

PLASTICS MATERIALS

SEVENTH EDITION

J. A. Brydson


*Former Head of the Department of Physical Sciences
and Technology,*

Polytechnic of North London (now known as the University of North London)

BUTTERWORTH
HEINEMANN

OXFORD AUCKLAND BOSTON JOHANNESBURG MELBOURNE NEW DELHI

Butterworth-Heinemann
Linacre House, Jordan Hill, Oxford OX2 8DP
225 Wildwood Avenue, Woburn, MA 01801-2041
A division of Reed Educational and Professional Publishing Ltd

 A member of the Reed Elsevier plc group

First published by Iliffe Books Ltd 1966
Second edition 1969
Reprinted 1970
Third edition 1975
Reprinted with revisions 1977
Reprinted 1979
Fourth edition published by Butterworth-Heinemann 1982
Reprinted 1985
Fifth edition 1989
Reprinted 1991, 1993
Sixth edition 1995
Reprinted 1995, 1996, 1998
Seventh edition 1999

© J. A. Brydson 1995, 1999

All rights reserved. No part of this publication may be reproduced in any material form (including photocopying or storing in any medium by electronic means and whether or not transiently or incidentally to some other use of this publication) without the written permission of the copyright holder except in accordance with the provisions of the Copyright Designs and Patents Act 1988 or under the terms of a licence issued by the Copyright Licensing Agency Ltd, 90 Tottenham Court Road, London, England W1P 9HE. Applications for the copyright holder's written permission to reproduce any part of this publication should be addressed to the publisher

British Library Cataloguing in Publication Data

Brydson, J. A. (John Andrew), 1932–
Plastics materials. – 7th ed.
I. Plastics
I. Title
668.4

ISBN 0 7506 4132 0

Library of Congress Cataloguing in Publication Data

Brydson, J. A.
Plastics materials/J.A. Brydson. – 7th ed.
p. cm.
Includes bibliographical references and index.
ISBN 0 7506 4132 0 (hbk.)
I. Plastics. I. Title.
TP1120 B7 99–30623
668.4—dc21 CIP

Preface to the Seventh Edition

I mentioned in the preface to the sixth edition that when I began preparation of the first edition of this book in the early 1960s world production of plastics materials was of the order of 9 million tonnes per annum. In the late 1990s it has been estimated at 135 million tonnes per annum! In spite of this enormous growth my prediction in the first edition that the likelihood of discovering new important general purposes polymers was remote but that new special purpose polymers would continue to be introduced has proved correct.

Since the last edition several new materials have been announced. Many of these are based on metallocene catalyst technology. Besides the more obvious materials such as metallocene-catalysed polyethylene and polypropylene these also include syndiotactic polystyrenes, ethylene-styrene copolymers and cycloolefin polymers. Developments also continue with condensation polymers with several new polyester-type materials of interest for bottle-blowing and/or degradable plastics. New phenolic-type resins have also been announced. As with previous editions I have tried to explain the properties of these new materials in terms of their structure and morphology involving the principles laid down in the earlier chapters.

This new edition not only includes information on the newer materials but attempts to explain in modifications to Chapter 2 the basis of metallocene polymerisation. Since it is also becoming apparent that successful development with these polymers involves consideration of molecular weight distributions an appendix to Chapter 2 has been added trying to explain in simple terms such concepts as number and molecular weight averages, molecular weight distribution and in particular concepts such as bi- and trimodal distributions which are becoming of interest.

As in previous editions I have tried to give some idea of the commercial importance of the materials discussed. What has been difficult is to continue to indicate major suppliers since there have been many mergers and transfers of manufacturing rights. There has also been considerable growth in manufacturing capacity in the Pacific Rim area and in Latin America. However this has tended to coincide with the considerable economic turmoil in these areas particularly during the period of preparation for this edition. For this reason most of the

figures on production and consumption is based on 1997 data as this was felt to be more representative than later, hopefully temporary, distortions.

In a book which has in effect been written over a period of nearly 40 years the author would request tolerance by the reader for some inconsistencies. In particular I am mindful about references. In the earlier editions these were dominated by seminal references to fundamental papers on the discovery of new materials, often by individuals, or classic papers that laid down the foundations relating properties to structure. In more recent editions I have added few new individual references since most announcements of new materials are the result of work by large teams and made by companies. For this reason I have directed the reader to reviews, particularly those by Rapra and those found in *Kunststoffe* for which translations in English are available. I am also aware that some of the graphs from early editions do not show data in SI units. Since in many cases the diagram is there to emphasise a relationship rather than to give absolute values and because changing data provided by other authors is something not to be undertaken lightly I would again request tolerance by the reader.

J. A. B
Brent Eleigh
Suffolk, 1999

Preface to the First Edition

There are at the present time many thousands of grades of commercial plastics materials offered for sale throughout the world. Only rarely are the properties of any two of these grades identical, for although the number of chemically distinct species (e.g. polyethylenes, polystyrenes) is limited, there are many variations within each group. Such variations can arise through differences in molecular structure, differences in physical form, the presence of impurities and also in the nature and amount of additives which may have been incorporated into the base polymer. One of the aims of this book is to show how the many different materials arise, to discuss their properties and to show how these properties can to a large extent be explained by consideration of the composition of a plastics material and in particular the molecular structure of the base polymer employed.

After a brief historical review in Chapter 1 the following five chapters provide a short summary of the general methods of preparation of plastics materials and follow on by showing how properties are related to chemical structure. These particular chapters are largely qualitative in nature and are aimed not so much at the theoretical physical chemist but rather at the polymer technologist and the organic chemist who will require this knowledge in the practice of polymer and compound formulation.

Subsequent chapters deal with individual classes of plastics. In each case a review is given of the preparation, structure and properties of the material. In order to prevent the book from becoming too large I have omitted detailed discussion of processing techniques. Instead, with each major class of material an indication is given of the main processing characteristics. The applications of the various materials are considered in the light of the merits and the demerits of the material.

The title of the book requires that a definition of plastics materials be given. This is however very difficult. For the purpose of this book I eventually used as a working definition 'Those materials which are considered to be plastics materials by common acceptance'. Not a positive definition but one which is probably less capable of being criticised than any other definition I have seen. Perhaps a rather more useful definition but one which requires clarification is

'Plastics materials are processable compositions based on macromolecules'. In most cases (certainly with all synthetic materials) the macromolecules are polymers, large molecules made by the joining together of many smaller ones. Such a definition does however include rubbers, surface coatings, fibres and glasses and these, largely for historical reasons, are not generally regarded as plastics. While we may arbitrarily exclude the above four classes of material the borderlines remain undefined. How should we classify the flexible polyurethane foams—as rubbers or as plastics? What about nylon tennis racquet filament?—or polyethylene dip coatings? Without being tied by definition I have for convenience included such materials in this book but have given only brief mention to coatings, fibres and glasses generally. The rubbers I have treated as rather a special case considering them as plastics materials that show reversible high elasticity. For this reason I have briefly reviewed the range of elastomeric materials commercially available.

I hope that this book will prove to be of value to technical staff who are involved in the development and use of plastics materials and who wish to obtain a broader picture of those products than they could normally obtain in their everyday work. Problems that are encountered in technical work can generally be classified into three groups; problems which have already been solved elsewhere, problems whose solutions are suggested by a knowledge of the way in which similar problems have been tackled elsewhere and finally completely novel problems. In practice most industrial problems fall into the first two categories so that the technologist who has a good background knowledge to his subject and who knows where to look for details of original work has an enhanced value to industry. It is hoped that in a small way the text of this book will help to provide some of the background knowledge required and that the references, particularly to more detailed monographs, given at the end of each chapter will provide signposts along the pathways of the ever thickening jungle of technical literature.

Acknowledgements for the Seventh Edition

As I have said in previous editions the information provided in this volume is a distillation of the work of very many scientists, technologists, engineers, economists and journalists without which this book could not have existed.

Over the years with the different editions I have received help from very many companies concerned with the production of plastics materials and from very many individuals. For this edition I should specifically like to thank Susan Davey, Academic Information Services Manager of the University of North London, Rebecca Dolbey and Ray Gill of Rapra Technology Ltd, Peter Lewis of the Open University, Simon Robinson of European Plastics News, Christopher Sutcliffe of Crystal Polymers Ltd and Graham Bonner of BP Chemicals.

Once again I should acknowledge that I have drawn heavily from the journals *European Plastics News*, *Kunststoffe*, *Modern Plastics International* and *Plastics and Rubber Weekly* for data on production and consumption statistics.

My thanks also go to the publishers Butterworth-Heinemann and particularly Rebecca Hammersley for their tolerance and help.

Once again I must also express my thanks to Wendy, my wife, who has had to tolerate me writing, at intervals, editions of this book for much of our married life.

Abbreviations for Plastics and Rubbers

Many abbreviations for plastics materials are in common use. Some of these have now been incorporated into national and international standards, including:

ISO 1043 (1978) Plastics—Symbols.

BS 3502 Common Names and Abbreviations for Plastics and Rubbers.

Part 1 Principal commercial plastics (1978).

(The 1978 revision was carried out in accordance with IS 1043 although the latter also deals with compounding ingredients.)

ASTM D 1600–83 Abbreviations of terms relating to plastics.

DIN 7728

Part 1 (1978) Symbols for terms relating to homopolymers, copolymers and polymer compounds.

Part 2 (1980) Symbols for reinforced plastics.

In *Table 1*, drawn up by the author, of abbreviations in common use those in **bold** type are in the main schedule of BS 3502. In this list the names given for the materials are the *commonly used scientific names*. This situation is further complicated by the adoption of a nomenclature by the International Union of Pure and Applied Chemistry for systematic names and a yet further nomenclature by the Association for Science Education which is widely used in British schools but not in industry. Some examples of these are given in *Table 2*. Because many rubbery materials have been referred to in this book, *Tables 3* and *4* list abbreviations for these materials.

Table 1 Common abbreviations for plastics

<i>Abbreviation</i>	<i>Material</i>	<i>Common name</i>
ABS	Acrylonitrile-butadiene-styrene polymer	ABS
ACS	Acrylonitrile-styrene and chlorinated polyethylene	
AES	Acrylonitrile-styrene and ethylene-propylene rubber	
ASA	Acrylonitrile-styrene and acrylic rubber	
CA	Cellulose acetate	Acetate
CAB	Cellulose acetate-butylate	CAB, butylate
CAP	Cellulose acetate-propionate	CAP
CN	Cellulose nitrate	Celluloid
CP	Cellulose propionate	CP, propionate
CPVC	Chlorinated polyvinyl chloride	
CTA	Cellulose triacetate	Triacetate
CS	Casein	Casein
DMC		Dough moulding compound (usually polyester)
EAA	Ethylene-acrylic acid	
EEA	Ethylene-ethyl acrylate	
EP	Epoxy resin	Epoxy
ETFE	Tetrafluoroethylene-ethylene copolymer	
EVAC	Ethylene-vinyl acetate	EVA
EVOH, EVAL, EVOL	Ethylene-vinyl alcohol	
FEP	Tetrafluoroethylene-hexafluoropropylene copolymer	
FRP, FRTP	Thermoplastic material reinforced, commonly with fibre	
GRP	Glass-fibre reinforced plastic based on a thermosetting resin	
HDPE	High-density polyethylene	
HIPS	High-impact polystyrene	
LDPE	Low-density polyethylene	
LLDPE	Linear low-density polyethylene	
MBS	Methacrylate-butadiene styrene	
MDPE	Medium-density polyethylene	
MF	Melamine-formaldehyde	Melamine
PA	Polyamide	Nylon (some types)
PAI	Polyamideimide	
PBTP, PBT, PTMT	Polybutylene terephthalate	Polyester
PC	Polycarbonate	Polycarbonate
PETP, PET	Polyethylene terephthalate	Polyester
PCT	Poly-(1,4-cyclohexylenediaminemethylene terephthalate)	
PCTFE	Polychlorotrifluoroethylene	
PE	Polyethylene	Polythene
PEBA	Polyether block amide	
PEEK	Polyether ether ketone	

Table 1 Continued

<i>Abbreviation</i>	<i>Material</i>	<i>Common name</i>
PEEKK	Polyether ether ketone ketone	
PEG	Polyethylene glycol	
PEI	Polyetherimide	
PEK	Polyether ketone	
PES	Polyether sulphone	
PETP, PET	Polyethylene terephthalate	Polyester
PF	Phenol-formaldehyde	Phenolic
PEA	Tetrafluoroethylene-perfluoroalkyl (usually propyl) vinyl ether copolymers	
PI	Polyimide	
PIB	Polyisobutylene	
PMMA, PMM	Polymethyl methacrylate	Acrylic
PMMI	Polymethylmethacrylimide	
POM	Polyacetal, polyoxymethylene, polyformaldehyde	Acetal
PP	Polypropylene	Propylene, polyprop
PPG	Polypropylene glycol	
PPO	Polyphenylene oxide	
PPO	Polypropylene oxide	
PPS	Polypropylene sulphide	
PS	Polystyrene	Styrene
PS, PSU	Polysulphone	
PTFE	Polytetrafluoroethylene	PTFE
PUR	Polyurethane	Polyurethane, urethane
PVA	Polyvinyl acetate	
PVA	Polyvinyl alcohol	
PVA	Polyvinyl acetal	
PVAC	Polyvinyl acetate	PVA
PVB	Polyvinyl butyral	
PVC	Polyvinyl chloride	PVC, vinyl
PVDC	Polyvinylidene chloride	
PVDF	Polyvinylidene fluoride	
PVF	Polyvinyl fluoride	
PVF	Polyvinyl formal	
PVP	Polyvinyl pyrrolidone	
P4MP1	Poly-4-methyl pentene-1	
RF	Resorcinol-formaldehyde	
SAN	Styrene-acrylonitrile	SAN
SI	Polysiloxane	Silicone
SMA	Styrene-maleic anhydride	
SMC		Sheet moulding compound (usually polyester)
TPS	Toughened polystyrene	
UF	Urea-formaldehyde	Urea
UP	Unsaturated polyester	Polyester
UPVC	Unplasticised PVC	
VLDPE	Very low density polyethylene	
XPS	Expanded polystyrene	

The Commission on Macromolecular Nomenclature of the International Union of Pure and Applied Chemistry has published a nomenclature for single-strand organic polymers (*Pure and Applied Chemistry*, **48**, 375 (1976)). In addition the Association for Science Education in the UK has made recommendations based on a more general IUPAC terminology, and these have been widely used in British schools. Some examples of this nomenclature compared with normal usage are given in *Table 2*.

Table 2

<i>Normal usage</i>	ASE	IUPAC
Polyethylene	Poly(ethene)	Poly(methylene)
Polypropylene	Poly(propene)	Poly(propylene)
Polystyrene	Poly(phenyl ethene)	Poly(1-phenyl ethylene)
Polyvinyl chloride	Poly(chloroethene)	Poly(1-chloroethylene)
Polymethyl methacrylate	Poly(methyl 2-methyl propenoate)	Poly[1-(methoxycarbonyl)-1-methyl ethylene]

In this book the policy has been to use *normal usage scientific terms*.

Table 3 Standard abbreviations for rubbery materials (based on ISO Recommendation and ASTM D 1418)

ABR	acrylate-butadiene rubber
ACM	copolymers of ethyl or other acrylates and a small amount of a monomer which facilitates vulcanization
ACSM	alkyl chlorosulphonated polyethylene
AECO	terpolymers of allyl glycidyl ether, ethylene oxide and epichlorohydrin
AEM	copolymers of ethyl or other acrylate and ethylene
AFMU	terpolymer of tetrafluoroethylene, trifluoronitrosomethane and nitroso-perfluorobutyric acid
ANM	copolymers of ethyl or other acrylate and acrylonitrile
AU	polyester urethanes
BIIR	bromo-isobutene-isoprene rubber (brominated butyl rubber)
BR	butadiene rubber
CFM	rubber with chlorotrifluoroethylene units in chain
CIIR	chloro-isobutene-isoprene rubber (chlorinated butyl rubber)
CM	chlorinated polyethylene
CO	epichlorohydrin rubber
CR	chloroprene rubber
CSM	chlorosulphonated polyethylene
ECO	ethylene oxide and epichlorohydrin copolymer
EAM	ethylene-vinyl acetate copolymer
EPDM	terpolymer of ethylene, propylene and a diene with the residual unsaturated portion of the diene in the side chain
EPM	ethylene-propylene copolymer
EU	polyether urethanes
FFKM	perfluororubbers of the polymethylene type, having all substituent groups on the polymer chain either fluoroperfluoroalkyl or perfluoroalkoxy
FKM	fluororubber of the polymethylene type, having substituent fluoro and perfluoroalkoxy groups on the main chain
FVMQ	silicone rubber having fluorine, vinyl and methyl substituent groups on the polymer chain
FZ	polyphosphazene with fluorinated side groups
GPO	polypropylene oxide rubbers

Table 3 Continued

IIR	isobutene–isoprene rubber (butyl rubber)
IM	polyisobutene
IR	isoprene rubber (synthetic)
MQ	silicone rubbers having only methyl substituent groups on the polymer chain
NBR	nitrile–butadiene rubber (nitrile rubber)
NIR	nitrile–isoprene rubber
NR	natural rubber
PBR	pyridine–butadiene rubber
PMQ	silicone rubbers having both methyl and phenyl groups on the polymer chain
PNR	polynorbornene rubber
PSBR	pyridine–styrene–butadiene rubber
PVMQ	silicone rubbers having methyl, phenyl and vinyl substituent groups on the polymer chain
PZ	polyphosphazene with phenolic side chains
Q	rubbers having silicon in the polymer chain
SBR	styrene–butadiene rubber
T	rubbers having sulphur in the polymer chain (excluding copolymers based on CR)
VMQ	silicone rubber having both methyl and vinyl substituent groups in the polymer chain
XNBR	carboxylic–nitrile butadiene rubber (carboxynitrile rubber)
XSBR	carboxylic–styrene butadiene rubber
Y	prefix indicating thermoplastic rubber
YBPO	thermoplastic block polyether–polyester rubbers

In addition to the nomenclature based on ISO and ASTM recommendations several other abbreviations are widely used. Those most likely to be encountered are shown in *Table 4*.

Table 4 Miscellaneous abbreviations used for rubbery materials

ENR	epoxidized natural rubber
EPR	ethylene–propylene rubbers (either EPM or EPDM)
EVA	ethylene–vinyl acetate copolymers (instead of EAM)
EVM	ethylene–vinyl acetate rubber (instead of EAM or EVA)
HNBR	hydrogenated nitrile rubber
PEBA	thermoplastic polyamide rubber, polyether block amide
SBS	styrene–butadiene–styrene triblock copolymer
SEBS	hydrogenated SBS
SIR	Standard Indonesian rubber
SIS	styrene–isoprene–styrene triblock copolymer
SMR	Standard Malaysian rubber
TOR	polyoctenamer
TPO	thermoplastic polyolefin rubber
TPU	thermoplastic polyurethane rubber

During the World War II the United States Government introduced the following system of nomenclature which continued in use, at least partially, until the 1950s and is used in many publications of the period.

GR-A	Government Rubber—Acrylonitrile	(modern equivalent NBR)
GR-I	Government Rubber—Isobutylene	(IIR)
GR-M	Government Rubber—Monovinyl acetylene	(CR)
GR-P	Government Rubber—Polysulphide	(T)
GR-S	Government Rubber—Styrene	(SBR)

Contents

<i>Preface to the Seventh Edition</i>	xvii
<i>Preface to the First Edition</i>	xix
<i>Acknowledgements for the Seventh Edition</i>	xxi
<i>Abbreviations for Plastics and Rubbers</i>	xxiii
1 The Historical Development of Plastics Materials	1
1.1 Natural Plastics	1
1.2 Parkesine and Celluloid	3
1.3 1900–1930	4
1.4 The Evolution of the Vinyl Plastics	6
1.5 Developments since 1939	7
1.6 Raw Materials for Plastics	9
1.7 The Market for Plastics	11
1.8 The Future for Plastics	15
2 The Chemical Nature of Plastics	19
2.1 Introduction	19
2.2 Thermoplastic and Thermosetting Behaviour	23
2.3 Further Consideration of Addition Polymerisation	24
2.3.1 Elementary kinetics of free-radical addition polymerisation	29
2.3.2 Ionic polymerisation	33
2.3.3 Ziegler–Natta and metallocene polymerisation	37
2.4 Condensation Polymerisation	39
3 States of Aggregation in Polymers	43
3.1 Introduction	43
3.2 Linear Amorphous Polymers	43
3.2.1 Orientation in linear amorphous polymers	47
3.3 Crystalline Polymers	49
3.3.1 Orientation and crystallisation	52
3.3.2 Liquid crystal polymers	53
3.4 Cross-linked Structures	53
3.5 Polyblends	55
3.6 Summary	57

4	Relation of Structure to Thermal and Mechanical Properties	59
4.1	Introduction	59
4.2	Factors Affecting the Glass Transition Temperature	59
4.3	Factors Affecting the Ability to Crystallise	64
4.4	Factors Affecting the Crystalline Melting Point	70
4.5	Some Individual Properties	73
4.5.1	Melt viscosity	73
4.5.2	Yield strength and modulus	74
4.5.3	Density	74
4.5.4	Impact strength	74
5	Relation of Structure to Chemical Properties	76
5.1	Introduction	76
5.2	Chemical Bonds	76
5.3	Polymer Solubility	80
5.3.1	Plasticisers	87
5.3.2	Extenders	89
5.3.3	Determination of solubility parameter	89
5.3.4	Thermodynamics and solubility	93
5.4	Chemical Reactivity	95
5.5	Effects of Thermal, Photochemical and High-energy Radiation	96
5.6	Aging and Weathering	99
5.7	Diffusion and Permeability	100
5.8	Toxicity	103
5.9	Fire and Plastics	104
6	Relation of Structure to Electrical and Optical Properties	110
6.1	Introduction	110
6.2	Dielectric Constant, Power Factor and Structure	110
6.3	Some Quantitative Relationships of Dielectrics	117
6.4	Electronic Applications of Polymers	119
6.5	Electrically Conductive Polymers	120
6.6	Optical Properties	120
	Appendix—Electrical Testing	122
7	Additives for Plastics	124
7.1	Introduction	124
7.2	Fillers	126
7.2.1	Coupling agents	128
7.3	Plasticisers and Softeners	131
7.4	Lubricants and Flow Promoters	132
7.5	Anti-aging Additives	134
7.5.1	Antioxidants	134
7.5.2	Antiozonants	143
7.5.3	Stabilisers against dehydrochlorination	143
7.5.4	Ultraviolet absorbers and related materials	143
7.6	Flame Retarders	145
7.7	Colorants	149
7.8	Blowing Agents	150
7.9	Cross-linking Agents	153
7.10	Photodegradants	154
7.11	2-Oxazolines	155

8	Principles of the Processing of Plastics	158
8.1	Introduction	158
8.2	Melt Processing of Thermoplastics	159
8.2.1	Hygroscopic behaviour	159
8.2.2	Granule characteristics	159
8.2.3	Thermal properties influencing polymer melting	161
8.2.4	Thermal stability	163
8.2.5	Flow properties	163
8.2.5.1	Terminology	164
8.2.5.2	Effect of environmental and molecular factors on viscous flow properties	167
8.2.5.3	Flow in an injection mould	170
8.2.5.4	Elastic effects in polymer melts	171
8.2.6	Thermal properties affecting cooling	174
8.2.7	Crystallisation	175
8.2.8	Orientation and shrinkage	175
8.3	Melt Processing of Thermosetting Plastics	176
8.4	Processing in the Rubbery State	179
8.5	Solution, Suspension and Casting Processes	181
8.6	Summary	182
9	Principles of Product Design	184
9.1	Introduction	184
9.2	Rigidity of Plastics Materials	184
9.2.1	The assessment of maximum service temperature	186
9.2.1.1	Assessment of thermal stability	186
9.2.1.2	Assessment of softening point	188
9.3	Toughness	190
9.3.1	The assessment of impact strength	192
9.4	Stress–Strain–Time Behaviour	195
9.4.1	The WLF equations	196
9.4.2	Creep curves	198
9.4.3	Practical assessment of long-term behaviour	200
9.5	Recovery from Deformation	201
9.6	Distortion, Voids and Frozen-in Stress	202
9.7	Conclusions	204
10	Polyethylene	205
10.1	Introduction	205
10.2	Preparation of Monomer	207
10.3	Polymerisation	208
10.3.1	High-pressure polymerisation	208
10.3.2	Ziegler processes	209
10.3.3	The Phillips process	210
10.3.4	Standard Oil Company (Indiana) process	211
10.3.5	Processes for making linear low-density polyethylene and metallocene polyethylene	211
10.4	Structure and Properties of Polyethylene	212
10.5	Properties of Polyethylene	217
10.5.1	Mechanical properties	217
10.5.2	Thermal properties	221
10.5.3	Chemical properties	223
10.5.4	Electrical properties	226
10.5.5	Properties of LLDPE and VLDPE	227
10.5.6	Properties of metallocene-catalysed polyethylenes	227

10.6	Additives	228
10.7	Processing	232
10.8	Polyethylenes of Low and High Molecular Weight	238
10.9	Cross-linked Polyethylene	239
10.10	Chlorinated Polyethylene	240
10.11	Applications	241
11	Aliphatic Polyolefins other than Polyethylene, and Diene Rubbers	247
11.1	Polypropylene	247
11.1.1	Preparation of polypropylene	248
11.1.2	Structure and properties of polypropylene	251
11.1.3	Properties of isotactic polypropylene	253
11.1.4	Additives for isotactic polypropylene	260
11.1.5	Processing characteristics	262
11.1.6	Applications	265
11.1.7	Atactic and syndiotactic polypropylene	267
11.1.8	Chlorinated polypropylene	268
11.2	Polybut-1-ene	268
11.2.1	Atactic polybut-1-ene	269
11.3	Polyisobutylene	269
11.4	Poly-(4-methylpent-1-ene)	270
11.4.1	Structure and properties	270
11.4.2	General properties	272
11.4.3	Processing	273
11.4.4	Applications	273
11.5	Other Aliphatic Olefin Homopolymers	273
11.6	Copolymers Containing Ethylene	275
11.6.1	Ethylene-carbon monoxide copolymers (ECO)	278
11.6.2	Ethylene-cyclo-olefin copolymers	280
11.7	Diene Rubbers	280
11.7.1	Natural rubber	285
11.7.2	Synthetic polyisoprene (IR)	289
11.7.3	Polybutadiene	290
11.7.4	Styrene-butadiene rubber (SBR)	291
11.7.4.1	'High styrene resins'	294
11.7.5	Nitrile rubber (NBR)	294
11.7.6	Chloroprene rubbers (CR)	295
11.7.7	Butadiene-pentadiene rubbers	296
11.8	Thermoplastic Diene Rubbers	296
11.9	Aliphatic Olefin Rubbers	299
11.9.1	Thermoplastic polyolefin rubbers	302
11.10	Rubbery Cyclo-olefin (Cyclo-alkene) Polymers	304
11.10.1	Aliphatic polyalkenamers	304
11.10.2	Polynorbomene	306
11.10.3	Chlorine-containing copolymers	307
11.11	1,2-Polybutadiene	307
11.12	Ethylene-styrene copolymers	308
11.13	Other elastomers	309
12	Vinyl Chloride Polymers	311
12.1	Introduction	311
12.2	Preparation of Vinyl Chloride	313
12.3	Polymerisation	315
12.4	Structure of Poly(vinyl chloride)	317
12.4.1	Characterisation of commercial polymers	320

12.5	Compounding Ingredients	325
12.5.1	Stabilisers	325
12.5.2	Plasticisers	330
12.5.3	Extenders	336
12.5.4	Lubricants	336
12.5.5	Fillers	337
12.5.6	Pigments	338
12.5.7	Polymeric impact modifiers and processing aids	338
12.5.8	Miscellaneous additives	342
12.5.9	Formulations	342
12.6	Properties of PVC Compounds	345
12.7	Processing	346
12.7.1	Plasticised PVC	347
12.7.2	Unplasticised PVC	349
12.7.3	Pastes	350
12.7.4	Copolymers	354
12.7.5	Latices	355
12.8	Applications	355
12.9	Miscellaneous Products	359
12.9.1	Crystalline PVC	359
12.9.2	Chlorinated PVC	359
12.9.3	Graft polymers based on PVC	360
12.9.4	Vinyl chloride–propylene copolymers	360
12.9.5	Vinyl chloride– <i>N</i> -cyclohexylmaleimide copolymers	360
13	Fluorine-containing Polymers	363
13.1	Introduction	363
13.2	Polytetrafluoroethylene	364
13.2.1	Preparation of monomer	364
13.2.2	Polymerisation	364
13.2.3	Structure and properties	365
13.2.4	General properties	367
13.2.5	Processing	369
13.2.6	Additives	371
13.2.7	Applications	372
13.3	Tetrafluoroethylene–Hexafluoropropylene Copolymers	373
13.4	Tetrafluoroethylene–Ethylene Copolymers (ETFE)	374
13.5	Polychlorotrifluoroethylene Polymers (PCTFE) and Copolymers with Ethylene (ECTFE)	374
13.6	Poly(vinyl fluoride) (PVF)	376
13.7	Poly(vinylidene fluoride)	376
13.8	Other Plastics Materials Containing Tetrafluoroethylene	377
13.9	Hexafluoroisobutylene–Vinylidene Fluoride Copolymers	379
13.10	Fluorine-containing Rubbers	379
13.11	Thermoplastic fluoroelastomers	383
13.12	Miscellaneous Fluoropolymers	384
14	Poly(vinyl acetate) and its Derivatives	386
14.1	Introduction	386
14.2	Poly(vinyl acetate)	386
14.2.1	Preparation of the monomer	386
14.2.2	Polymerisation	388
14.2.3	Properties and uses	389
14.3	Poly(vinyl alcohol)	389
14.3.1	Structure and properties	390
14.3.2	Applications	391

14.4	The Poly(vinyl acetals)	391
14.4.1	Poly(vinyl formal)	392
14.4.2	Poly(vinyl acetal)	393
14.4.3	Poly(vinyl butyral)	393
14.5	Ethylene–Vinyl Alcohol Copolymers	394
14.6	Poly(vinyl cinnamate)	395
14.7	Other Organic Vinyl Ester Polymers	397
15	Acrylic Plastics	398
15.1	Introduction	398
15.2	Poly(methyl methacrylate)	400
15.2.1	Preparation of monomer	400
15.2.2	Polymerisation	401
15.2.3	Structure and properties	405
15.2.4	General properties of poly(methyl methacrylate)	405
15.2.5	Additives	409
15.2.6	Processing	409
15.2.7	Applications	411
15.3	Methyl Methacrylate Polymers with Enhanced Impact Resistance and Softening Point	413
15.4	Nitrile Resins	415
15.5	Acrylate Rubbers	417
15.6	Thermosetting Acrylic Polymers	418
15.7	Acrylic Adhesives	419
15.8	Hydrophilic Polymers	420
15.9	Poly(methacrylimide)	420
15.10	Miscellaneous Methacrylate and Chloroacrylate Polymers and Copolymers	421
15.11	Other Acrylic Polymers	423
16	Plastics Based on Styrene	425
16.1	Introduction	425
16.2	Preparation of the Monomer	426
16.2.1	Laboratory preparation	426
16.2.2	Commercial preparation	427
16.3	Polymerisation	429
16.3.1	Mass polymerisation	429
16.3.2	Solution polymerisation	431
16.3.3	Suspension polymerisation	431
16.3.4	Emulsion polymerisation	432
16.3.5	Grades available	432
16.4	Properties and Structure of Polystyrene	433
16.5	General Properties	434
16.6	High-impact Polystyrenes (HIPS) (Toughened Polystyrenes (TPS))	437
16.7	Styrene–Acrylonitrile Copolymers	441
16.8	ABS Plastics	441
16.8.1	Production of ABS materials	442
16.8.2	Processing of ABS materials	447
16.8.3	Properties and applications of ABS plastics	447
16.9	Miscellaneous Rubber-modified Styrene–Acrylonitrile and Related Copolymers	448
16.10	Styrene–Maleic Anhydride Copolymers	450
16.11	Butadiene–Styrene Block Copolymers	450
16.12	Miscellaneous Polymers and Copolymers	452
16.13	Stereoregular Polystyrene	454
16.13.1	Syndiotactic polystyrene	454

16.14	Processing of Polystyrene	455
16.15	Expanded Polystyrene	457
	16.15.1 Structural foams	459
16.16	Oriented Polystyrene	461
16.17	Applications	462
17	Miscellaneous Vinyl Thermoplastics	466
17.1	Introduction	466
17.2	Vinylidene Chloride Polymers and Copolymers	466
	17.2.1 Properties and applications of vinylidene chloride–vinyl chloride copolymers	468
	17.2.2 Vinylidene chloride–acrylonitrile copolymers	470
17.3	Coumarone–Indene resins	471
17.4	Poly(vinyl carbazole)	472
17.5	Poly(vinyl pyrrolidone)	474
17.6	Poly(vinyl ethers)	475
17.7	Other Vinyl Polymers	476
18	Polyamides and Polyimides	478
18.1	Polyamides: Introduction	478
18.2	Intermediates for Aliphatic Polyamides	480
	18.2.1 Adipic acid	480
	18.2.2 Hexamethylenediamine	481
	18.2.3 Sebacic acid and Azelaic acid	481
	18.2.4 Caprolactam	482
	18.2.5 ω -Aminoundecanoic acid	483
	18.2.6 ω -Aminoanthanic acid	484
	18.2.7 Dodecanelactam	485
18.3	Polymerisation of Aliphatic Polyamides	486
	18.3.1 Nylons 46, 66, 69, 610 and 612	486
	18.3.2 Nylon 6	486
	18.3.3 Nylon 11	487
	18.3.4 Nylon 12	487
	18.3.5 Nylon 7	487
18.4	Structure and Properties of Aliphatic Polyamides	487
18.5	General Properties of the Nylons	490
18.6	Additives	496
18.7	Glass-filled Nylons	498
	18.7.1 Comparison of nylons 6 and 66 in glass-filled compositions	500
18.8	Processing of the Nylons	500
18.9	Applications	502
18.10	Polyamides of Enhanced Solubility	505
18.11	Other Aliphatic Polyamides	507
18.12	Aromatic Polyamides	509
	18.12.1 Glass-clear polyamides	509
	18.12.2 Crystalline aromatic polyamides	513
	18.12.2.1 Poly- <i>m</i> -xylylene adipamide	513
	18.12.2.2 Aromatic polyamide fibres	514
	18.12.2.3 Polyphthalamide plastics	516
18.13	Polyimides	516
18.14	Modified Polyimides	521
	18.14.1 Polyamide–imides	524
	18.14.2 Polyetherimides	525
18.15	Elastomeric Polyamides	526
18.16	Polyesteramides	528

19	Polyacetals and Related Materials	531
19.1	Introduction	531
19.2	Preparation of Formaldehyde	532
19.3	Acetal Resins	533
19.3.1	Polymerisation of formaldehyde	533
19.3.2	Structure and properties of acetal resins	536
19.3.3	Properties of acetal resins	538
19.3.4	Processing	542
19.3.5	Additives	543
19.3.6	Acetal–polyurethane alloys	544
19.3.7	Applications of the acetal polymers and copolymers	544
19.4	Miscellaneous Aldehyde Polymers	546
19.5	Polyethers from Glycols and Alkylene Oxides	546
19.5.1	Elastomeric polyethers	547
19.6	Oxetane Polymers	549
19.7	Polysulphides	551
20	Polycarbonates	556
20.1	Introduction	556
20.2	Production of Intermediates	557
20.3	Polymer Preparation	558
20.3.1	Ester exchange	558
20.3.2	Phosgenation process	560
20.4	Relation of Structure and Properties	561
20.4.1	Variations in commercial grades	564
20.5	General Properties	567
20.6	Processing Characteristics	573
20.7	Applications of Bis-phenol A Polycarbonates	575
20.8	Alloys based on Bis-phenol A Polycarbonates	578
20.9	Polyester Carbonates and Block Copolymers	579
20.10	Miscellaneous Carbonic Ester Polymers	580
21	Other Thermoplastics Containing <i>p</i> -Phenylene Groups	584
21.1	Introduction	584
21.2	Polyphenylenes	584
21.3	Poly- <i>p</i> -xylylene	586
21.4	Poly(phenylene oxides) and Halogenated Derivatives	586
21.5	Alkyl Substituted Poly(phenylene oxides) including PPO	586
21.5.1	Structure and properties of poly-(2,6-dimethyl- <i>p</i> -phenylene oxide) (PPO)	587
21.5.2	Processing and application of PPO	589
21.5.3	Blends based in polyphenylene oxides	589
21.5.4	Styrenic PPOs	590
21.5.5	Processing of styrenic PPOs	591
21.5.6	Polyamide PPOs	592
21.5.7	Poly(2,6-dibromo-1,4-phenylene oxide)	592
21.6	Polyphenylene Sulphides	593
21.6.1	Amorphous polyarylene sulphides	596
21.7	Polysulphones	596
21.7.1	Properties and structure of polysulphones	599
21.7.2	General properties of polysulphones	600
21.7.3	Processing of polysulphones	601
21.7.4	Applications	601
21.7.5	Blends based on polysulphones	602
21.8	Polyarylether Ketones	602
21.9	Phenoxy Resins	607
21.10	Linear Aromatic Polyesters	607

21.11	Polyhydantoin Resins	609
21.12	Poly(parabanic acids)	610
21.13	Summary	611
22	Cellulose Plastics	613
22.1	Nature and Occurrence of Cellulose	613
22.2	Cellulose Esters	616
22.2.1	Cellulose nitrate	616
22.2.2	Cellulose acetate	621
22.2.3	Other cellulose esters	627
22.3	Cellulose Ethers	629
22.3.1	Ethyl cellulose	629
22.3.2	Miscellaneous ethers	632
22.4	Regenerated Cellulose	632
22.5	Vulcanised Fibre	634
23	Phenolic Resins	635
23.1	Introduction	635
23.2	Raw Materials	635
23.2.1	Phenol	636
23.2.2	Other phenols	638
23.2.3	Aldehydes	639
23.3	Chemical Aspects	639
23.3.1	Novolaks	639
23.3.2	Resols	641
23.3.3	Hardening	641
23.4	Resin Manufacture	643
23.5	Moulding Powders	645
23.5.1	Compounding ingredients	646
23.5.2	Compounding of phenol-formaldehyde moulding compositions	648
23.5.3	Processing characteristics	649
23.5.4	Properties of phenolic mouldings	652
23.5.5	Applications	652
23.6	Phenolic Laminates	654
23.6.1	The properties of phenolic laminates	656
23.6.2	Applications of phenolic laminates	658
23.7	Miscellaneous Applications	659
23.8	Resorcinol-Formaldehyde Adhesives	662
23.9	Friedel-Crafts and Related Polymers	662
23.10	Phenolic Resin Fibres	666
23.11	Polybenzoxazines	666
24	Aminoplastics	668
24.1	Introduction	668
24.2	Urea-Formaldehyde Resins	669
24.2.1	Raw materials	669
24.2.2	Theories of resinification	670
24.2.3	U-F moulding materials	671
24.2.4	Adhesives and related uses	677
24.2.5	Foams and firelighters	679
24.2.6	Other applications	679
24.3	Melamine-Formaldehyde Resins	680
24.3.1	Melamine	680
24.3.2	Resinification	682
24.3.3	Moulding powders	684
24.3.4	Laminates containing melamine-formaldehyde resin	688
24.3.5	Miscellaneous applications	688

24.4	Melamine–Phenolic Resins	689
24.5	Aniline–Formaldehyde Resins	690
24.6	Resins Containing Thiourea	691
25	Polyesters	694
25.1	Introduction	694
25.2	Unsaturated Polyester Laminating Resins	696
25.2.1	Selection of raw materials	696
25.2.2	Production of resins	701
25.2.3	Curing systems	702
25.2.4	Structure and properties	704
25.2.5	Polyester–glass fibre laminates	704
25.2.6	Water-extended polyesters	708
25.2.7	Allyl resins	708
25.3	Polyester Moulding Compositions	709
25.4	Fibre-forming and Film-forming Polyesters	713
25.5	Poly(ethylene terephthalate) Moulding Materials	720
25.5.1	Poly(ethylene naphthalate) (PEN)	723
25.6	Poly(butylene terephthalate)	724
25.7	Poly(trimethylene terephthalate)	728
25.8	Poly-(1,4-cyclohexylenedimethyleneterephthalate) (PCT)	728
25.8.1	Poly-(1,4-cyclohexylenedimethyleneterephthalate-co-isophthalate)	729
25.9	Highly Aromatic Linear Polyesters	730
25.9.1	Liquid crystal polyesters	733
25.10	Polyester Thermoplastic Elastomers	737
25.11	Poly(pivalolactone)	739
25.12	Polycaprolactones	740
25.13	Surface Coatings, Plasticisers and Rubbers	740
26	Epoxide Resins	744
26.1	Introduction	744
26.2	Preparation of Resins from Bis-phenol A	745
26.3	Curing of Glycidyl Ether Resins	751
26.3.1	Amine hardening systems	753
26.3.2	Acid hardening systems	758
26.3.3	Miscellaneous hardener systems	761
26.3.4	Comparison of hardening systems	761
26.4	Miscellaneous Epoxide Resins	761
26.4.1	Miscellaneous glycidyl ether resins	761
26.4.2	Non-glycidyl ether epoxides	764
26.5	Diluents, Flexibilisers and other Additives	768
26.6	Structure and Properties of Cured Resins	772
26.7	Applications	772
27	Polyurethanes and Polyisocyanurates	778
27.1	Introduction	778
27.2	Isocyanates	779
27.3	Fibres and Crystalline Moulding Compounds	782
27.4	Rubbers	784
27.4.1	Cast polyurethane rubbers	784
27.4.2	Millable gums	788
27.4.3	Properties and applications of cross-linked polyurethane rubbers	788
27.4.4	Thermoplastic polyurethane rubbers and Spandex fibres	789
27.5	Flexible Foams	791
27.5.1	One-shot polyester foams	792
27.5.2	Polyether prepolymers	793

	27.5.3	Quasi-prepolymer polyether foams	794
	27.5.4	Polyether one-shot foams	794
	27.5.5	Properties and applications of flexible foams	799
27.6		Rigid and Semi-rigid Foams	800
	27.6.1	Self-skinning foams and the RIM process	803
27.7		Coatings and Adhesives	805
27.8		Polyisocyanurates	805
27.9		Polycarbodi-imide Resins	807
27.10		Polyurethane–Acrylic Blends	808
27.11		Miscellaneous Isocyanate-Based Materials	808
28		Furan Resins	810
	28.1	Introduction	810
	28.2	Preparation of Intermediates	810
	28.3	Resinification	811
	28.4	Properties of the Cured Resins	812
	28.5	Applications	812
29		Silicones and Other Heat-resisting Polymers	814
	29.1	Introduction	814
		29.1.1 Nomenclature	815
		29.1.2 Nature of chemical bonds containing silicon	816
	29.2	Preparation of Intermediates	817
		29.2.1 The Grignard method	818
		29.2.2 The direct process	818
		29.2.3 The olefin addition method	820
		29.2.4 Sodium condensation method	820
		29.2.5 Rearrangement of organochlorosilanes	820
	29.3	General Methods of Preparation and Properties of Silicones	821
	29.4	Silicone Fluids	823
		29.4.1 Preparation	823
		29.4.2 General properties	824
		29.4.3 Applications	826
	29.5	Silicone Resins	828
		29.5.1 Preparation	828
		29.5.2 Properties	828
		29.5.3 Applications	829
	29.6	Silicone Rubbers	832
		29.6.1 Dimethylsilicone rubbers	832
		29.6.2 Modified polydimethylsiloxane rubbers	832
		29.6.3 Compounding	836
		29.6.4 Fabrication and cross-linking	837
		29.6.5 Properties and applications	838
		29.6.6 Liquid silicone rubbers	839
		29.6.7 Polysiloxane–polyetherimide copolymers	840
	29.7	Polymers for use at High Temperatures	841
		29.7.1 Fluorine-containing polymers	841
		29.7.2 Inorganic polymers	842
		29.7.3 Cross-linked organic polymers	846
		29.7.4 Linear polymers with <i>p</i> -phenylene groups and other ring structures	847
		29.7.5 Ladder polymers and spiro polymers	848
		29.7.6 Co-ordination polymers	850
		29.7.7 Summary	851

30	Miscellaneous Plastics Materials	853
30.1	Introduction	853
30.2	Casein	853
30.2.1	Chemical nature	854
30.2.2	Isolation of casein from milk	855
30.2.3	Production of casein plastics	856
30.2.4	Properties of casein	858
30.2.5	Applications	859
30.3	Miscellaneous Protein Plastics	860
30.4	Derivatives of Natural Rubber	860
30.5	Gutta Percha and Related Materials	865
30.6	Shellac	867
30.6.1	Occurrence and preparation	867
30.6.2	Chemical composition	868
30.6.3	Properties	868
30.6.4	Applications	869
30.7	Amber	870
30.7.1	Composition and properties	870
30.8	Bituminous Plastics	871
31	Selected Functional Polymers	874
31.1	Introduction	874
31.2	Thermoplastic Elastomers	874
31.2.1	Applications of thermoplastic elastomers	878
31.2.2	The future for thermoplastic elastomers	880
31.3	Degradable Plastics	880
31.3.1	Polyhydroxybutyrate–valerate copolymers (PHBV)	883
31.3.2	The future for degradable plastics	886
31.4	Intrinsically Electrically Conducting Polymers (ICPs)	886
32	Material Selection	890
32.1	Introduction	890
32.2	Establishing Operational Requirements	891
32.3	Economic Factors Affecting Material Choice	891
32.4	Material Data Sources	892
32.4.1	Computer-aided selection	894
32.5	A Simple Mechanistic Non-computer Selection System	895
32.6	A Simple Pathway-based Non-computer Selection System	895
	Appendix	898
	Index	899

The Historical Development of Plastics Materials

1.1 NATURAL PLASTICS

Historians frequently classify the early ages of man according to the materials that he used for making his implements and other basic necessities. The most well known of these periods are the Stone Age, the Iron Age and the Bronze Age. Such a system of classification cannot be used to describe subsequent periods for with the passage of time man learnt to use other materials and by the time of the ancient civilisations of Egypt and Babylonia he was employing a range of metals, stones, woods, ceramics, glasses, skins, horns and fibres. Until the 19th century man's inanimate possessions, his home, his tools, his furniture, were made from varieties of these eight classes of material.

During the last century and a half, two new closely related classes of material have been introduced which have not only challenged the older materials for their well-established uses but have also made possible new products which have helped to extend the range of activities of mankind. Without these two groups of materials, rubbers and plastics, it is difficult to conceive how such everyday features of modern life such as the motor car, the telephone and the television set could ever have been developed.

Whereas the use of natural rubber was well established by the start of the twentieth century, the major growth period of the plastics industry has been since 1930. This is not to say that some of the materials now classified as plastics were unknown before this time since the use of the natural plastics may be traced well into antiquity.

In the book of *Exodus* (Chapter 2) we read that the mother of Moses 'when she could no longer hide him, she took for him an ark of bullrushes and daubed it with slime and with pitch, and put the child therein and she laid it in the flags by the river's brink'. Biblical commentaries indicate that slime is the same as bitumen but whether or not this is so we have here the precursor of our modern fibre-reinforced plastics boat.

The use of bitumen is mentioned even earlier. In the book of *Genesis* (Chapter 11) we read that the builders in the plain of Shinar (i.e. Babylonia) 'had brick for

2 The Historical Development of Plastics Materials

stone and slime they had for mortar'. In *Genesis* (Chapter 14) we read that 'the vale of Siddim was full of slimepits; and the Kings of Sodom and Gomorrah fled, and fell there; and they that remained fled to the mountain'.

In Ancient Egypt mummies were wrapped in cloth dipped in a solution of bitumen in oil of lavender which was known variously as Syrian Asphalt or Bitumen of Judea. On exposure to light the product hardened and became insoluble. It would appear that this process involved the action of chemical cross-linking, which in modern times became of great importance in the vulcanisation of rubber and the production of thermosetting plastics. It was also the study of this process that led Niepce to produce the first permanent photograph and to the development of lithography (see Chapter 14).

In Ancient Rome, Pliny the Elder (c. A.D. 23–79) dedicated 37 volumes of *Natural History* to the emperor Titus. In the last of these books, dealing with gems and precious stones, he describes the properties of the fossil resin, amber. The ability of amber to attract dust was recognised and in fact the word electricity is derived from *elektron*, the Greek for amber.

Further east another natural resin, lac, had already been used for at least a thousand years before Pliny was born. Lac is mentioned in early Vedic writings and also in the *Kama Sutra* of Vatsyayana. In 1596 John Huyglen von Linschoeten undertook a scientific mission to India at the instance of the King of Portugal. In his report he describes the process of covering objects with shellac, now known as Indian turnery and still practised:

'Thence they dresse their besteds withall, that is to say, in turning of the woode, they take a peece of Lac of what colour they will, and as they turme it when it commeth to his fashion they spread the Lac upon the whole peece of woode which presently, with the heat of the turning (melteth the waxe) so that it entreth into the crestes and cleaveth unto it, about the thickness of a mans naile: then they burnish it (over) with a broad straw or dry rushes so (cunningly) that all the woode is covered withall, and it shineth like glasse, most pleasant to behold, and continueth as long as the woode being well looked unto: in this sort they cover all kind of household stufte in India, as Bedsteddes, Chaires, stoolles, etc. . . .'

Early records also indicate that cast mouldings were prepared from shellac by the ancient Indians. In Europe the use of sealing wax based on shellac can be traced back to the Middle Ages. The first patents for shellac mouldings were taken out in 1868.

The introduction to western civilisation of another natural resin from the east took place in the middle of the 17th century. To John Tradescant (1608–1662), the English traveller and gardener, is given the credit of introducing gutta percha. The material became of substantial importance as a cable insulation material and for general moulding purposes during the 19th century and it is only since 1940 that this material has been replaced by synthetic materials in undersea cable insulation.

Prior to the eastern adventures of Linschoeten and Tradescant, the sailors of Columbus had discovered the natives of Central America playing with lumps of natural rubber. These were obtained, like gutta percha, by coagulation from a latex; the first recorded reference to natural rubber was in Valdes *La historia natural y general de las Indias*, published in Seville (1535–1557). In 1731 la Condamine, leading an expedition on behalf of the French government to study the shape of the earth, sent back from the Amazon basin rubber-coated cloth prepared by native tribes and used in the manufacture of waterproof shoes and flexible bottles.

The coagulated rubber was a highly elastic material and could not be shaped by moulding or extrusion. In 1820 an Englishman, Thomas Hancock, discovered that if the rubber was highly sheared or masticated, it became plastic and hence capable of flow. This is now known to be due to severe reduction in molecular weight on mastication. In 1839 an American, Charles Goodyear, found that rubber heated with sulphur retained its elasticity over a wider range of temperature than the raw material and that it had greater resistance to solvents. Thomas Hancock also subsequently found that the plastic masticated rubber could be regenerated into an elastic material by heating with molten sulphur. The rubber-sulphur reaction was termed vulcanisation by William Brockendon, a friend of Hancock. Although the work of Hancock was subsequent to, and to some extent a consequence of, that of Goodyear, the former patented the discovery in 1843 in England whilst Goodyear's first (American) patent was taken out in 1844.

In extensions of this work on vulcanisation, which normally involved only a few per cent of sulphur, both Goodyear and Hancock found that if rubber was heated with larger quantities of sulphur (about 50 parts per 100 parts of rubber) a hard product was obtained. This subsequently became known variously as ebonite, vulcanite and hard rubber. A patent for producing hard rubber was taken out by Nelson Goodyear in 1851.

The discovery of ebonite is usually considered as a milestone in the history of the rubber industry. Its importance in the history of plastics materials, of which it obviously is one, is generally neglected. Its significance lies in the fact that ebonite was the first thermosetting plastics material to be prepared and also the first plastics material which involved a distinct chemical modification of a natural material. By 1860 there was a number of manufacturers in Britain, including Charles Macintosh who is said to have started making ebonite in 1851. There are reports of the material having been exhibited at the Great Exhibition of 1851.

1.2 PARKESINE AND CELLULOID

While Hancock and Goodyear were developing the basic processes of rubber technology, other important discoveries were taking place in Europe. Following earlier work by Pelouze, Schönbein was able to establish conditions for controlled nitration of cellulose. The product soon became of interest as an explosive and in the manufacture of collodion, a solution in an alcohol-ether mixture. In the 1850s the English inventor Alexander Parkes 'observed after much research, labour and investigation that the solid residue left on the evaporation of the solvent of photographic collodion produced a hard, horny elastic and waterproof substance'. In 1856 he patented the process of waterproofing woven fabrics by the use of such solutions.

In 1862 the Great International Exhibition was held in London and was visited by six million people. At this exhibition a bronze medal was awarded to Parkes for his exhibit Parkesine. This was obtained by first preparing a suitable cellulose nitrate and dissolving it in a minimum of solvent. The mixture was then put on a heated rolling machine, from which some of the solvent was then removed. While still in the plastic state the material was then shaped by 'dies or pressure'. In 1866 the Parkesine Co., Ltd was formed but it failed in 1868. This appears in part due to the fact that in trying to reduce production costs products inferior to

4 *The Historical Development of Plastics Materials*

those exhibited in 1862 were produced. Although the Parkesine Company suffered an economic failure, credit must go to Parkes as the first man to attempt the commercial exploitation of a chemically modified polymer as a thermoplastics material.

One year after the failure of the Parkesine Company a collaborator of Parkes, Daniel Spill, formed the Xylonite Company to process materials similar to Parkesine. Once again economic failure resulted and the Company was wound up in December 1874. Undaunted, Spill moved to a new site, established the Daniel Spill Company and working in a modest way continued production of Xylonite and Ivoride.

In America developments were also taking place in the use of cellulose nitrate. In 1865 John Wesley Hyatt who, like Parkes and Spill, had had no formal scientific training, but possessed that all-important requirement of a plastics technologist—inventive ingenuity—became engrossed in devising a method for producing billiard balls from materials other than ivory. Originally using mixtures of cloth, ivory dust and shellac, in 1869 he patented the use of collodion for coating billiard balls. The inflammability of collodion was quickly recognised. In his history of plastics, Kaufman¹ tells how Hyatt received a letter from a Colorado billiard saloon proprietor commenting that occasionally the violent contact of the balls would produce a mild explosion like a percussion guncap. This in itself he did not mind but each time this happened 'instantly every man in the room pulled a gun'.

Products made up to this time both in England and the United States suffered from the high shrinkage due to the evaporation of the solvent. In 1870 J. W. Hyatt and his brother took out US Patent 105338 for a process of producing a horn-like material using cellulose nitrate and camphor. Although Parkes and Spill had mentioned camphor in their work it was left to the Hyatt brothers to appreciate the unique value of camphor as a plasticiser for cellulose nitrate. In 1872 the term celluloid was first used to describe the product, which quickly became a commercial success. The validity of Hyatts patents was challenged by Spill and a number of court actions took place between 1877 and 1884. In the final action it was found that Spill had no claim on the Hyatt brothers, the judge opining that the true inventor of the process was in fact Alexander Parkes since he had mentioned the use of both camphor and alcohol in his patents. There was thus no restriction on the use of these processes and any company, including the Hyatts Celluloid Manufacturing Company, were free to use them. As a result of this decision the Celluloid Manufacturing Company prospered, changed its name to the American Celluloid and Chemical Corporation and eventually became absorbed by the Celanese Corporation.

It is interesting to note that during this period L. P. Merriam and Spill collaborated in their work and this led to the formation in 1877 of the British Xylonite Company. Although absorbed by the Distillers organisation in 1961, and subsequently subjected to further industrial take-overs, this company remains an important force in the British plastics industry.

1.3 1900–1930

By 1900 the only plastics materials available were shellac, gutta percha, ebonite and celluloid (and the bitumens and amber if they are considered as plastics). Early experiments leading to other materials had, however, been carried out. The

first group of these to bear fruit were those which had been involved with the milk protein, casein. About 1897 there was a demand in German schools for what may only be described as a white blackboard. As a result of efforts to obtain such a product, Krische and Spitteler were able to take out patents describing the manufacture of casein plastics by reacting casein with formaldehyde. The material soon became established under the well-known trade names of Galalith and later Erinoid and today casein plastics still remain of interest to the button industry.

The ability of formaldehyde to form resinous substances had been observed by chemists in the second half of the 19th century. In 1859 Butlerov described formaldehyde polymers while in 1872 Adolf Bayer reported that phenols and aldehydes react to give resinous substances. In 1899 Arthur Smith took out British Patent 16 274, the first dealing with phenol–aldehyde resins, in this case for use as an ebonite substitute in electrical insulation. During the next decade the phenol–aldehyde reaction was investigated, mainly for purely academic reasons, but, on occasion, in the hope of commercial exploitation. In due course Leo Hendrik Baekeland discovered techniques of so controlling and modifying the reaction that useful products could be made. The first of his 119 patents on phenol–aldehyde plastics was taken out in 1907, and in 1910 the General Bakelite Company was formed in the United States. Within a very few years the material had been established in many fields, in particular for electrical insulation. When Baekeland died in 1944 world production of phenolic resins was of the order of 175 000 tons per annum and today annual consumption of the resins is still substantial.

Whereas celluloid was the first plastics material obtained by chemical modification of a polymer to be exploited, the phenolics were the first commercially successful fully synthetic resins. It is interesting to note that in 1963, by a merger of two subsidiary companies of the Union Carbide and the Distillers organisations, there was formed the Bakelite Xylonite Company, an intriguing marriage of two of the earliest names in the plastics industry.

The success of phenol–formaldehyde mouldings stimulated research with other resins. In 1918 Hans John prepared resins by reacting urea with formaldehyde. The reaction was studied more fully by Pollak and Ripper in an unsuccessful attempt to produce an organic glass during the period 1920–1924. At the end of this period the British Cyanides Company (later to become British Industrial Plastics), who were in financial difficulties, were looking around for profitable outlets for their products. E. C. Rossiter suggested that they might investigate the condensation of thiourea, which they produced, with formaldehyde. Although at the time neither thiourea–formaldehyde nor urea–formaldehyde resins proved of value, resins using urea and thiourea with formaldehyde were made which were successfully used in the manufacture of moulding powders. Unlike the phenolics, these materials could be moulded into light-coloured articles and they rapidly achieved commercial success. In due course the use of thiourea was dropped as improvements were made in the simpler urea–formaldehyde materials. Today these resins are used extensively for moulding powders, adhesives and textile and paper finishing whilst the related melamine–formaldehyde materials are also used in decorative laminates.

During the time of the development of the urea-based resins, a thermoplastic, cellulose acetate, was making its debut. The material had earlier been extensively used as an aircraft dope and for artificial fibres. The discovery of suitable

plasticisers in 1927 led to the introduction of this material as a non-inflammable counterpart of celluloid. During the next ten years the material became increasingly used for injection moulding and it retained its pre-eminent position in this field until the early 1950s.

1.4 THE EVOLUTION OF THE VINYL PLASTICS

The decade 1930–1940 saw the initial industrial development of four of today's major thermoplastics: polystyrene, poly(vinyl chloride) (PVC), the polyolefins and poly(methyl methacrylate). Since all these materials can be considered formally as derivatives of ethylene they have, in the past, been referred to as ethenoid plastics; however, the somewhat inaccurate term *vinyl plastics* is now usually preferred.

About 1930 I.G. Farben, in Germany, first produced polystyrene, whilst at the same time the Dow Chemical Company commenced their ultimately successful development of the material.

Commercial interest in PVC also commenced at about this time. The Russian, I. Ostromislensky, had patented the polymerisation of vinyl chloride and related substances in 1912, but the high decomposition rate at processing temperatures proved an insurmountable problem for over 15 years. Today PVC is one of the two largest tonnage plastics materials, the other being polyethylene.

The discovery and development of polyethylene provides an excellent lesson in the value of observing and following up an unexpected experimental result. In 1931 the research laboratories of the Alkali Division of Imperial Chemical Industries designed an apparatus to investigate the effect of pressures up to 3000 atmospheres on binary and ternary organic systems. Many systems were investigated but the results of the experiments did not show immediate promise. However, E. W. Fawcett and R. O. Gibson, the chemists who carried out the research programme, noticed that in one of the experiments in which ethylene was being used a small amount of a white waxy solid had been formed. On analysis this was found to be a polymer of ethylene.

In due course attempts were made to reproduce this polymer. It was eventually discovered that a trace of oxygen was necessary to bring about the formation of polyethylene. In the original experiment this had been present accidentally, owing to a leak in the apparatus. Investigation of the product showed that it was an excellent electrical insulator and that it had very good chemical resistance. At the suggestion of B. J. Habgood its value as a submarine cable insulator was investigated with the assistance of J. N. Dean (later Sir John Dean) and H. F. Wilson of the Telegraph Construction and Maintenance Company (Telcon).

Polyethylene was soon seen to have many properties suitable for this purpose and manufacture on a commercial scale was authorised. The polyethylene plant came on stream on 1st September 1939, just before the outbreak of World War II.

During this period, the ICI laboratories were also making their other great contribution to the range of plastics materials—the product which they marketed as Perspex, poly(methyl methacrylate). As a result of work by two of their chemists, R. Hill and J. W. C. Crawford, it was found that a rigid transparent thermoplastics material could be produced at a commercially feasible cost. The material became invaluable during World War II for aircraft glazing and to a lesser extent in the manufacture of dentures. Today poly(methyl methacrylate) is

produced in many countries and used for a wide variety of applications particularly where transparency and/or good weathering resistance are important.

1.5 DEVELOPMENTS SINCE 1939

The advent of war brought plastics more into demand, largely as substitutes for materials, such as natural rubber and gutta percha, which were in short supply. In the United States the crash programme leading to the large-scale production of synthetic rubbers resulted in extensive research into the chemistry underlying the formation of polymers. A great deal of experience was also obtained on the large-scale production of such materials.

New materials also emerged. Nylon, developed brilliantly by W. H. Carothers and his team of research workers for Du Pont as a fibre in the mid-1930s, was first used as a moulding material in 1941. Also in 1941 a patent taken out by Kinetic Chemical Inc. described how R. J. Plunkett had first discovered polytetrafluoroethylene. This happened when, on one occasion, it was found that on opening the valve of a supposedly full cylinder of the gas tetrafluoroethylene no gas issued out. On subsequently cutting up the cylinder it was found that a white solid, polytetrafluoroethylene (PTFE), had been deposited on the inner walls of the cylinder. The process was developed by Du Pont and, in 1943, a pilot plant to produce their product Teflon came on stream.

Interesting developments were also taking place in the field of thermosetting resins. The melamine-formaldehyde materials appeared commercially in 1940 whilst soon afterwards in the United States the first 'contact resins' were used. With these materials, the forerunners of today's polyester laminating resins, it was found possible to produce laminates without the need for application of external pressure. The first experiments in epoxide resins were also taking place during this period.

The first decade after the war saw the establishment of the newer synthetics in many applications. Materials such as polyethylene and polystyrene, originally rather expensive special purpose materials, were produced in large tonnages at low cost and these started to oust some of the older materials from established uses. The new materials were, however, not only competitive with the older plastics but with the more traditional materials such as metals, woods, glasses and leathers. In some instances the use of plastics materials was unwise but in others the use of plastics was of great value both technically and economically. The occasional misuse of plastics was damaging to the industry and plastics became surrounded with an aura of disrepute for many years. In due course it was appreciated that it was unfair to blame the plastics themselves. Slowly there has developed an understanding of the advantages and limitations of the individual plastics in the way that we have for many years appreciated the good and bad features of our traditional materials. Wood warps and rots, iron rusts and much glass is brittle yet no one disputes the enormous value of these materials.

In the period 1945-1955, while there was a noticeable improvement in the quality of existing plastics materials and an increase in the range of grades of such materials, few new plastics were introduced commercially. The only important newcomer was high-impact polystyrene and, at the time of its introduction, this was a much inferior material to the variants available today.

In the mid-1950s a number of new thermoplastics with some very valuable properties became available. High-density polyethylenes produced by the Phillips process and the Ziegler process were marketed and these were shortly followed by the discovery and rapid exploitation of polypropylene. These polyolefins soon became large tonnage thermoplastics. Somewhat more specialised materials were the acetal resins, first introduced by Du Pont, and the polycarbonates, developed simultaneously but independently in the United States and Germany. Further developments in high-impact polystyrenes led to the development of ABS polymers.

The discovery and development of polypropylene, the one genuinely new large tonnage thermoplastics material developed since World War II, forms part of what is arguably the most important episode in the history of polymer science. For many years it had been recognised that natural polymers were far more regular in their structure than synthetic polymers. Whilst there had been some improvement in controlling molecular architecture, the man-made materials, relative to the natural materials, were structurally crude.

The work which was eventually to put the structure of the synthetics within striking distance of the natural polymers started as long ago as the late 1920s when Karl Ziegler became interested in the then relatively obscure area of organometallic chemistry. At that time the possibility of a connection with the infant plastics industry was not even considered. In 1943 Ziegler was made Director of the Max Planck Institute for Coal Research, a post he accepted with some reluctance because of his wish to continue his research without having to have regard for the relevance of this work to coal. In the event he was allowed to pursue his studies and eventually he found that he was able to grow long hydrocarbon chains by linking a series of ethylene molecules onto aluminum alkyls. These materials had molecular weights up to about 1000, about one-thirtieth of that required for a useful polyethylene. At this stage it appears that Ziegler and his colleagues believed that some impurity was inhibiting further growth and in an attempt to track it down they found quite fortuitously that if titanium tetrachloride was added there was an increase in the reaction rate and furthermore it became possible to produce high molecular weight materials.

Further investigation showed that these new polyethylenes had distinctive properties compared with the older materials developed by ICI. They had a higher softening point, were stiffer and had a higher density. This method of using organometallic compounds in conjunction with a second material such as a titanium halide was then developed by Giulio Natta working at the Polytechnic Institute in Milan. He found that, by varying the detailed form of the catalyst, varying types of polypropylene could be produced, one variety of which, isotactic polypropylene, was found to exhibit particularly useful properties. In addition Natta was able to polymerise several other monomers that had previously been reluctant to polymerise, again into diverse structural forms. The work also led to the production of polymers with a fine structure much closer to that of the natural rubber molecule than had been hitherto achieved and to the preparation of the now important ethylene-propylene rubbers. In due course Ziegler and Natta were both awarded the Nobel Prize for Chemistry for the development of what are now known as Ziegler-Natta catalysts.

In attempts to understand more fully the mechanism of Ziegler-Natta polymerisations chemists came to develop what have become known as metallocene catalysts for polymerisation. In due course it was found possible to

control more closely polymer structure than with previous systems. This has resulted in the appearance in the late 1990s of a number of interesting polymers based, mainly, on ethylene, propylene and styrene. The potential of such polymers has yet to be fully realised but intensive development work is currently underway.

As the author pointed out in the first edition of this book, the likelihood of discovering new important general purpose materials was remote but special purpose materials could be expected to continue to be introduced. To date this prediction has proved correct and the 1960s saw the introduction of the polysulphones, the PPO-type materials, aromatic polyesters and polyamides, the ionomers and so on. In the 1970s the new plastics were even more specialised in their uses. On the other hand in the related fields of rubbers and fibres important new materials appeared, such as the aramid fibres and the various thermoplastic rubbers. Indeed the division between rubbers and plastics became more difficult to draw, with rubbery materials being handled on standard thermoplastics-processing equipment.

The lack of new plastics in the late 1960s did not deter the growth of the plastics industries around the world and production reached levels an order of magnitude higher than 20 years before. Then in 1973 came the first serious check to growth that had been seen by the industry since the war. This arose from the oil crisis and it is now pertinent to consider the dependence of plastics on oil and other raw materials.

1.6 RAW MATERIALS FOR PLASTICS

Today, the plastics industry is heavily integrated with the oil industry. In fact a popular view is that it would not be able to produce plastics if oil were not available. This is very different from the situation 40–50 years ago when the plastics industry was being described as a ‘scavenger of raw materials’.

Before World War II the most important class of thermoplastics, the cellulose, were produced from vegetable sources, cellulose being an important constituent of vegetable matter. From waste oat husks were produced the furane plastics whilst routes to the nylons were also developed from this raw material. Henry Ford had experimented with soya bean plastics and several plastics had been derived from natural rubber. After the war ICI produced a protein fibre, Ardil, from ground nuts whilst vegetable oils became a source for producing some of the acids used in nylon manufacture. Early grades of polyethylene were obtained from sugar cane via molasses, ethyl alcohol and ethylene. Some of these processes are still of importance but their relative significance has declined. On the other hand they could be revived and extended should the need arise.

There is rather less scope for the re-emergence of the animal-based plastics such as casein, shellac and the blood albumin products.

Until the mid-1950s the main raw material source for the European plastics industry was coal. On destructive distillation coal yields four products: coal tar, coke, coal gas and ammonia. Coal tar was an important source of aromatic chemicals such as benzene, toluene, phenol, naphthalene and related products. From these materials other chemicals such as adipic acid, hexamethylenediamine, caprolactam and phthalic anhydride could be produced, leading to such important plastics as the phenolic resins, polystyrene and the nylons.

Reaction of coke with calcium oxide gives calcium carbide, which on treatment with water produces acetylene. This was for many years an important starting point for the production of acrylonitrile, vinyl chloride, vinyl acetate and other vinyl monomers. Furthermore, during World War II, Reppe developed routes for many other monomers although these were not viable under normal economic conditions.

The development of the petrochemical industry is probably the greatest single contributing factor in the growth of the plastics industry, the two industries today having a remarkable degree of interdependence. In the first instance the growth potential of plastics stimulated research into the production of monomers and other intermediates from petroleum. As a result there became available cheap and abundant intermediates which in turn stimulated further growth of the plastics industry in a way which would not have been possible if the industry had been dependent on coal alone.

The petrochemical industry was founded shortly after the World War I to produce solvents from olefins which were then merely waste-products of 'cracking'—the process of breaking down higher molecular weight petroleum fractions into lower molecular weight products, such as gasoline. By the advent of World War II petrochemicals were also being used to produce ethylene dichloride, vinyl chloride, ethylene glycol, ethylene oxide and styrene. During World War II the large synthetic rubber industry created in the United States used butadiene and styrene, the former entirely and the latter partly derived from petroleum. Whilst in its early days polyethylene was produced from molasses via ethyl alcohol and ethylene, today ethylene used for polymerisation, and for other purposes, is obtained almost entirely from petroleum.

With each succeeding year in the 1950s and 1960s there was a swing away from coal and vegetable sources of raw materials towards petroleum. Today such products as terephthalic acid, styrene, benzene, formaldehyde, vinyl acetate and acrylonitrile are produced from petroleum sources. Large industrial concerns that had been built on acetylene chemistry became based on petrochemicals whilst coal tar is no longer an indispensable source of aromatics.

There are three general routes for producing intermediates from petroleum:

- (1) Separation of individual saturated hydrocarbons from the petroleum fractions and subsequent conversion to more useful products. Important examples are n-butane to butadiene and cyclohexane to nylon intermediates.
- (2) Separation of olefins produced by cracking operations and subsequent conversion. This is the major route to aliphatic petrochemicals.
- (3) Formation of aromatic structures such as benzene and its homologues by 'platforming' and other processes. This route is of ever increasing importance in the production of aromatic materials.

These three initial classes of product may then be converted to other chemicals by oxidation, halogenation, alkylation, hydration, carbonylation, telomerisation and many other reactions. There are nowadays few intermediates for plastics that cannot be produced more cheaply from petroleum than from other sources.

During the 1960s and early 1970s the choice was not so much petroleum *versus* coal but which petroleum route to use. However, there has now arisen a growing awareness of the fact that petroleum resources are not unlimited. This led to substantial increases in petroleum prices.

1.7 THE MARKET FOR PLASTICS

Some idea of the spectacular growth in the plastics industry may be obtained from consideration of *Table 1.1*. Whilst growth in percentage terms was greatest before 1973, it has remained high in tonnage terms up to the present time.

Table 1.2, based on *Modern Plastics sources*, provides USA consumption figures (based on sales data) for the main groups of plastics materials. The figures probably underestimate the global importance of the major tonnage thermoplastics since these are also manufactured in quantity in developing countries and OPEC countries.

The similarity between USA and Western Europe data is quite striking. In recent years the dominance of these two areas, which traditionally accounted for at least two-thirds of the market, has decreased and by 1998 was closer to 50% of the market. This was as a result of growth in production in petroleum-exporting countries, in Latin America and, particularly, in the Pacific Rim area. However, the economic turmoil which particularly affected the latter from 1997 is in early 1999 having an influence whose consequences are not yet clear.

One recurring problem has been that a perceived shortage of a particular material has led to plans by more than one company to build large plants to produce that material, so that a shortage is then followed by a period of severe excess capacity and depressed polymer prices.

As already mentioned, much of the use for plastics just after World War II was as a cheap substitute for traditional materials, and in other cases the material was used for its novelty value. In many instances the result was detrimental to the industry and it required several years of painstaking work by the technical service departments of the major plastics materials manufacturers before confidence was regained in the use of plastics. Even today the public image of plastics is not entirely positive and the significant contribution of plastics to raising the standard of living and quality of life is not fully recognised.

Table 1.1 World and USA production of plastics materials (Much of the earlier data are based on long tons; later data are in tonnes. The USA figures are based on estimates published in *Modern Plastics*, apart from those for 1967, which are from US government sources. The global figures are from various sources, with the 1992 figure being based on RAPRA statistics.)

Year	World	USA
1939	300 000	90 000
1951	2 000 000	810 000
1957	4 600 000	1 920 000
1960	6 200 000	2 480 000
1963	8 500 000	3 730 000
1967	18 000 000	5 567 000
1973	—	13 182 000
1980	50 000 000	16 117 000
1986	—	22 522 000*
1992	91 237 000	29 890 000*
1998	135 000 000	33 500 000

*These figures are based on sales figures, not production.

Table 1.2 Relative importance of major plastics materials in the USA and Western Europe. Consumption data based on estimates published in *Modern Plastics International*.

Material	'000 tonnes				
	USA		Western Europe 1997		
	1987	1997			
Polyethylene (LD and LLD)	4322	7118	13 226	6219	
Polyethylene (HD)	3560	6108			3850
PVC and copolymers		3665	6395	5575	
Polypropylene and copolymers		2945	5905	5801	
Styrene polymers					
Polystyrene	2210	2907	3547	1989	
ABS/SAN	589	6640			580
Other	—	—			720
Polyurethane	1220	2190		not available	
Polyamides	214	533		532	
Polyacetals	—	167		140	
Acrylics	303	277		256	
Polycarbonates including blends	176	436		662	
Thermoplastic polyesters	819	1844		1203	
Polyesters (unsaturated)	598	760		449	
Phenolics	1258				
Aminoplastics	712				
Epoxide resins	184				

NB Data for the three important thermosetting materials (phenolics, aminoplastics and epoxide resins) were not covered in the 1998 review on which the 1997 data was based. The 1987 figures for these materials do include a substantial percentage of use in adhesive, surface coating and laminate applications.

In some outlets plastics materials have been long established. A prime example is in the electrical industries where the combination of excellent insulation properties with toughness, durability and, where desired, flame retardant characteristics have led to wide acceptance for plugs, sockets, wire and cable insulation. The ability of polyethylene to act as an excellent insulator at high frequencies was of great significance in the early development of radar. In this area three recent trends are discernible. Firstly there has been increasing acceptance of plastics for housing electrical and electronic equipment, leading to increased use of the more general purpose plastics. Secondly the development of microprocessors and the silicon chip has meant that components are becoming smaller and thus less plastics materials per part are used and in some cases even eliminated. Thirdly plastics are finding use in sophisticated techniques. For example, the photoconductive behaviour of poly(vinyl carbazole) is made use of in electrostatic copying equipment and in the preparation of holographs whilst the peculiar piezo-electric and pyro-electric properties of poly(vinylidene fluoride) are being utilised in transducers, loudspeakers and detectors.

In the building industry there was much emphasis in the early 1960s on the all-plastics house although the raw material suppliers who sponsored their design probably thought of them primarily as publicity exercises. As the plastics industry has matured it has been realised that it is better to emphasise those applications where plastics are preferable to traditional materials and this

approach has led to widespread acceptance. Uses include piping, guttering and conduit, damp course layers, flooring, insulation, wall cladding and window frames. Quite rightly government organisations have been concerned about possible fire risks and although regulations have seemed unduly restrictive to some, others will feel that they have avoided unjustified excesses in the use of plastics.

Plastics have been widely accepted as packaging materials. Plastics bottles have been particularly appreciated in the bathroom, where breakage of glass containers has led to many serious accidents. The ability of many materials to withstand the most corrosive chemicals has been of benefit to the chemical and related industries whilst the light weight compared with a glass bottle reduces the energy required for transportation. Small containers are also widely made from plastics and for medicines, particularly in tablet form, the use of closures that cannot be prised open by young children is particularly valuable. The wide use of plastics films for wrapping, for bags and sacks is almost too well known for comment. The sheer quantity of plastics used in this area nevertheless attracts critical comment, in particular that some goods are overpackaged and that waste plastics film left lying around is likely to be an all-too-durable eyesore. In many countries paper bag manufacturers have stressed the environmental desirability of using their products and in turn this has stimulated research into biodegradable plastics.

The automotive industry is now a major user of plastics, with the weight of plastics being used per car increasing year by year. It has recently been stated that in the early 1990s the average car contained some 75 kg of plastics. For many years the main uses were associated with car electrical equipment such as batteries, flex, plugs, switches and distributor caps. Plastics then became established in light fittings, seating upholstery and interior body trim. In recent times there has been increased use in under-the-bonnet (under-the-hood) applications such as radiator fans, drain plugs, petrol tubing and coolant water reservoirs. In many applications the weight of material used is small. For example, it has been stated that in one small European car there were 450 different parts made from polyacetal plastics but which had a total weight of only one kilogram. The requirements of fuel economy demanding lighter cars and of increased occupant safety have led to a substantially increased use of plastics materials for bumpers, radiator grilles and fascia assemblies. Indeed if it were not for the trend towards fabric rather than leathercloth upholstery most parts of the car within reach of the driver other than the windows would be made from rubbers and plastics, and even then the fabric and the glass are polymeric!

Plastics also find increasing use in vehicles for both water and air transport. Glass-fibre-reinforced plastic boats are widely used as a result of their economy in manufacture, ease of maintenance, lightness of weight and, for military purposes, antimagnetic characteristics. The non-corrosive nature of plastics also leads to their widespread use in boat fixtures and fittings. In aircraft, plastics are particularly useful on account of their low density.

Domestic and commercial furniture and fittings form another important market. Uses include stacking chairs, armchair body shells, foam upholstery and desk and cupboard drawers, whilst chipboard and decorative laminates are very widely used. The variety of finishes possible at a relatively low cost compared to traditional materials as well as ease of maintenance are important in raising standards of living around the world. As with other applications the use of plastics in furniture is not without its detractors and in particular there is concern

about the inflammability of those plastics that are used in a form which has a high surface-to-volume ratio, such as polyurethane foams. Whilst most of the problem appears to lie in the correct choice of covering fabric the matter continues to require attention.

Industrial equipment is a continuing area of development for plastics. Pipes, pumps, valves and sight glasses, made from such materials as PVC, PTFE and poly-4-methylpent-1-ene, have become well established on account of their corrosion resistance. The nylons are used for such diverse applications as mine conveyor belts and main drive gears for knitting machines and paper-making equipment. These and other materials are widely used where such features as toughness, abrasion resistance, corrosion resistance, non-stick properties, electrical insulation capability and transparency are of importance.

In the general area of medicine uses range from spare-part surgery, such as hip joints and heart valves, through catheters, injection syringes and other sterilisable equipment, to more mundane but nevertheless desirable uses such as quiet-running curtain rails.

In agriculture and horticulture plastics are most widely known in film form but they also find use for water piping containers, automatic watering equipment and potato chitting trays to name but a few uses.

What may loosely be described as the leisure industries are widespread users of plastics. The photographic industry was of course one of the earliest users of plastics, for photographic film. There has also been widespread use of plastics in darkroom equipment for many years. More recently there has been increasing acceptance of plastics in cameras, both inexpensive and expensive. It is now recognised that well-designed camera bodies made from the correct plastics materials are more able to withstand rough usage than metal camera bodies, particularly in resistance to denting. In the audio field use of plastics for tapes and compact discs is well-established whilst plastics are now almost standard for the housings of reproduction equipment. Sports equipment makes increasing use of glass- and even carbon-fibre-reinforced materials for such diverse articles as fishing rods, canoes, racquets and so on. Toys and games (both for children and adults!) make wide use of the materials that form the subject of this book.

The widespread use of plastics film for printing paper appears to be only a remote possibility in the near future. There is, however, the prospect of the establishment of polyethylene film for use in service manuals, maps and other printed articles which are required to be resistant to water, oils and other liquids.

Whilst natural and synthetic fibres will no doubt remain the major materials for clothing, plastics will be more widely employed. Footwear will provide the major outlet; not only are plastics likely to be used in soles and uppers but there is an increasing use of the all-plastics moulded shoe, which although unacceptable for general wear in Britain is in high demand in under-developed regions of the world. In rainwear, plastics and rubbers will continue to be used for waterproof lining and in the manufacture of the all-plastics packable mackintosh. Polyurethane foam will find increased use as the insulation layer in cold-weather apparel and for giving 'body' to clothing, whilst other plastics will be widely used for stiffening of light fabrics.

The above paragraphs indicate some of the major uses of plastics materials, but these materials also find applications in a variety of other areas. In addition, closely related materials such as rubbers, fibres, surface coatings and adhesives are of considerable importance.

1.8 THE FUTURE FOR PLASTICS

This section was written for the fourth edition published in 1982 at a time when there had just been a further sharp increase in the price of petroleum. At the time I was optimistic about the future for plastics, although I did not anticipate the slump in oil prices that has taken place since then. Oil remains a finite resource and sooner or later prices will rise again. Apart from changing one word and inserting one other for technical reasons, I see no reason to otherwise change what I wrote then.

The advent of the oil crisis of 1973 led to dire predictions about the future of plastics materials, which to date have not been realised. Before attempting to predict what will happen in the next few years it is worthwhile to consider why the growth of plastics was so spectacular during the period 1945–1973.

In essence the reason for the spectacular growth lay in the interaction of three factors:

- (1) A growing understanding of the characteristics and capabilities of plastics materials.
- (2) An improving capability of plastics due to the appearance of new materials, improved qualities with existing types and better processing equipment.
- (3) A steady reduction in the cost of basic plastics raw materials relative to the cost of such traditional materials as leather, paper, metals and ceramics.

With respect to the first factor it is difficult in one paragraph to summarise the properties of plastics because they are so diverse in their behaviour. It is, however, possible to make a few rough generalisations on the characteristics of plastics. They are:

- (1) Because most plastics may be fabricated in the melt and at quite low temperatures (e.g. 200°C) the energy requirements for processing are low. Since plastics generally have low densities, costs of transportation and general handling are also relatively low.
- (2) Through the development of such techniques as injection moulding it is possible to make highly complex parts in one operation without the need for assembly work or the generation of more than a notional amount of scrap material.
- (3) Colouring is not usually restricted to the surface but is throughout the mass so that damage due to scratching and abrasion is less obvious than with coated metals.
- (4) An extremely wide range of surface finishes is possible which may not only simulate non-plastics materials but in addition produce novel effects.
- (5) The materials are generally excellent thermal insulators, being particularly useful in expanded form.
- (6) Many plastics are superb electrical insulators including, in many instances, good insulation characteristics at high frequencies.
- (7) Plastics are available in a wide range of strengths, flexibilities and degrees of toughness. Many fibre-reinforced grades have strength per unit weight figures as high as those of many metals.
- (8) Plastics are available in a wide range of chemical and solvent resistances. Some materials are available that are water soluble whilst others will withstand such aggressive materials as hydrofluoric acid.

The above are of course only some of the most common characteristics. Individual materials may have special properties such as photoconductivity, very low coefficient of friction to steel, high dielectric constant, high ultraviolet light transmission and so on.

The second factor listed above that affects the growth of plastics, namely improved capability, is self-explanatory, but the third, the decrease in relative costs for plastics, requires some explanation, particularly as this may have relevance to future prospects.

It may be argued that there were four main reasons why in general the price of plastics raw materials declined relatively, and often absolutely, between 1945 and 1973. These are:

- (1) The world-wide growth of the petrochemical industry which enabled plastics to be produced at lower cost than from other materials such as coal.
- (2) The economies of scale that follow from large reactors producing more economically than smaller ones.
- (3) Improvements in the methods of making polymers and their intermediate chemicals.
- (4) Intensive world-wide competition as first the major chemical companies in the main industrial countries entered the field of plastics manufacture, this being followed by the policy of many less industrialised countries to become involved in this area.

In the 1970s these reasons lost some of their force. Oil became more expensive, economies of scale appear to have reached a limiting value, improvements in manufacturing methods tend to have only a marginal effect whilst in some, but not all, areas there has been some abatement in the intensity of competition. This analysis does not, however, lead to a prediction of a bleak future for plastics. Apart from the oil cost these factors largely indicate that the plastics industry has become a mature industry, the future growth of which will be increasingly dependent on the global economic situation. In the case of oil a cost of 35 dollars a barrel is only equivalent to about 10 cents or five pence a pound. The cost of converting this oil to plastics materials and of transporting and processing them will often be much less than for similar activities with traditional materials. Hence provided that the price of plastics increases at a lower rate than for competitive alternative materials, and there is reason to believe that this will be the case, plastics may be expected to increase in their importance.

Another problem confronting the plastics industry, and in fact civilisation as a whole, which first came to the foreground in the 1970s, was the concern for the environment. There has been an increasing awareness of the need for conservation of resources, of the evils of pollution and of the fact that it is the quality of life rather than material possessions which is the criterion by which civilisation should be judged. As a result of this the chemical industries of the world have come under critical scrutiny and some of this has been reflected on to plastics. Unlike many lower molecular weight chemicals, plastics do not cause pollution, except where they may foul up water channels and underwater machinery. Like glass, metals and many other materials of civilisation they can be a litter problem. Because of their longevity, plastics packagings have received much criticism as causes of litter and while there may be some justification for this it is as well to realise the hazards of sharp metal and glass

objects which are also liable to litter the surfaces of the earth. Slums, car dumps and many older factories are much greater eyesores than plastics can ever be. There are also areas where the use of plastics can make a positive contribution in this connection. Every ton of metal removed from the earth necessitates the removal of hundreds of tons of earth and a severe despoliation of the landscape. Replacement by plastics made from petroleum taken from below the sea-bed helps to preserve the countryside or at least helps to conserve valuable metal resources for the future. There is also little doubt that the use of plastics has helped to raise the quality of life for very many people. The telephone, the gramophone record, the tape recorder, the photographic film, the radio and television which help us to see and hear things which few of us could see or hear at first hand depend on the existence of plastics. Many other objects which are common in industrialised societies, such as cars, refrigerators and small boats, would be afforded by far fewer people were it not for such materials as PVC, expanded and high-impact polystyrene and glass-reinforced polyesters. The mass production possible with plastics has enabled improvements in the standard of living in the much less wealthy areas of the world, whilst the use of plastics in surgery and medicine should eventually be of universal benefit.

A cautionary note is necessary here. Modern society has become highly dependent on petroleum as a cheap source of energy and raw materials. Progressive price increases and the growing shortage of this commodity occurring before the effective development of alternative energy sources are bound to have far-reaching effects on society in general and the plastics industry in particular. It is perhaps fortunate that plastics may be made from such diverse renewable vegetable products as cellulose, natural rubber, seaweed, oat husks, soya bean and molasses. Nevertheless it is to be hoped that it will be some time before we have to resort to such materials as our major sources of raw materials for plastics.

The widespread use of plastics has not been achieved without large-scale investment in research and development by those concerned. Polymer properties have been closely studied and slowly a relationship has been built up between structure and properties of polymers. In some instances the properties of a polymer were predicted before it was ever prepared. Studies of polymerisation methods have enabled a greater control to be made of the properties and structure of established polymers and have also led to the production of new polymers. It is sometimes said that 'once we polymerised monomers in solution, today we polymerise the solvent', for indeed polymers of acetone and tetrahydrofuran have been prepared. Many polymers would have remained of academic interest had not chemists devised new economic syntheses from raw materials. The polymers produced have been investigated by the technologist and methods of processing and compounding requirements developed. Mathematicians have assisted in interpreting the rheological and heat transfer data important for processing, engineers have developed machines of ever increasing sophistication, whilst suggested new applications have been vigorously pursued by sales organisations, often in conjunction with experts in aesthetics and design.

In this way chemist, physicist, mathematician, technologist, engineer, salesman and designer have all played a vital part. In many instances the tasks of these experts overlap but even where there is a clearer delineation it is important that the expert in one field should have a knowledge of the work of his counterparts in other fields. It is hoped that this volume will be of some assistance in achieving this end.

References

1. KAUFMAN, M., *The First Century of Plastics—Celluloid and its Sequel*, The Plastics Institute, London (1963)

Bibliography

- DINGLEY, C. S., *The Story of B.I.P.*, British Industrial Plastics, Birmingham (1963)
- FIELDING, T. J., *History of Bakelite Ltd.* Bakelite Ltd., London (c. 1948)
- HANCOCK, T., *Personal Narrative of the Origin and Progress of the Caoutchouc or India Rubber Manufacturers in England*, Longmans, London (1857). Centenary Edn (1920)
- HANCOCK, T., *Fourteen Patents*, Barclay, London (1853)
- HAYNES, W., *Cellulose—the Chemical that Grows*, Doubleday, New York (1953)
- KAUFMAN, M., *The First Century of Plastics—Celluloid and its Sequel*, The Plastics Institute, London (1963)
- SCHIDROWITZ, P. and DAWSON, T. R., *History of the Rubber Industry*. The Institution of the Rubber Industry, London (1952)
- Booklets published by British Xylonite Ltd. on the 50th and 75th anniversaries of the Company *Landmarks of the Plastics Industry* (1862–1962), ICI Plastics Division, Welwyn Garden City (1962)
- The Telcon Story, 1850–1950*, Telegraph Construction and Maintenance Co. Ltd., London (1950)

2

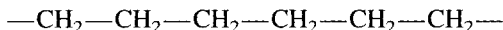
The Chemical Nature of Plastics

2.1 INTRODUCTION

Although it is very difficult and probably of little value to produce an adequate definition of the word 'plastics', it is profitable to consider the chemical structure of known plastics materials and try to see if they have any features in common.

When this is done it is seen that in all cases plastics materials, before compounding with additives, consist of a mass of very large molecules. In the case of a few naturally occurring materials, such as bitumen, shellac and amber, the compositions are heterogeneous and complex but in all other cases the plastics materials belong to a chemical family referred to as high polymers.

For most practical purposes a *polymer* may be defined as a large molecule built up by repetition of small, simple chemical units. In the case of most of the existing thermoplastics there is in fact only one species of unit involved. For example the polyethylene molecule consists essentially of a long chain of repeating $\text{---}(\text{CH}_2)\text{---}$ (methylene) groups, viz.



The lengths of these chains may be varied but in commercial polymers chains with from 1000 to 10 000 of these methylene groups are generally encountered. These materials are of high molecular weight and hence are spoken of as *high polymers* or *macromolecules*.

As a further illustration of the concept of polymers *Table 2.1* gives the repeating units of a number of other well-known plastics.

In addition to plastics materials, many fibres, surface coatings and rubbers are also basically high polymers, whilst in nature itself there is an abundance of polymeric material. Proteins, cellulose, starch, lignin and natural rubber are high polymers. The detailed structures of these materials are complex and highly sophisticated; in comparison the synthetic polymers produced by man are crude in the quality of their molecular architecture.

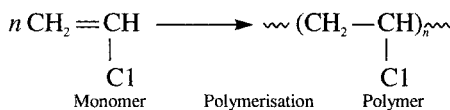
There are basically three ways by which polymers may be produced synthetically from simple starting materials. These techniques are referred to as

Table 2.1 Repeating units of some well-known polymers

Polymer	Repeating unit
Poly(vinyl chloride) Polystyrene	$\begin{array}{c} -\text{CH}_2 - \text{CHCl} - \\ -\text{CH}_2 - \text{CH} - \\ \\ \text{C}_6\text{H}_5 \end{array}$
Polypropylene	$\begin{array}{c} -\text{CH}_2 - \text{CH} - \\ \\ \text{CH}_3 \end{array}$
Nylon 66 Acetal resin	$\begin{array}{c} -(\text{CH}_2)_4\text{CONH}(\text{CH}_2)_6\text{NHOC}- \\ -\text{CH}_2 - \text{O} - \end{array}$

addition polymerisation, condensation polymerisation and rearrangement polymerisation.

In *addition polymerisation* a simple, low molecular weight molecule, referred to in this context as a *monomer*, which possesses a double bond, is induced to break the double bond and the resulting free valences are able to join up to other similar molecules. For example poly(vinyl chloride) is produced by the double bonds of vinyl chloride molecules opening up and linking together (*Figure 2.1*).

*Figure 2.1*

In these cases the monomer is converted into polymer, and no side products are formed. This approach is used with the major thermoplastics materials (*Figure 2.2*) such as polyethylene (a polymer of ethylene), polystyrene (a polymer of styrene) and poly(methyl methacrylate) (a polymer of methyl methacrylate).

In the above examples the polymerisation takes place by the opening of a carbon-carbon double bond. It is also possible to open carbonyl carbon-oxygen double bonds and nitrile carbon-nitrogen triple bonds. An example of the former is the polymerisation of formaldehyde to give polyformaldehyde (also known as polyoxymethylene and polyacetal) (*Figure 2.3*).

One other variant in double-bond polymerisations may be mentioned here. Many conjugated dienes may be polymerised in such a way as to generate long chain molecules with residual double bonds in the chain. Well-known examples of such dienes are buta-1,3-diene and isoprene, which yield 1,4-polybutadiene and 1,4-polyisoprene respectively (*Figure 2.4*). Natural rubber has a formula corresponding to the 1,4-polyisoprene.

An alternative technique is that of *condensation polymerisation*. A simple example of this is seen in the manufacture of linear polyesters. Here a dibasic acid is reacted with a dihydroxy compound, e.g. a glycol (*Figure 2.5*).

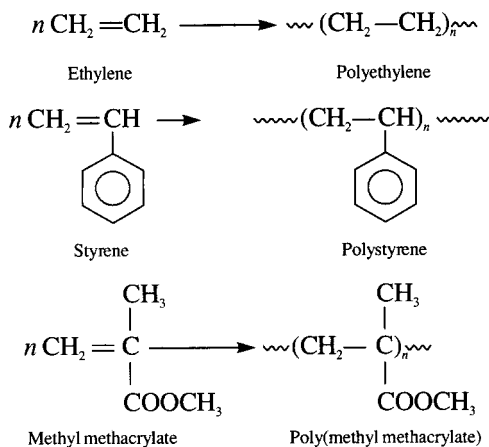


Figure 2.2

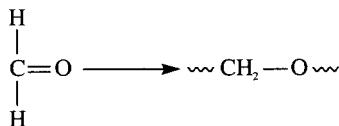


Figure 2.3

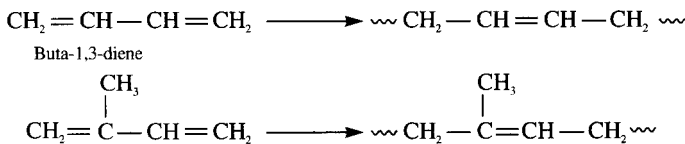


Figure 2.4

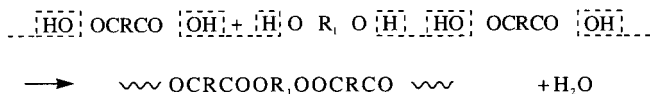


Figure 2.5

In this case each acid group reacts with a hydroxyl group with the elimination of water to form an ester linkage. As each molecule has two ends that can react in this way long chain molecules are progressively built up. Condensation polymerisation differs from addition polymerisation in that some small molecule is split out during the reaction. Furthermore, it is not essential that the monomer should contain a double bond. Two further examples that may be given of condensation polymerisation are in the manufacture of polyamides and of polysulphides (*Figure 2.6*).

In the first case a dibasic acid is reacted with diamine to give a polyamide. A specific example is the formation of nylon 66 by the reaction of adipic acid and hexamethylenediamine.

in these instances the kinetics are more akin to those of double bond polymerisation. An interesting feature of the three examples cited is that the polymer formed may also be produced by other methods, the first by addition polymerisation and the second and third by condensation methods.

It may also be mentioned that a number of commercial polymers are produced by chemical modification of other polymers, either natural or synthetic. Examples are cellulose acetate from the naturally occurring polymer cellulose, poly(vinyl alcohol) from poly(vinyl acetate) and chlorosulphonated polyethylene (Hypalon) from polyethylene.

2.2 THERMOPLASTIC AND THERMOSETTING BEHAVIOUR

In all of the examples given so far in this chapter the product of polymerisation has been a long chain molecule, a linear polymer. With such materials it should be possible for the molecules to slide past each other under shear forces above a certain temperature such that the molecules have enough energy to overcome the intermolecular attractions. In other words above a certain temperature the material is capable of flow, i.e. it is essentially plastic, whereas below this temperature it is to all intents and purposes a solid. Such materials are referred to as *thermoplastics* and today these may be considered to be the most important class of plastics material commercially available.

It is, however, possible to produce other structures. For example, if phthalic acid is condensed with glycerol, the glycerol will react at each point (*Figure 2.9*).

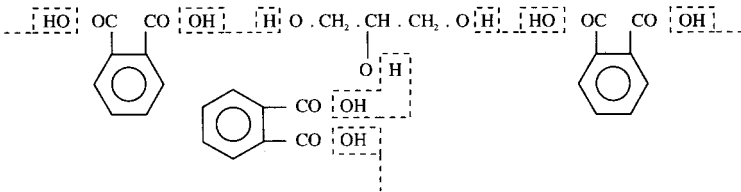


Figure 2.9

This will lead initially to branched chain structures such as indicated schematically in *Figure 2.10*, G indicating a glycerol residue and P a phthalic acid residue. In due course these branched molecules will join up, leading to a *cross-linked* three-dimensional product.

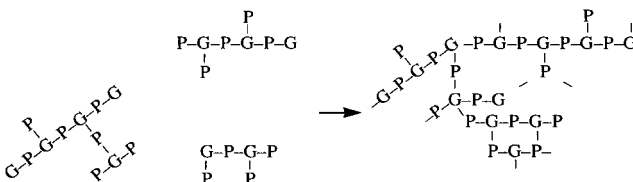


Figure 2.10

It is quite easy to take such a reaction to the cross-linked stage in one step but in practice it is often more convenient to first produce relatively low molecular weight structures sometimes referred to as *A-stage resins*. These small branched molecules, which are comparatively stable at room temperature, are first deformed to shape and then under the influence of either heat or catalysts the molecules join together and some cross-linking occurs to yield *C-stage resins*. These materials are usually referred to as *thermosetting plastics* and important commercial examples include the phenolics, the aminoplastics, epoxy resins and many polyesters. Although in fact most of these commercial polymers are made by condensation polymerisation this need not necessarily be the case. For example, it is possible to polymerise diallyl phthalate (*Figure 2.11*) through both of its double bonds and produce a thermoset polymer.

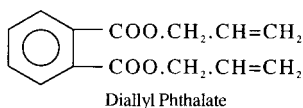


Figure 2.11

Whilst the term *thermosetting plastics* arose out of the fact that early products of this type were cross-linked by subjecting the intermediate-stage materials to elevated temperature, the term is also widely used where cross-linking takes place at normal ambient temperatures.

An alternative route to cross-linking is to start with a linear polymer and then cross-link the molecules by 'tying' the molecule through some reactive group. For example, it is possible to cross-link unsaturated polyesters by an addition polymerisation across the double bond as shown schematically in *Figure 2.12*.

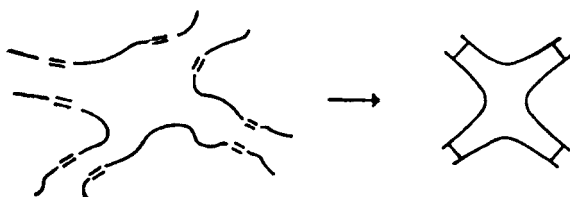


Figure 2.12

The *vulcanisation* of natural rubber, a long chain polyisoprene, with sulphur involves a similar type of cross-linking.

2.3 FURTHER CONSIDERATION OF ADDITION POLYMERISATION

Addition polymerisation is effected by the activation of the double bond of a *vinyl monomer*, thus enabling it to link up to other molecules. It has been shown that this reaction occurs in the form of a chain addition process with initiation, propagation and termination steps.

The *initiation* stage may be activated by free-radical or ionic systems. In the following example a free-radical system will be discussed. In this case a material which can be made to decompose into free radicals on warming, or in the presence of a promoter or by irradiation with ultraviolet light, is added to the monomer and radicals are formed. Two examples of such materials are benzoyl peroxide and azodi-isobutyronitrile, which decompose as indicated in *Figure 2.13*.

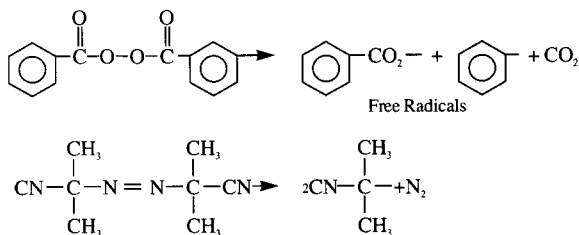
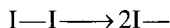


Figure 2.13

Such free-radical formation may be generally indicated as



The rate of formation of radicals will depend on a number of features, including the concentration of initiator, temperature and the presence of other agents. Since subsequent stages of polymer growth occur almost instantaneously it is the relative slowness of this stage which causes the overall conversion times in most polymerisations to be at least 30 minutes and sometimes much longer.

The radicals formed may then react with a monomer molecule by addition, producing another radical.



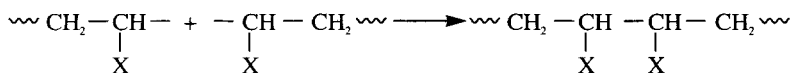
This radical then reacts with a further molecule of monomer, generating yet another free radical of the same order of reactivity.



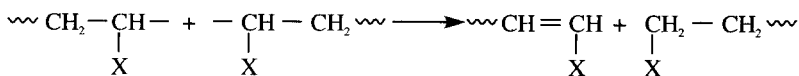
This reaction may then repeat itself many times so that several thousand monomer units are joined together in a time of the order of 1 second, leading to a long chain free radical. This is the *propagation* or *growth* stage.

Termination may be effected in a number of ways, including:

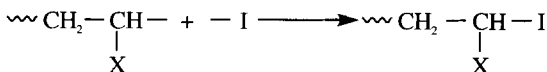
(1) Mutual combination of two growing radicals



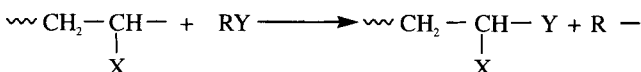
(2) Disproportionation between growing radicals



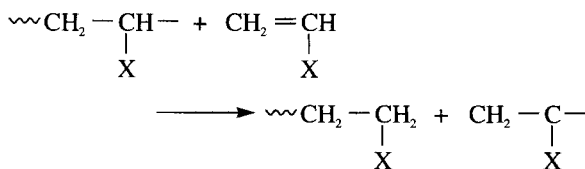
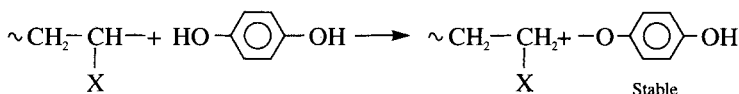
(3) Reaction with an initiator radical



(4) Chain transfer with a modifier



(This reaction terminates growth of a chain but there is no net loss in the radical concentration and it does not therefore affect the velocity of the reaction.)

(5) Chain transfer with monomer (*Figure 2.14*).*Figure 2.14*(6) Reaction with a molecule to form a stable free radical, e.g. hydroquinone (*Figure 2.15*).*Figure 2.15*

Termination by mechanisms (1) and (2) above are most common, whilst mechanisms (4) and (6) are of particular technological importance. Although it is generally possible to reduce molecular weight to some extent by increasing the polymerisation temperature, there is a limit to the amount that this can be done. In addition, raising the polymerisation temperature often causes undesirable side reactions to occur. On the other hand, by incorporating small quantities of a *modifier* a method of regulating the amount of chain growth is employed which does not interfere with the rate of the reaction. Such materials are also spoken of as *chain transfer agents* and *regulators*, and include chlorinated materials such as carbon tetrachloride and trichlorethylene and mercaptans such as dodecyl mercaptan.

In the case of mechanism (6) there are materials available which completely prevent chain growth by reacting preferentially with free radicals formed to produce a stable product. These materials are known as *inhibitors* and include quinone, hydroquinone and tertiary butylcatechol. These materials are of particular value in preventing the premature polymerisation of monomer whilst in storage, or even during manufacture.

It may be noted here that it is frequently possible to polymerise two monomers together so that residues from both monomers occur together in the same polymer chain. In addition polymerisation this normally occurs in a somewhat random fashion and the product is known as a *binary copolymer**. It is possible to copolymerise more than two monomers together and in the case of three monomers the product is referred to as a *ternary copolymer* or *terpolymer*. The term *homopolymer* is sometimes used to refer to a polymer made from a single monomer.

Other copolymer forms are *alternating copolymers*, *block copolymers* and *graft polymers*.

Figure 2.16 illustrates some possible ways in which two monomers A and B can be combined together in one chain.

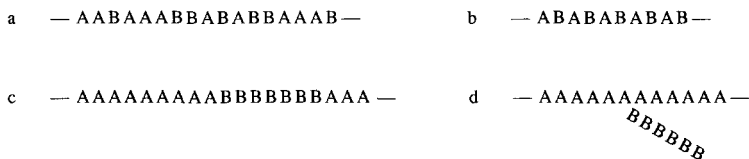


Figure 2.16. (a) Random copolymer, (b) alternating copolymer, (c) block copolymer, (d) graft copolymer

Polymerisation may be carried out in bulk, in solution in a suitable solvent, in suspension or emulsion. Detailed considerations with individual polymers are given in later chapters but a number of general points may be made here. *Bulk* polymerisation is, in theory, comparatively straightforward and will give products of as good a clarity and electrical insulation characteristics as can be expected of a given material. However, because polymerisation reactions are exothermic and because of the very low thermal conductivity of polymers there are very real dangers of the reactants overheating and the reaction getting out of control.

Reactions in bulk are used commercially but careful control of temperature is required. Polymerisation in a suitable solvent will dilute the concentration of reacting material and this together with the capability for convective movement or stirring of the reactant reduces exotherm problems. There is now, however, the necessity to remove solvent and this leads to problems of solvent recovery. Fire and toxicity hazards may also be increased.

An alternative approach to solving the exotherm problem is to polymerise in *suspension*. In this case the monomer is vigorously stirred in water to form tiny droplets. To prevent these droplets from cohering at the stage when the droplet is a sticky mixture of polymer and monomer, suspension or dispersion agents

* Binary copolymers are commonly referred to simply as copolymers.

such as talc, poly(vinyl alcohol) or gelatine are added to provide a protective coating for each droplet. Polymerisation occurs within each droplet, providing a monomer-soluble initiator is employed, and the polymer is produced as small beads reasonably free from contaminants.

The reaction is considerably modified if the so-called *emulsion polymerisation* technique is used. In this process the reaction mixture contains about 5% soap and a water-soluble initiator system. The monomer, water, initiator, soap and other ingredients are stirred in the reaction vessel. The monomer forms into droplets which are emulsified by some of the soap molecules. Excess soap aggregates into micelles, of about 100 molecules, in which the polar ends of the soap molecules are turned outwards towards the water whilst the non-polar hydrocarbon ends are turned inwards (*Figure 2.17*).

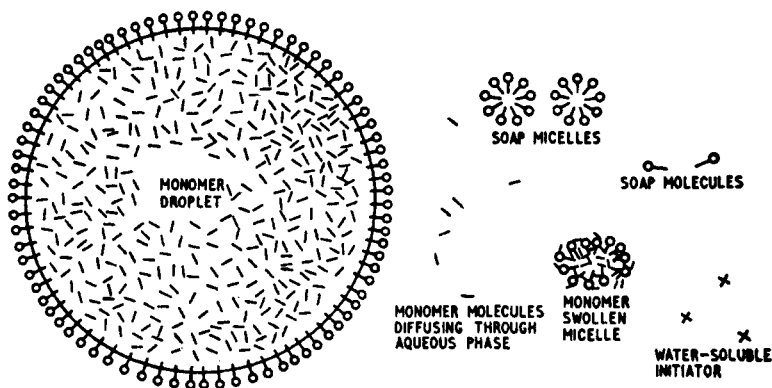


Figure 2.17. Structures present during emulsion polymerisation

Monomer molecules, which have a low but finite solubility in water, diffuse through the water and drift into the soap micelles and swell them. The initiator decomposes into free radicals which also find their way into the micelles and activate polymerisation of a chain within the micelle. Chain growth proceeds until a second radical enters the micelle and starts the growth of a second chain. From kinetic considerations it can be shown that two growing radicals can survive in the same micelle for a few thousandths of a second only before mutual termination occurs. The micelles then remain inactive until a third radical enters the micelle, initiating growth of another chain which continues until a fourth radical comes into the micelle. It is thus seen that statistically the micelle is active for half the time, and as a corollary, at any one time half the micelles contain growing chains.

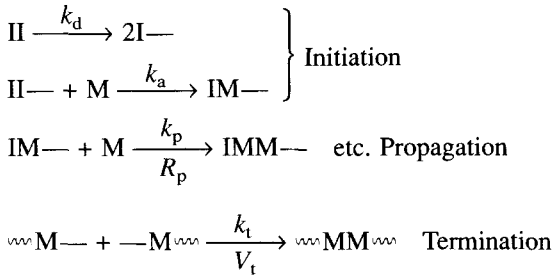
As reaction proceeds the micelles become swollen with monomer and polymer and they eject polymer particles. These particles which are stabilised with soap molecules taken from the micelles become the loci of further polymerisation, absorbing and being swollen by monomer molecules.

The final polymerised product is formed in particles much smaller (50–500 nm) than produced with suspension polymerisation. Emulsion polymerisation can lead to rapid production of high molecular weight polymers but the unavoidable occlusion of large quantities of soap adversely affects the electrical insulation properties and the clarity of the polymer.

2.3.1 Elementary Kinetics of Free-radical Addition Polymerisation

Polymerisation kinetics will be dealt with here only to an extent to be able to illustrate some points of technological significance. This will involve certain simplifications and the reader wishing to know more about this aspect of polymer chemistry should refer to more comprehensive studies.¹⁻⁴

In a simple free-radical-initiated addition polymerisation the principal reactions involved are (assuming termination by combination for simplicity)



where M, I, M· and I· indicate monomers, initiators and their radicals respectively, each initiator yielding two radicals.

The rate of initiation, V_i , i.e. the rate of formation of growing polymer radicals, can be shown to be given by

$$V_i = 2fk_d[\text{I}] \tag{2.1}$$

where f is the fraction of radicals which initiate chains, i.e. the initiator efficiency, and $[\text{I}]$ is the initiator concentration.

The propagation rate is governed by the concentrations of growing chains $[\text{M}\cdot]$ and of monomers $[\text{M}]$. Since this is in effect the rate of monomer consumption it also becomes the overall rate of polymerisation

$$R_p = k_p[\text{M}] [\text{M}\cdot] \tag{2.2}$$

In mutual termination the rate of reaction is determined by the concentration of growing radicals and since two radicals are involved in each termination the reaction is second order.

$$V_t = k_t[\text{M}\cdot]^2 \tag{2.3}$$

In practice it is found that the concentration of radicals rapidly reaches a constant value and the reaction takes place in the steady state. Thus the rate of radical formation V_i becomes equal to the rate of radical disappearance V_t . It is thus possible to combine equations (2.1) and (2.3) to obtain an expression for $[\text{M}\cdot]$ in terms of the rate constants

$$[\text{M}\cdot] = \left(2f \frac{k_d}{k_t} [\text{I}] \right)^{1/2} \tag{2.4}$$

This may then be substituted into equation 2.2 to give

$$R_p = \left(2f \frac{k_d}{k_t} \right)^{1/2} k_p [\text{M}] [\text{I}]^{1/2} \tag{2.5}$$

This equation indicates that the reaction rate is proportional to the square root of the initiator concentration and to the monomer concentration. It is found that the relationship with initiator concentration is commonly borne out in practice (see *Figure 2.18*) but that deviations may occur with respect to monomer concentration. This may in some cases be attributed to the dependency of f on monomer concentration, particularly at low efficiencies, and to the effects of certain solvents in solution polymerisations.

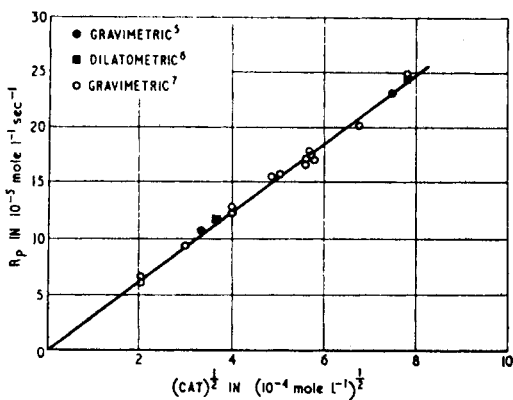


Figure 2.18. Rate of polymerisation R_p of methyl methacrylate with azobisisobutyronitrile at 60°C as measured by various workers.⁷ (Copyright 1955 by the American Chemical Society and reprinted by permission of the copyright owner)

The *average kinetic chain length* r is defined as the number of monomer units consumed per active centre formed and is given by R_p/V_i (or R_p/V_t).

Therefore combining equations (2.1) and (2.5)

$$r = \frac{k_p}{(2fk_d k_t)^{1/2}} \cdot \frac{[M]}{[I]^{1/2}} \quad (2.6)$$

The *number average degree of polymerisation* \bar{x}_n is defined as the average number of monomer units per polymer chain. Therefore if termination is by disproportionation $r = \bar{x}$, but if by combination $r = \frac{1}{2}\bar{x}$.

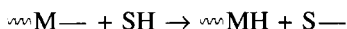
It is seen from equations (2.5) and (2.6) that while an increase in concentration of initiator *increases* the polymerisation rate it *decreases* the molecular weight.

In many technical polymerisations transfer reactions to modifier, solvent, monomer and even initiator may occur. In these cases whereas the overall propagation rate is unaffected the additional ways of terminating a growing chain will cause a reduction in the degree of polymerisation.

The degree of polymerisation may also be expressed as

$$\bar{x}_n = \frac{\text{rate of propagation}}{\text{combined rate of all termination reactions}}$$

For modes of transfer with a single transfer reaction of the type



the rate equation, where $[S]$ is the concentration of transfer agent SH, is

$$V_s = k_s[M-][S] \quad (2.7)$$

Thus

$$\bar{x} = \frac{R_p}{V_t + V_s} = \frac{R_p}{V_i + V_s}$$

$$\frac{1}{\bar{x}} = r + \frac{V_s}{R_p} = r + \frac{k_s[S]}{k_p[M]} \quad (2.8)$$

Thus the greater the transfer rate constant and the concentration of the transfer agent the lower will be the molecular weight (*Figure 2.19*).

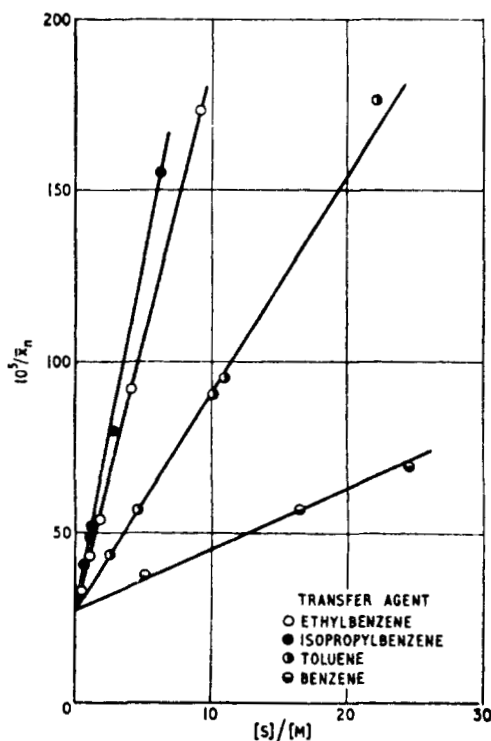


Figure 2.19. Effect of chain transfer solvents on the degree of polymerisation of polystyrene. (After Gregg and Mayo⁸)

An increase in temperature will increase the values of k_d , k_p and k_t . In practice it is observed that in free-radical-initiated polymerisations the overall rate of conversion is approximately doubled per 10°C rise in temperature (see *Figure 2.20*). Since the molecular weight is inversely related to k_d and k_t it is observed in practice that this decreases with increase in temperature.

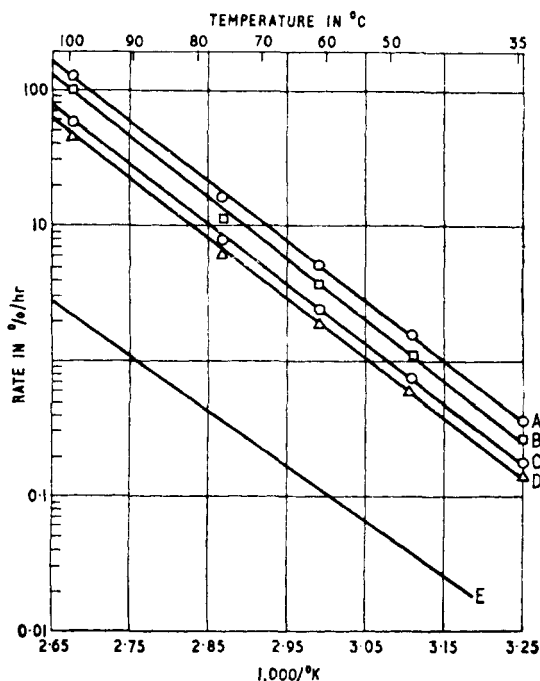


Figure 2.20. Rates of catalysed and uncatalysed polymerisation of styrene at different temperatures. Catalysts used (all at 0.0133 mole/l). A, bis-(2,4-dichlorobenzoyl) peroxide; B, lauroyl peroxide; C, benzoyl peroxide; D, bis-(*p*-chlorobenzoyl) peroxide; E, none. (After Boundy and Boyer⁹)

The most important technological conclusions from these kinetic studies may be summarised as follows:

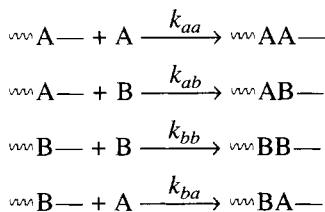
- (1) The formation of a polymer molecule takes place virtually instantaneously once an active centre is formed. At any one time the reacting system will contain monomer and complete polymer with only a small amount of growing radicals. Increase of reaction time will only increase the degree of conversion (of monomer to polymer) and to first approximation will not affect the degree of polymerisation. (In fact at high conversions the high viscosity of the reacting medium may interfere with the ease of termination so that polymers formed towards the end of a reaction may have a somewhat higher molecular weight.)
- (2) An increase in initiator concentration or in temperature will increase the rate of conversion but decrease molecular weight.
- (3) Transfer reactions will reduce the degree of polymerisation without affecting the rate of conversion.
- (4) The statistical nature of the reaction leads to a distribution of polymer molecular weights. Figures quoted for molecular weights are thus averages of which different types exist. The number average molecular weight takes into account the numbers of molecules of each size when assessing the average whereas the weight average molecular weight takes into account the fraction of each size by weight. Thus the presence of 1% by weight of monomer would have little effect on the weight average but since it had a

great influence on the number of molecules present per unit weight it would greatly influence the number average. The ratio of the two averages will provide a measure of the molecular weight distribution.

In the case of *emulsion polymerisation*, half the micelles will be reacting at any one time. The conversion rate is thus virtually independent of radical concentration (within limits) but dependent on the number of micelles (or swollen polymer particles).

An increase in the rate of radical production in emulsion polymerisation will reduce the molecular weight since it will increase the frequency of termination. An increase in the number of particles will, however, reduce the rate of entry of radicals into a specific micelle and increase molecular weight. Thus at constant initiator concentration and temperature an increase in micelles (in effect in soap concentration) will lead to an increase in molecular weight and in rate of conversion.

The kinetics of *copolymerisation* are rather complex since four propagation reactions can take place if two monomers are present



Since these reactions rarely take place at the same rate one monomer will usually be consumed at a different rate from the other.

If k_{aa}/k_{ab} is denoted by r_a and k_{bb}/k_{ba} by r_b then it may be shown that the relative rates of consumption of the two monomers are given by

$$\frac{d[A]}{d[B]} = \frac{[A] r_a [A] + [B]}{[B] r_b [B] + [A]} \quad (2.9)$$

When it is necessary that the same copolymer composition is maintained throughout the entire reaction, it is necessary that one of the monomers in the reaction vessel be continually replenished in order to maintain the relative rates of consumption. This is less necessary where r_1 and r_2 both approximate to unity and 50/50 compositions are desired.

An alternative approach is to copolymerise only up to a limited degree of conversion, say 40%. In such cases although there will be some variation in composition it will be far less than would occur if the reaction is taken to completion.

2.3.2 Ionic Polymerisation

A number of important addition polymers are produced by ionic mechanisms. Although the process involves initiation, propagation and termination stages the growing unit is an ion rather than a radical.

The electron distribution around the carbon atom (marked with an asterisk in *Figure 2.21*) of a growing chain may take a number of forms. In *Figure 2.21* (a)

there is an unshared electron and it acts as a free radical. *Figure 2.21 (b)* is a positively charged carbonium ion, unstable as it lacks a shared pair of electrons and *Figure 2.21 (c)* is a negatively charged carbanion, unstable as there exists an unshared electron pair.

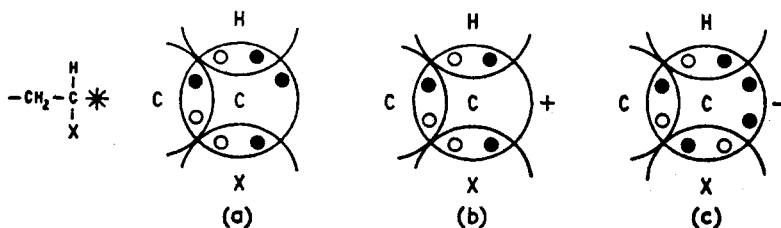
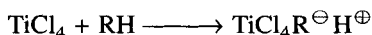


Figure 2.21. (a) Free radical. (b) Carbonium ion. (c) Carbanion

Both carbonium ions and carbanions may be used as the active centres for chain growth in polymerisation reactions (cationic polymerisation and anionic polymerisation respectively). The mechanisms of these reactions are less clearly understood than free-radical polymerisations because here polymerisation often occurs at such a high rate that kinetic studies are difficult and because traces of certain ingredients (known in this context as *cocatalysts*) can have large effects on the reaction. Monomers which have electron-donating groups attached to one of the double bond carbon atoms have a tendency to form carbonium ions in the presence of proton donors and may be polymerised by cationic methods whilst those with electron-attracting substituents may be polymerised anionically. Free-radical polymerisation is somewhat intermediate and is possible when substituents have moderate electron-withdrawing characteristics. Many monomers may be polymerised by more than one mechanism.

Cationic polymerisation, used commercially with polyformaldehyde, polyisobutylene and butyl rubber, is catalysed by Friedel–Crafts agents such as aluminium chloride (AlCl_3), titanium tetrachloride (TiCl_4) and boron trifluoride (BF_3) (these being strong electron acceptors) in the presence of a cocatalyst. High molecular weight products may be obtained within a few seconds at -100°C . Although the reactions are not fully understood it is believed that the first stage involves the reaction of the catalyst with a cocatalyst (e.g. water) to produce a complex acid



This donates a proton to the monomer to produce a carbonium ion (*Figure 2.22*)

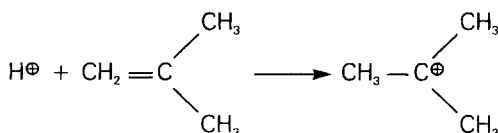


Figure 2.22

In turn this ion reacts with a further monomer molecule to form another reactive carbonium ion (Figure 2.23)

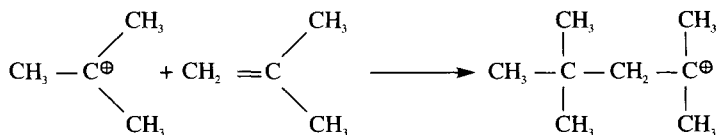


Figure 2.23

The reaction is repeated over and over again with the rapid growth of a long chain ion. Termination can occur by rearrangement of the ion pair (Figure 2.24) or by monomer transfer.

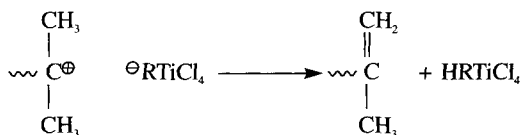
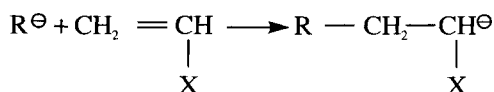


Figure 2.24

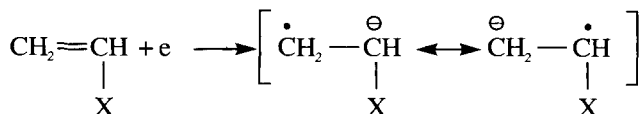
The process of *anionic polymerisation* was first used some 60 or more years ago in the sodium-catalysed production of polybutadiene (Buna Rubbers). Typical catalysts include alkali metals, alkali metal alkyls and sodium naphthalene, and these may be used for opening either a double bond or a ring structure to bring about polymerisation. Although the process is not of major importance with the production of plastics materials, it is very important in the production of synthetic rubbers. In addition the method has certain special features that make it of particular interest.

Today the term anionic polymerisation is used to embrace a variety of mechanisms initiated by anionic catalysts and it is now common to use it for all polymerisations initiated by organometallic compounds (other than those that also involve transition metal compounds). Anionic polymerisation does not necessarily imply the presence of a free anion on the growing polymer chain.

Anionic polymerisation is more likely to proceed when there are electron-withdrawing substituents present in the monomer (e.g.—CN,—NO₂ and phenyl). In principle initiation may take place either by addition of an anion to the monomer, viz:



or by addition of an electron to produce an anion radical



The most common initiators are the alkyl and aryl derivatives of alkali metals. With some of these derivatives the bond linking the metal to the hydrocarbon portion of the molecule may exhibit a substantial degree of covalency whilst others are more electrovalent. In other words the degree of attachment of the counterion to the anion varies from one derivative to another. Where there is a strong attachment steric and other factors can impose restrictions on the manner in which monomer adds on to the growing chain and this can lead to more regular structures than usually possible with free-radical polymerisations. It is also not surprising that the solvent used in polymerisation (anionic polymerisations are often of the solution type) can also influence the metal-hydrocarbon bond and have a marked influence on the polymer structure. The considerable importance of alkyl lithium catalysts is a reflection of the directing influence of the metal-hydrocarbon bond.

In the absence of impurities there is frequently no termination step in anionic polymerisations. Hence the monomer will continue to grow until all the monomer is consumed. Under certain conditions addition of further monomer, even after an interval of several weeks, will cause the dormant polymerisation process to proceed. The process is known as *living polymerisation* and the products as *living polymers*. Of particular interest is the fact that the follow-up monomer may be of a different species and this enables block copolymers to be produced. This technique is important with certain types of thermoplastic elastomer and some rather specialised styrene-based plastics.

A further feature of anionic polymerisation is that, under very carefully controlled conditions, it may be possible to produce a polymer sample which is virtually *monodisperse*, i.e. the molecules are all of the same size. This is in contrast to free-radical polymerisations which, because of the randomness of both chain initiation and termination, yield polymers with a wide molecular size distribution, i.e. they are said to be *polydisperse*. In order to produce monodisperse polymers it is necessary that the following requirements be met:

- (1) All the growing chains must be initiated simultaneously.
- (2) All the growing chains must have equal growth rates.
- (3) There must be no transfer or termination reactions so that all chains continue to grow until all of the monomer is consumed.

It follows immediately that the number average degree of polymerisation is given by:

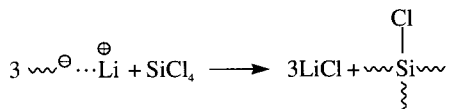
$$\bar{x}_n = nx \frac{[M]}{[I]}$$

where [M] and [I] are the monomer and initiator concentrations respectively, n is equal to 1 or 2 depending on whether the initiator forms mono- or di-anions and x is the fraction of monomer converted into polymer.

In principle it is possible to extend the method to produce block copolymers in which each of the blocks is monodisperse but the problems of avoiding impurities become formidable. Nevertheless, narrow size distributions, if not monodisperse ones, are achievable.

Yet another feature of anionic polymerisation is the possibility of coupling chains together at their 'living ends'. Where the coupling agent is bifunctional

a stable non-living linear polymer is produced which on average has (approximately) twice the average length of the non-coupled molecules. However, where the coupling agent is trivalent a T-shaped molecule will be obtained whilst a tetrafunctional agent will produce X-shaped molecules. Where agents of higher functionalities are used star-shaped polymers will be produced. An example is the coupling of a butyl-lithium-initiated polystyrene with silicon tetrachloride:



Other coupling agents include the tri- and tetrachloromethylbenzenes and divinylbenzene.

The system may be used for homopolymers and for block copolymers. Some commercial SBS triblock thermoplastic rubbers and the closely related K-resins produced by Phillips are of this type. Anionic polymerisation methods are of current interest in the preparation of certain diene rubbers.

2.3.3 Ziegler-Natta and Metallocene Polymerisation

As a result of the work of Ziegler in Germany, Natta in Italy and Pease and Roedel in the United States, the process of *co-ordination polymerisation*, a process related to ionic polymerisation, became of significance in the late 1950s. This process is today used in the commercial manufacture of polypropylene and polyethylene and has also been used in the laboratory for the manufacture of many novel polymers. In principle the catalyst system used governs the way in which a monomer and a growing chain approach each other and because of this it is possible to produce stereoregular polymers.

One way in which such stereospecificity occurs is by the growing polymer molecule forming a complex with a catalyst which is also complexed with a monomer molecule. In this way growing polymers and monomers are brought together in a highly specific fashion. The product of reaction of the growing polymer molecule and the monomer molecule is a further growing molecule which will then again complex itself with the catalyst and the cycle may be repeated.

The catalysts used are themselves complexes produced by interaction of alkyls of metals in Groups I–III of the Periodic Table with halides and other derivatives of Groups IV–VIII metals. Although soluble co-ordination catalysts are known, those used for the manufacture of stereoregular polymers are usually solid or adsorbed on solid particles.

A number of olefins may be polymerised using certain metal oxides supported on the surface of an inert solid particle. The mechanism of these polymerisation reactions is little understood but is believed to be ionic in nature.

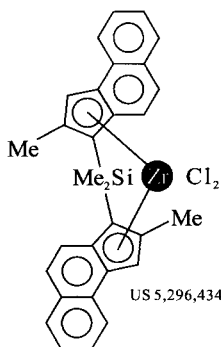
Following the considerable commercial success of Ziegler-Natta polymerisation systems which made possible high density polyethylene, polypropylene, ethylene-propylene rubbers and a number of speciality materials, a considerable

body of research was devoted to attempt a better understanding of the polymerisation mechanism. Cossee proposed that a metal atom in the catalyst system formed a temporary bond simultaneously with a growing polymer chain and with the double bond of the monomer. This caused the chain end to be electrically attracted to the monomer resulting in fusion of chain end and monomer generating a new chain end and allowing the process to repeat. The Ziegler–Natta catalysts were, however, complex mixtures of solid and liquid compounds and so attempts were made to produce model systems for study using a catalyst of uniform structure containing a single metal atom. Such systems are referred to as being single-sited and the Ziegler–Natta systems as multi-sited.

Research work eventually concentrated around what became known as metallocene systems. At risk of considerable over-simplification these may be regarded as consisting of a metal atom, usually titanium or zirconium, linked to two rings of 5-carbon atoms and to two other groups, usually single carbon atoms with attached hydrogens. The 5-carbon rings are hinged together by other atoms in a form reminiscent of a partly opened clamshell and these partly enclose the metal atom. By varying the nature of the hinge atoms, by the use of substituents on the 5-carbon rings, by modifying the symmetry of the ‘clam-shell’ by the positioning of the substituents and by the use of cocatalysts such as methyl aluminoxanes, the accessibility of monomer, and in due course, polymer chain to the metal atom can be carefully controlled. In turn this can lead to control of the following factors:

- what monomer can be polymerised (it may be possible to polymerise just one of a mixture of monomers);
- the frequency of termination reactions leading to narrow molecular weight distributions;
- the direction of approach of monomer to the chain end leading to closely controlled stereoregular polymers. (The main types of stereoregular polymer are discussed further in Section 4.3.)

An example of a metallocene catalyst (patented by Targor and of particular interest for polymerising propylene) is illustrated in *Figure 2.25*.



rac.-Dimethylsilylenebis(2-methyl-1-benz[e]indenyl)zirconium dichloride

Figure 2.25 A metallocene catalyst

2.4 CONDENSATION POLYMERISATION

In this form of polymerisation, initiation and termination stages do not exist and chain growth occurs by random reaction between two reactive groups. Thus in contradistinction to addition polymerisation an increase in reaction time will produce a significant increase in average molecular weight. An increase in temperature and the use of appropriate catalysts, by increasing the reactivity, will also increase the degree of polymerisation achieved in a given time.

In the case of linear polymers it is often difficult to obtain high molecular weight polymers. The degree of polymerisation \bar{x} will be given by

$$\bar{x} = \frac{\text{No. of groups available for reaction}}{\text{No. of groups not reacted}} \quad (2.10)$$

If p , the extent of reaction, is the fraction of groups that have reacted, then

$$\bar{x} = \frac{1}{1 - p} \quad (2.11)$$

Thus when 95% of the groups have reacted ($p = 0.95$) the degree of polymerisation will be only 20.

Even lower molecular weights will be obtained where there is an excess of one reactive group, since these will eventually monopolise all the chain ends and prevent further reaction. The presence of monofunctional ingredients will have similar effects and they are sometimes added deliberately to control molecular weight (see for example Section 20.4.1).

It is to be noted that only one condensation reaction is necessary to convert two molecules with values of $\bar{x} = 100$ to one molecule with $\bar{x} = 200$. A similar reaction between two dimers will produce only tetramers ($\bar{x} = 4$). Thus although the concentration of reactive groups may decrease during reaction, individual reactions at later stages of the reaction will have greater effect.

As with addition polymers, molecules with a range of molecular weights are produced. In the condensation of bifunctional monomers

$$\frac{\bar{x}_w}{\bar{x}_n} = (1 + p) \quad (2.12)$$

where \bar{x}_w and \bar{x}_n are the weight average and number average degrees of polymerisation respectively. Thus as the reaction goes towards completion the ratio of the degrees of polymerisation and hence the molecular weights approaches 2.

In the case of trifunctional monomers the situation is more complex. From the schematic diagrams (*Figure 2.26*) it will be seen that the polymers have more functional groups than the monomers.

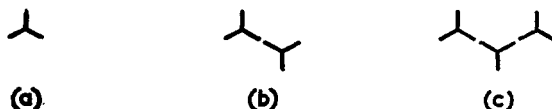


Figure 2.26

It is seen that the *functionality* (no. of reactive groups = f) is equal to $n+2$ where n is the degree of polymerisation. Thus the chance of a specific 100-mer (102 reactive groups) reacting is over 30 times greater than a specific monomer (3 reactive groups) reacting. Large molecules therefore grow more rapidly than small ones and form even more reactive molecules. Thus 'infinitely' large, cross-linked molecules may suddenly be produced while many monomers have not even reacted. This corresponds to the 'gel point' observed with many processes using thermosetting resins. It may in fact be shown that at the gel point with a wholly trifunctional system $\bar{x}_w = \infty$ whilst \bar{x}_n is only 4.

Appendix – A note on molecular weight averages and molecular weight distribution

(Although the term *molecular mass* is now often preferred to the term *molecular weight* the latter term is still commonly used in the context of polymers and the author has decided to retain the latter term again for this edition.)

A mass of polymer will contain a large number of individual molecules which will vary in their molecular size. This will occur in the case, for example, of free-radically polymerised polymers because of the somewhat random occurrence of chain termination reactions and in the case of condensation polymers because of the random nature of the chain growth. There will thus be a distribution of molecular weights; the system is said to be *polydisperse*.

The *molecular weight distribution* may be displayed graphically by plotting the frequency at which each molecular weight occurs against that molecular weight (or more practically the frequency within a narrow molecular weight band). When this is done certain characteristics may be established. These include:

- (i) A measure of the central tendency of the distribution. While this could be expressed using such statistical terms as a mode or median an average (mean) molecular weight is more useful; but see below.
- (ii) The breadth of distribution. It is common to refer to polymers having a narrow- or a broad-molecular weight distribution. While this could be quantified in terms of statistical parameters such as standard deviation, mean deviation or inter-quartile range, such data is seldom made available by the polymer supplier and is also of somewhat limited value if the distribution deviates significantly from being symmetrical.
- (iii) The symmetry of the distribution. As pointed out in the previous section on condensation polymerisation, large polymer molecules can grow rapidly, particularly where there are trifunctional monomers. This can lead to a positively skewed distribution, i.e. a distribution with a long high molecular weight tail. Other polymerisation methods may leave a significant amount of unreacted monomer which would give a negative skew.
- (iv) The modality of the distribution. In the example given in the previous sentence the distribution would probably have two peaks or modes, one corresponding to the monomer molecular weight and the other related to an average polymer molecular weight. Such a *bimodal distribution* can also occur if two polymer samples of different average molecular weight are blended together. Trimodal, tetramodal, pentamodal distributions, and so on, could similarly be envisaged.

While breadth, skewness and modality of a distribution are all of some interest the most important parameter is the average molecular weight. This however can be defined in a number of different ways. Conceptually the simplest is the *number average molecular weight*, invariably given the symbol \bar{M}_n . This is essentially the same as the arithmetic mean molecular weight where the sum of the weights of all the molecules are divided by the number of molecules. This is the same as saying that \bar{M}_n is the sum of the product of the number fraction of each molecular weight (n_i) times the molecular weight (M_i) i.e.

$$\bar{M}_n = \sum n_i M_i$$

For some purposes this average may be less useful than the *weight average molecular weight* defined by \bar{M}_w which considers the fraction by weight of each molecular size i.e.

$$\bar{M}_w = \sum w_i M_i$$

This can best be explained by taking a somewhat extreme theoretical example. Let us consider a tiny sample of polymer consisting of 1 molecule with a molecular weight of 100 000 and 999 molecules with a molecular weight of 100. In this case the *number average molecular weight* will be

$$(0.001) (100\,000) + (0.999)(100) = c.199$$

However, a moments consideration makes clear that over half the mass of the polymer consists of the molecule with the molecular weight of 100 000 and that this would have an important influence on the properties of the polymer mass not reflected in the number average figure which is in any case totally unrepresentative of any of the molecules. In this case the *weight average molecular weight* will be

$$(100\,000/199\,900) (100\,000) + (99\,900/199\,900) (100) = c. 50\,125$$

While this example shows an extreme difference in the two molecular weight averages, the other extreme is where all of the molecules have the same size, i.e. they are said to be *monodisperse*. In this case the two averages will have the same value.

The molecular weight ratio \bar{M}_w/\bar{M}_n can thus be considered as a crude measure of the breadth of the molecular weight distribution and is often used for this purpose.

One further point might be made here. Although the example illustrates the difference between the two types of molecular weight average, the weight average molecular weight in this example cannot be said to be truly representative, an essential requirement of any measure of central tendency. In such circumstances where there is a bimodal, i.e. two-peaked, distribution additional data should be provided such as the *modal values* (100 and 100 000 in this case) of the two peaks.

References

1. BILLMEYER, F. W., *Textbook of Polymer Science*, Interscience, New York (1962)
2. JENKINS, A. D. (Ed.), *Polymer Science*, North-Holland, Amsterdam (1972)
3. FLORY, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953)
4. TUDÓS, F. (Ed.), *Kinetics and Mechanisms of Polyreactions*, Akadémiai, Kiadó, Budapest (1971)
5. BAYSAL, B. and TOBOLSKY, A. V., *J. Polymer Sci.*, **8**, 529 (1952)
6. BONSALL, E. P., VALENTINE L., and MELVILLE H. W., *Trans. Faraday Soc.*, **48**, 763 (1952)
7. O'BRIEN, J. L., and GORNICK, F., *J. Am. Chem. Soc.*, **77**, 4757 (1955)
8. GREGG, R. A., and MAYO, F. R., *Disc. Faraday Soc.*, **2**, 328 (1947)
9. BOUNDY, R. H., and BOYER, R. F., *Styrene, its Polymers, Copolymers and Derivatives*, Rheinhold, New York (1952)
10. COSSEE, P. *Tetrahedron letters* **12**, 17 (1960); *J. Catal.* **3**, 80 (1964)

Bibliography

- ALGER, M. S. M., *Polymer Science Dictionary*, 2nd edn, Chapman & Hall (1996)
- ALLPORT, D. C., and JANES, W. H., *Block Copolymers*, Applied Science, London (1973)
- BILLMEYER, F. W., *Textbook of Polymer Science*, 3rd edn, Interscience, New York (1984)
- COWIE, J. M. G., *Polymers: Chemistry and Physics of Modern Materials*, 2nd, edn, Blackie, London (1991)
- FLORY, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953)
- HAWARD, R. N., *Developments in Polymerisation*, Vols 1 and 2, Applied Science, London (1979)
- JENKINS, A. D. (Ed.), *Polymer Science* (2 volumes), North-Holland, Amsterdam (1972)
- LENZ, R. W., *Organic Chemistry of Synthetic High Polymers*, Interscience, New York (1967)
- MOORE, W. R., *An Introduction to Polymer Chemistry*, University of London Press, London (1963)
- PLESCH, P. H., *Cationic Polymerisation*, Pergamon Press, Oxford (1963)
- SMITH, D. A. (Ed.), *Addition Polymers: Formation and Characterization*, Butterworths, London (1968)

3

States of Aggregation in Polymers

3.1 INTRODUCTION

In the previous chapter the various methods of synthesising polymers were briefly discussed. In this chapter the physical states of aggregation of these polymers will be considered, whilst in the three subsequent chapters the effect of molecular structure on the properties of polymers will be investigated.

Simple molecules like those of water, ethyl alcohol and sodium chloride can exist in any one of three physical states, i.e. the solid state, the liquid state and the gaseous state, according to the ambient conditions. With some of these materials it may be difficult to achieve the gaseous state or even the liquid state because of thermal decomposition but in general these three phases, with sharply defined boundaries, are discernible. Thus at a fixed ambient pressure, the melting point and the boiling point of a material such as pure water occur at definite temperatures. In polymers, changes of state are less well defined and may well occur over a finite temperature range. The behaviour of linear amorphous polymers, crystalline polymers and thermosetting structures will be considered in turn.

3.2 LINEAR AMORPHOUS POLYMERS

A specific linear amorphous polymer, such as poly(methyl methacrylate) or polystyrene, can exist in a number of states according to the temperature and the average molecular weight of the polymer. This is shown diagrammatically in *Figure 3.1*. At low molecular weights (e.g. M_1) the polymer will be solid below some given temperature whilst above that temperature it will be liquid. The melting point for such polymers will be quite sharp and is the temperature above which the molecules have sufficient energy to move independently of each other, i.e. they are capable of viscous flow. Conversely, below this temperature the molecules have insufficient energy for flow and the mass behaves as a rigid solid. At some temperature well above the melting point, the material will start to boil provided this is below the decomposition temperature. In high polymers this is rarely, if ever, the case.

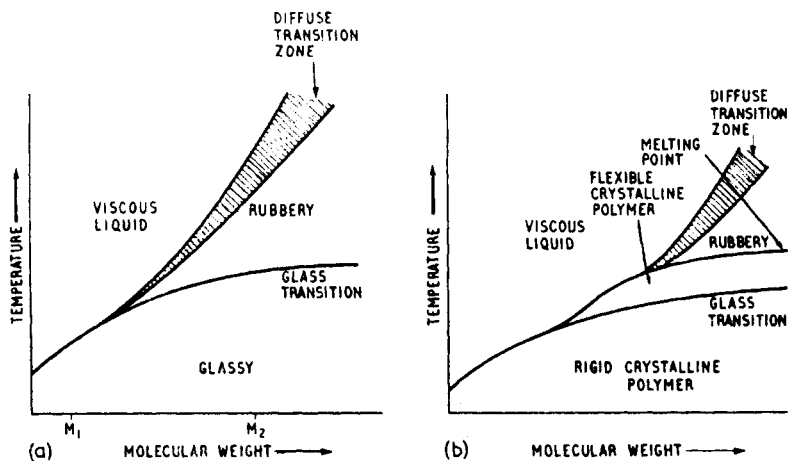


Figure 3.1. Temperature-molecular weight diagrams for (a) amorphous and (b) moderately crystalline polymers (with highly crystalline polymers the glass transition is less apparent)

At high molecular weights (e.g. M_2) such a clearly defined melting point no longer occurs and a rubbery intermediate zone is often observed. In this case two transition temperatures may be observed; firstly a rigid solid-rubber transition (usually known as the *glass transition temperature*) and secondly a generally very indefinite rubber-liquid transition, sometimes referred to as the flow temperature. (The term melting point will be reserved for crystalline polymers.)

It is instructive to consider briefly the three states and then to consider the processes which define the transition temperatures. In the solid state the polymer is hard and rigid. Amorphous polymers, under discussion in this section, are also transparent and thus the materials are glass-like and the state is sometimes referred to as the *glassy state*. Molecular movement other than bond vibrations are very limited. Above the glass transition temperature the molecule has more energy and movement of molecular segments becomes possible. It has been established that, above a given molecular weight, movement of the complete molecule as a unit does not take place. Flow will occur only when there is a co-operative movement of the molecular segments. In the rubbery range such co-operative motion leading to flow is very limited because of such features as entanglements and secondary (or even primary) cross-linking. (In crystalline polymers, discussed in the next section, crystalline zones may also restrict flow.) In the rubbery state the molecules naturally take up a random, coiled conformation as a result of free rotation about single covalent bonds (usually C—C bonds) in the chain backbone. On application of a stress the molecules tend to uncoil and in the absence of crystallisation or premature rupture the polymer mass may be stretched until the molecules adopt the fully stretched conformation. In tension, elongations as high as 1200% are possible with some rubbery polymers. On release of the stress the free rotations about the single bonds cause the molecule to coil up once again. In commercial rubbery materials chain coiling and uncoiling processes are substantially complete within a small fraction of a second. They are, nevertheless, not instantaneous and the deformation changes lag behind the application and removal of stress. Thus the deformation characteristics are somewhat dependent on the rate of stressing.

Chain uncoiling, and the converse process of coiling, is conveniently considered as a unimolecular chemical reaction. It is assumed that the rate of uncoiling at any time after application of a stress is proportional to the molecules still coiled. The deformation $D_{HE}(t)$ at time t after application of stress can be shown to be related to the equilibrium deformation $D_{HE}(\infty)$ by the equation

$$D_{HE}(t) = D_{HE}(\infty) (1 - e^{-t/\tau_m}) \quad (3.1)$$

when τ_m , a reaction rate constant, is the time taken for the deformation to reach $(1-1/e)$ of its final value (*Figure 3.2*). Since different molecules will vary in their orientation time depending on their initial disposition this value is an average time for all the molecules.

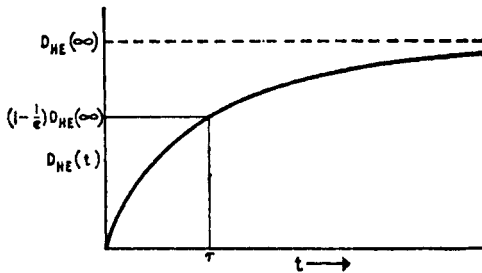


Figure 3.2. Application of stress to a highly elastic body. Rate of chain uncoiling with time

Whether or not a polymer is rubbery or glass-like depends on the relative values of t and τ_m . If t is much less than τ_m , the *orientation time*, then in the time available little deformation occurs and the rubber behaves like a solid. This is the case in tests normally carried out with a material such as polystyrene at room temperature where the orientation time has a large value, much greater than the usual time scale of an experiment. On the other hand if t is much greater than τ_m there will be time for deformation and the material will be rubbery, as is normally the case with tests carried out on natural rubber at room temperature. It is, however, vital to note the dependence on the time scale of the experiment. Thus a material which shows rubbery behaviour in normal tensile tests could appear to be quite stiff if it were subjected to very high frequency vibrational stresses.

The rate constant τ_m is a measure of the ease at which the molecule can uncoil through rotation about the C—C or other backbone bonds. This is found to vary with temperature by the exponential rate constant law so that

$$\tau_m = A e^{E/RT} \quad (3.2)$$

If this is substituted into equation (3.1), equation (3.3) is obtained.

$$D_{HE}(t) = D_{HE}(\infty) \left[1 - \exp \left(\frac{-t}{A e^{E/RT}} \right) \right] \quad (3.3)$$

In effect this equation indicates that the deformation can be critically dependent on temperature, and that the material will change from a rubbery to a glass-like

state over a small drop in temperature. Frith and Tuckett¹ have illustrated (*Figure 3.3*) how a polymer of $\tau_m = 100$ sec at 27°C and an activation energy E of 60 kcal will change from being rubbery to glass-like as the temperature is reduced from about 30°C to about 15°C. The time of stressing in this example was 100 s.

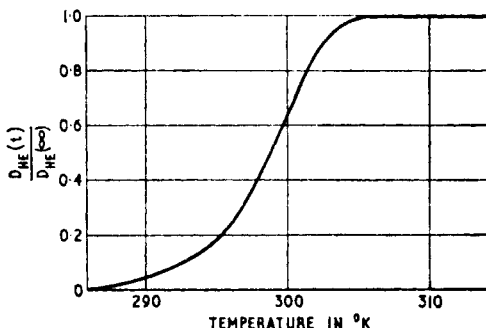


Figure 3.3. The ratio $D_{HE}(t)/D_{HE}(\infty)$ and its variation with temperature. (After Frith and Tuckett,¹ reproduced by permission of Longmans, Green and Co. Ltd.)

It is now possible to understand the behaviour of real polymers and to interpret various measurements of the glass transition temperature. This last named property may be thus considered as the temperature at which molecular segment rotations do not occur within the time scale of the experiment. There are many properties which are affected by the transition from the rubbery to the glass-like state as a result of changes in the molecular mobility. Properties which show significant changes include specific volume, specific heat, thermal conductivity, power factor (see Chapter 6), nuclear magnetic resonance, dynamic modulus and simple stress-strain characteristics. The fact that measurements of the effect of temperature on these properties indicate different glass transition temperatures is simply due to the fact that the glass temperature is dependent on the time scale of the experiment. This is illustrated by results obtained for polyoxacyclobutane (poly-3,3-bischloromethyloxacyclobutane), showing how transition temperatures depend on the frequency (or speed) of the test (*Table 3.1*).²

It should be pointed out that the view of the glass transition temperature described above is not universally accepted. In essence the concept that at the glass transition temperature the polymers have a certain molecular orientation time is an iso-elastic approach while other theories are based on iso-viscous,

Table 3.1 Influence of experimental time scale on the glass transition point of a polyoxacyclobutane²

	Frequency (Hz)	Glass temperature (°C)
Electrical tests	1000	32
Mechanical vibration	89	25
Slow tensile	3	15
Dilatometry	10^{-2}	7

iso-free volume and statistical mechanical considerations. Of these the iso-free volume approach is widely quoted and in the writer's view³ provides an alternative way of looking at the glass transition rather than providing a contradictory theory. The iso-free volume theory states that below the glass transition temperature there is only a very small fraction of space in a polymer mass which is unoccupied by the polymer molecules. Therefore polymer flow and chain uncoiling will be negligible since such spaces are necessary to allow polymer segments to move. At the glass transition temperature the free volume begins to increase quite rapidly with temperature, the glass transition temperature being characterised by the fact that all polymers have the same free volume at this temperature. It has been found in practice that many polymers do appear to have equal free volumes at their glass transition temperature although some exceptions, such as the polycarbonate of bis-phenol A, have been found. Some important semi-empirical consequences of the iso-free volume nature of the glass transition temperature will be considered in Chapter 4.

Electrical and dynamic mechanical tests often reveal transition temperatures additional to the glass transition temperature (and in the case of crystalline polymers the crystal melting point). These occur because at temperatures below the glass transition temperature, side chains, and sometimes small segments of the main chain, require less energy for mobility than the main segments associated with the glass transition temperature. Various types of nomenclature are used, one of the most common being to label the transitions α , β , γ , δ and so on in descending order of temperature, the α -transition normally corresponding to the glass transition temperature. It must be stressed that simply to label a transition as a β -transition does not imply any particular type of mechanism and the mechanism for a β -transition in one polymer could correspond to a γ -transition in a second polymer.

Boyer⁴ has suggested the use of the symbol T_{cg} to indicate a transition due to a crankshaft mechanism proposed by Schatzki.⁵ Schatzki has postulated that, in a randomly oriented polymer, potentially co-linear bonds will be separated by four methylene groups; providing there is sufficient rotational energy and free volume this segment can rotate between the co-linear bonds in the manner of a crankshaft. A T_{cg} transition may be observed in many polymers containing at least four linked methylene groups. To avoid any commitment to any particular mechanism the transition is sometimes referred to as the 'glass II transition'.

3.2.1 Orientation in Linear Amorphous Polymers

If a sample of an amorphous polymer is heated to a temperature above its glass transition point and then subjected to a tensile stress the molecules will tend to align themselves in the general direction of the stress. If the mass is then cooled below its transition temperature while the molecule is still under stress the molecules will become frozen whilst in an oriented state. Such an orientation can have significant effects on the properties of the polymer mass. Thus if a filament of polystyrene is heated, stretched and frozen in this way a thinner filament will be produced with aligned molecules. The resultant filament has a tensile strength which may be five times that of the unoriented material because on application of stress much of the strain is taken up by covalent bonds forming the chain backbone. On the other hand the tensile strength will be lower in the directions perpendicular to the orientation. The polymer is thus anisotropic.

Anisotropic behaviour is also exhibited in optical properties and orientation effects can be observed and to some extent measured by birefringence methods. In such oriented materials the molecules are in effect frozen in an unstable state and they will normally endeavour to take up a more coiled conformation due to rotation about the single bonds. If an oriented sample is heated up the molecules will start to coil as soon as they possess sufficient energy and the mass will often distort. Because of this oriented materials usually have a lower heat distortion temperature than non-oriented polymers.

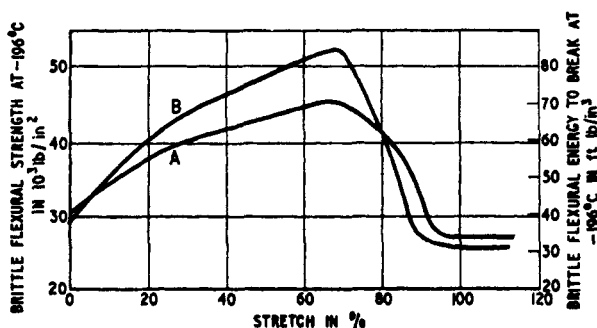


Figure 3.4. Biaxial orientation of polymethyl methacrylate. Variation of (a) brittle flexural strength and (b) brittle flexural energy with percentage stretch. (After Ladbury⁶)

In addition to monoaxial orientation, *biaxial stretching* of amorphous polymers is possible. For example if poly(methyl methacrylate) sheet is heated above its glass temperature and stretched in two directions simultaneously there will be a planar disposition of the molecules. It has been found that with poly(methyl methacrylate) sheet such properties as tensile strength and brittle flexural strength increase with increased orientation up to a percentage stretch of about 70% (Figure 3.4).⁶ Above this value there is a decrease in the numerical value of these properties, presumably due to the increase in flaws between the layers of molecules. Properties such as impact strength (Figure 3.5)⁶ and solvent crazing resistance, which are less dependent on these flaws than other properties, continue to improve with increased orientation.

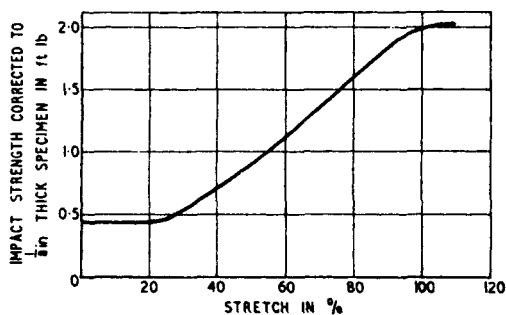


Figure 3.5. Biaxial orientation of polymethyl methacrylate. Variation of impact strength with percentage stretch. (After Ladbury⁶)

In addition to the deliberate monoaxial or biaxial orientation carried out to produce oriented filament or sheet, orientation will often occur during polymer processing whether desired or not. Thus in injection moulding, extrusion or calendering the shearing of the melt during flow will cause molecular orientation. If the plastic mass 'sets' before the individual molecules have coiled then the product will contain frozen-in orientation with built-in, often undesirable, stresses. It is in order to reduce these frozen-in stresses that warm moulds and fast injection rates are preferred in injection moulding. In the manipulation of poly(methyl methacrylate) sheet to form baths, light fittings and other objects biaxial stretching will frequently occur. Such acrylic products produced by double curvature forming will revert completely to the original flat sheet from which they were prepared if they are heated above their glass transition temperature.

3.3 CRYSTALLINE POLYMERS

If a polymer molecule has a sufficiently regular structure it may be capable of some degree of crystallisation. The factors affecting regularity will be discussed in the next chapter but it may be said that crystallisation is limited to certain linear or slightly branched polymers with a high structural regularity. Well-known examples of crystalline polymers are polyethylene, acetal resins and polytetrafluoroethylene.

From a brief consideration of the properties of the above three polymers it will be realised that there are substantial differences between the crystallisation of simple molecules such as water and copper sulphate and of polymers such as polyethylene. The lack of rigidity, for example, of polyethylene indicates a much lower degree of crystallinity than in the simple molecules. In spite of this the presence of crystalline regions in a polymer has large effects on such properties as density, stiffness and clarity.

The essential difference between the traditional concept of a crystal structure and crystalline polymers is that the former is a single crystal whilst the polymer is polycrystalline. By a single crystal is meant a crystalline particle grown without interruption from a single nucleus and relatively free from defects. The term polycrystallinity refers to a state in which clusters of single crystals are involved, developed from the more or less simultaneous growth of many nuclei. The resulting conglomerate may possess no readily discernible symmetry. Polycrystallinity occurs not only in polymers but also in metals and, unless care is taken, in the large-scale commercial crystallisation of materials such as sucrose and sodium chloride.

There have been, over the years, profound changes in the theories of crystallisation in polymers. For many years it was believed that the crystallinity present was based on small crystallites of the order of a few hundred Ångström units in length. This is very much less than the length of a high polymer molecule and it was believed that a single polymer molecule actually passed through several crystallites. The crystallites thus consisted of a bundle of segments from separate molecules which had packed together in a highly regular order. The method of packing was highly specific and could be ascertained from X-ray diffraction data. It was believed that in between the crystallites the polymer passed through amorphous regions in which molecular disposition was random. Thus there is the general picture of crystallites embedded in an amorphous matrix

(Figure 3.6). This theory known as the fringed micelle theory or fringed crystallite theory helped to explain many properties of crystalline polymers but it was difficult to explain the formation of certain larger structures such as spherulites which could possess a diameter as large as 0.1 mm.

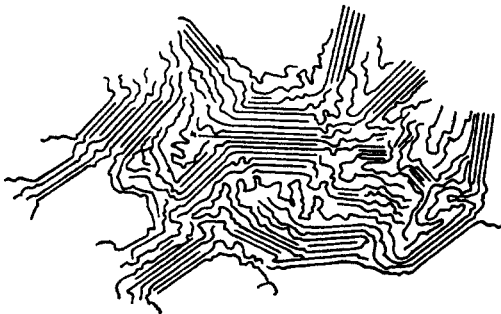


Figure 3.6. Two-dimensional representation of molecules in a crystalline polymer according to the fringed micelle theory showing ordered regions (crystallites) embedded in an amorphous matrix. (After Bryant⁷)

As a result of work based initially on studies of polymer single crystals, it became realised that the fringed micelle theory was not entirely correct. It was found that in many circumstances the polymer molecules folded upon themselves at intervals of about 100 \AA to form lamellae which appear to be the fundamental units in a mass of crystalline polymer. Crystallisation spreads by the growth of individual lamellae as polymer molecules align themselves into position and start to fold. For a variety of reasons, such as a point of branching or some other irregularity in the structure of the molecule, growth would then tend to proceed in many directions. In effect this would mean an outward growth from the nucleus and the development of spherulites. In this concept it is seen that a spherulite is simply caused by growth of the initial crystal structure, whereas in the fringed micelle theory it is generally postulated that formation of a spherulite required considerable reorganisation of the disposition of the crystallites. Both theories are consistent with many observed effects in crystalline polymers. The closer packing of the molecules causes an increased density. The decreased intermolecular distances will increase the secondary forces holding the chain together and increase the value of properties such as tensile strength, stiffness and softening point. If it were not for crystallisation, polyethylene would be rubbery at room temperature and many grades would be quite fluid at 100°C .

The properties of a given polymer will very much depend on the way in which crystallisation has taken place. A polymer mass with relatively few large spherulitic structures will be very different in its properties to a polymer with far more, but smaller, spherulites. It is thus useful to consider the factors affecting the formation of the initial nuclei for crystallisation (nucleation) and on those which affect growth.

Homogeneous nucleation occurs when, as a result of statistically random segmental motion, a few segments have adopted the same conformation as they would have in a crystallite. At one time it was considered that the likelihood of the formation of such nuclei was greatest just above the transition temperature

whilst the rate of growth was greatest just below the melting point. This provided an explanation of the common observation that the overall crystallisation rate is greatest at a temperature about half-way between the glass transition temperature and the melting point. It is, however, now believed that both nucleation rates and growth rates are dependent on temperature in the same way so that the overall crystallisation rate–temperature curve is of the same form as the nucleation–temperature and growth–temperature curve (*Figure 3.7*). By definition no crystallisation occurs above the melting point.

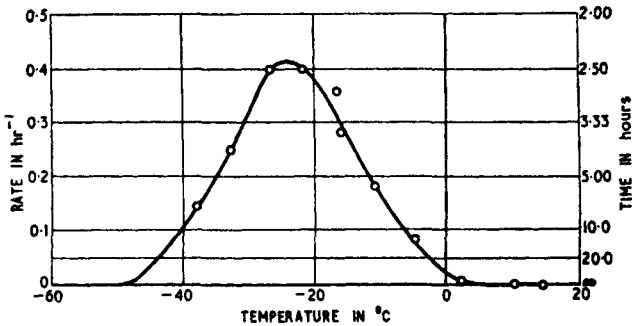


Figure 3.7. Rate of crystallisation of natural rubber as a function of temperature. (After Wood⁸)

There are certain differences between the properties of a polymer crystallised under conditions of high nucleation/growth ratios as compared with those made under the opposite conditions. In the latter case the polymer develops large crystal structures which may be sufficiently large to interfere with light waves and cause opacity. It may also be somewhat brittle. In the former case the polymer mass, with smaller structures, is generally more transparent. The properties of the polymer will also depend on the time available for cooling. In the case of a polymer such as the bis-phenol A polycarbonate (Chapter 20) the glass temperature is about 140°C. There is in this case little time for crystallisation to develop in cooling from the melt after injection moulding and extrusion and transparent polymers are usually obtained.

On the other hand crystalline polymers with a glass temperature below that of the ambient temperature in which the polymer is to be used will continue to crystallise until equilibrium is reached. For this reason nylon 66, which has a glass temperature slightly below that of usual room temperature, will exhibit after-shrinkage for up to two years after manufacture unless the sample has been specially annealed. In the case of the polyacetals (polyformaldehydes) the shrinkage is to all intents and purposes complete within 48 hours. The reason for this is that the glass transition point for the polyacetals is as low as -13°C (some authors also quote -73°C). Therefore at the common ambient temperatures of about 20°C crystallisation rates are much faster for polyacetals than for nylon 66. The problems of slow after-shrinkage of nylon 66 may be avoided by heating the polymer for a short period at a temperature at which crystallisation proceeds rapidly (about 120°C).

Because polymers have a very low thermal conductivity, compared with metals, cooling from the melt proceeds unevenly, the surface cooling more

rapidly than the centre. This will be particularly marked with thick injection moulded sections and with piping and other extrusions which have been extruded into cold water. In these cases the morphology (fine structure) of crystalline polymers will vary across the cooled polymer mass and hence the physical properties will also vary. One consequence of this is that a surface produced by a machining operation may have quite different hardness, abrasion resistance and coefficient of friction than a moulded surface.

In many polymer products it is desirable to have a high degree of crystallinity but with small spherulite size. A high homogeneous nucleation rate, however, requires the polymers to be held at a temperature midway between the glass temperature and the melting point. Processing operations, however, demand a quick 'cooling' operation and it would be desirable to speed up the freezing operation. High nucleation rates can be achieved together with high growth if *heterogeneous nucleation* is employed. In this case nucleation is initiated by seeding with some foreign particle. This can be of many types but is frequently a polymer of similar cohesive energy density (see Chapter 5) to that being crystallised but of a higher melting point. Nucleating agents are now widely used in commercial products. They have the overall effect of promoting rapid freezing, giving a high degree of crystallisation, good clarity in polymer films, controlling skin effects and reducing formation of voids which can occur in conjunction with large morphological structures.

Mention may be made of the effect of the glass transition on the properties of a crystalline polymer. In a highly crystalline polymer there is little scope for segmental motion since most of the segments are involved in a lattice formation in which they have low mobility. Such polymers are comparatively rigid in the mass and there is little difference in properties immediately above and below the glass transition. In fact with some highly crystalline polymers it is difficult to find the glass temperature. With less crystalline materials some distinction may be possible because of the greater number of segments in a less organised state. Thus above the glass transition point the polymer may be flexible and below it quite stiff.

3.3.1 Orientation and Crystallisation

If a rubbery polymer of regular structure (e.g. natural rubber) is stretched, the chain segments will be aligned and crystallisation is induced by orientation. This crystallisation causes a pronounced stiffening in natural rubber on extension. The crystalline structures are metastable and on retraction of the sample they disappear.

On the other hand if a polymer such as nylon 66 is stretched at some temperature well below its melting point but above its transition temperature, e.g. at room temperature, additional crystallisation will be induced and the crystalline structure will generally be aligned in the direction of extension. As a result, oriented crystalline filaments or fibres are much stronger than the unoriented product. This is the basis of the 'cold-drawing' process of the synthetic fibre industry. Poly(ethylene terephthalate) (e.g. Terylene) with a transition temperature of 67°C has to be cold-drawn at some higher temperature. The tensile strengths of nylon 66 and poly(ethylene terephthalate) fibres approach 10^5 lbf/in² (700 MPa), many times greater than those of the unoriented polymers.

Biaxial orientation effects are of importance in the manufacture of films and sheet. Biaxially stretched poly(ethylene terephthalate) (e.g. Melinex),

poly(vinylidene chloride) (Saran) and polypropylene films are strong films of high clarity, the orientation-induced crystallisation producing structures which do not interfere with the light waves.

Much of the success of the poly(ethylene terephthalate) bottle has arisen from the control of the biaxial orientation that occurs during manufacture to give a product both strong and of low gas permeability.

3.3.2 Liquid Crystal Polymers

When normal non-polymeric crystalline solids melt they do so abruptly and the material becomes liquid. This is associated with both a collapse of the overall positional order of the lattice array and the onset of what is, to all intents and purposes, free rotation of the particles. There are, however, a number of non-polymeric materials where this sharp transition does not occur and intermediate stages are identifiable. Materials that show this behaviour are said to be *mesomorphic*. Whilst a spectrum of mesomorphic states may be envisaged there are two basic states which are usually identified, plastic crystals and liquid crystals. In *plastic crystals* an overall solid condition is maintained with a general retention of lattice order but the individual molecules have rotational and diffusional mobilities approaching those of liquids. With *liquid crystals* the materials flow like liquids but retain some long-range order due to restricted rotational mobility of the molecules. Where the mesomorphic phase is brought about by thermal changes, the phenomenon is known as *thermotropic mesomorphism*. Where the solid lattice has been disturbed by the presence of solvents, the phenomenon is known as *lyotropic mesomorphism*.

During the 1970s a number of polymers were produced which showed long-range order in the melt analogous to that exhibited by non-polymeric liquid crystals. Prominent amongst thermotropic materials are certain aromatic polyesters which might be considered as copolymers based on *p*-hydroxybenzoic acid, whilst lyotropic mesomorphism is shown by such materials as poly-*p*-benzamide and poly(γ -benzyl-L-glutamate) in appropriate solvents.

The liquid crystal polymers consist of rod-like molecules which, during shear, tend to orient in the direction of shear. Because of the molecular order the molecules flow past each other with comparative ease and the melts have a low viscosity. When the melt is cooled the molecules retain their orientation, giving self-reinforcing materials that are extremely strong in the direction of orientation.

The homopolymers of *p*-hydroxybenzoic acid have such a high value for the T_m that they are somewhat intractable. Useful materials may, however, be made by copolymerising with a view to introducing some molecular flexibility or reducing chain packing or introducing some non-linear links. Commercially important liquid crystal polyesters are discussed in Chapter 25.

3.4 CROSS-LINKED STRUCTURES

A cross-linked polymer can generally be placed into one of two groups:

- (1) Lightly cross-linked materials.
- (2) Highly cross-linked materials.

In the lightly cross-linked polymers (e.g. the vulcanised rubbers) the main purpose of cross-linking is to prevent the material deforming indefinitely under load. The chains can no longer slide past each other, and flow, in the usual sense of the word, is not possible without rupture of covalent bonds. Between the cross-links, however, the molecular segments remain flexible. Thus under appropriate conditions of temperature the polymer mass may be rubbery or it may be rigid. It may also be capable of crystallisation in both the unstressed and the stressed state.

However, if the degree of cross-linking is increased the distance between cross-links decreases and a tighter, less flexible network will be formed. Segmental motion will become more restricted as the degree of cross-linking increases so that the transition temperature will eventually reach the decomposition temperature. In polymers of such a degree of cross-linking only the amorphous rigid (glass-like) state will exist. This is the state commonly encountered with, for example, the technically important phenolic, aminoplastic and epoxide resins.

Most cross-linking carried out with commercial polymers involves the production of covalent bonds to link the polymer molecules. Such a process imposes certain limitations on the processing of the polymer. For example, the shaping operation will have to be followed by a chemical cross-linking process which may have to be undertaken on additional plant. Furthermore, once polymers are covalently cross-linked, it is seldom possible to regenerate uncross-linked polymers suitable for reprocessing by selectively breaking the cross-link bonds but not breaking main chain bonds.

These and other considerations have led to attempts to produce materials which effectively cross-link on cooling to room temperature after processing but which on reheating appear to lose their cross-links. Several approaches to such fugitive cross-linking have been made in recent years of which the following have come to, or at least near to, commercial fruition:

- (1) *Ionic cross-linking*. This technique was first developed by Du Pont and resulted in the marketing of their Surlyn A ionomers in 1963. Ethylene is copolymerised with a small amount of a monomer containing carboxyl groups. On mixing the copolymer with a suitable metal salt, the carboxyl group becomes ionised and ionic links between the metal cation and the anionic carboxyl groups are formed. Such links are strong at normal ambient temperatures but become weaker and progressively disappear on heating. On cooling, new links form and the process may be repeated.
- (2) *Hydrogen bonding* (see also Chapter 5). Many polymers such as the nylons, poly(vinyl alcohols) and cellulose exhibit a form of cross-linking by hydrogen bonding. It is also probable that in a way PVC may be considered to be cross-linked by hydrogen bonding via plasticisers such as tritolyl phosphate. It is thought that some thermoplastic polyurethanes may involve a hydrogen bonding type of cross-linking.
- (3) *Triblock copolymers*.⁹ The most well-known example is provided by the 'thermoelastomers' developed by the Shell Company. A block copolymer is produced comprising three portions, a middle portion consisting of a chain of butadiene or isoprene segments with a glass transition temperature in the case of the butadiene segments well below -40°C , and two end portions of styrene segments with a glass transition temperature of about $+80^{\circ}\text{C}$. The polystyrene ends tend to congregate in glassy domains which act somewhat

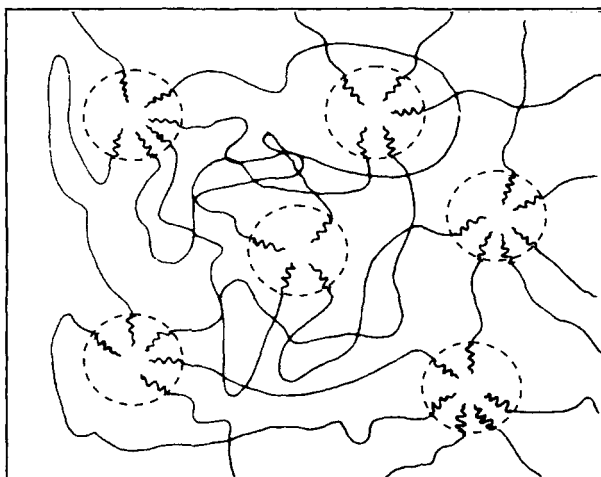


Figure 3.8. Schematic representation of the polystyrene domain structure in styrene-butadiene-styrene triblock copolymers. (After Holden, Bishop and Legge¹⁰)

like end-of-chain cross-links (Figure 3.8). When the temperature is raised above the glass transition of the polystyrene segments the glassy domains also become rubbery and, providing the molecular weight is not too high, further raising of the temperature enables flow to occur. On cooling, glassy domains are re-formed and the material, once again, is effectively cross-linked. (Unlike covalently cross-linked polymers such a system can, however, be dissolved without degradation in appropriate solvents.) Further reduction of the temperature below the glass transition temperature of the butadiene segments will render the whole mass rigid. (See also Chapter 11.)

- (4) *Multiblock systems.* A somewhat similar approach is involved in the production of thermoplastic polyurethane elastomers. In this case the chain contains soft segments that are largely aliphatic polyether in nature and also hard segments that are primarily polyurea (see Chapter 27).

In the 1970s the concept was extended to the thermoplastic polyether-ester rubbers typified by the Du Pont product Hytrel. As with the polyurethanes there are more than three blocks in the polymer. Some of these are polyether and are highly flexible while others are aromatic polyester. Although the T_g of the polyester group is not high this is not so important since the block, being regular in structure, is also crystallisable. As is normal the T_m for the block is much higher than the T_g and the 'hard' polyester segments retain their identity until this point is reached.

(Thermoplastic elastomers are further reviewed in Chapter 31.)

3.5 POLYBLENDS

Whilst the volume production of completely new polymers which have achieved commercial viability in recent years has been small, the development of polymer blends has been highly significant. Of these the most important involve a glassy

or near-glassy resin in conjunction with a rubbery polymer. When suitably paired it has been possible to produce rigid compounds with a high degree of toughness, particularly on impact, a combination of properties which tends to be lacking in most polymers. Such compositions, frequently referred to as polyblends, may be exemplified by such well-known products as high-impact polystyrene, ABS and impact-modified PVC. In some cases the blends are essentially physical mixtures but often the situation can be complex and involve block and graft copolymers.

In most cases the rubbery component forms droplets in a continuous glassy matrix and this results in a composition of enhanced toughness. Any explanation of this phenomenon needs to take into account the following facts:

- (1) Although the glassy resins form the continuous phase quite high extensions are possible in tensile tests, particularly at high strain rates.
- (2) Greatest improvements are obtained where the polymers are neither too compatible nor too incompatible.
- (3) Similar effects are not obtained with either gaseous or hard droplets embedded into the resin.
- (4) Crazeing is observed at stresses below those at which cracking occurs. The crazes are formed at right angles to the applied stress and consist of microscopic interconnected voids interlaced with strands of polymer which have been oriented in the direction of the stress. The term microfibrillation would usefully describe this phenomenon. In glassy polymers the crazeing stress is only slightly less than the fracture stress whilst with polyblends the crazeing stress is much lower.
- (5) The more the rubber present, the greater the reinforcing effect. The toughening does, however, appear to depend more on the number of particles of rubber than on the total volume of rubber present.
- (6) There appears to be an optimum particle size of 'rubber' for a given system (0.10–1.0 μm for ABS and 1–10 μm for high-impact polystyrene).

For many years the rubber-bridge theory of Merz, Claver and Baer¹¹ was widely accepted. This stipulated that when the polyblend was stressed to an extent to cause crack initiation, the propagating cracks reached a rubber particle and passed through it. During cracking the fractured surfaces tended to separate and the rubber particles became extended in tension. This extension of the rubber particle absorbed energy and resisted further crack growth. Such a mechanism required a good bond between resin and rubber, as otherwise the crack would simply propagate round the resin–rubber interface. Such a theory could not, however, explain the ductility of many blends and, furthermore, calculations have shown that the energy absorbed in this way could not account for the large increases in toughness observed.

Other theories¹² proposed dissipation of energy through crack interaction; localised heating causing the material to be raised to above the glass transition temperature in the layers of resin between the rubber droplets; and a proposal that extension causes dilation so that the free volume is increased and the glass transition temperature drops to below the temperature of the polyblend.

At the present time it is generally accepted that the toughening effect is associated with the crazeing behaviour.^{12–15} Because of the presence of the low-modulus rubber particles most of the loading caused when a polyblend is subject to mechanical stress is taken up by the rigid phase (at least up to the moment of

crazing). This high stress concentration will lead to a low craze initiation stress (averaged out over the whole load area). At the same time the fracture initiation stress is not reduced. The reason for this appears to be a consequence of the following:

- (1) Because the rubber is not too compatible it exists in droplets, rather than in a molecular scale mixture with the glassy polymer.
- (2) When a craze occurs around a rubber droplet the droplet is stressed not only in a direction parallel to the applied stress but also in the plane of the craze perpendicular to the applied stress (see *Figure 3.9*). Such a triaxial stress leading to dilation of the particle would be resisted by the high bulk modulus of the rubber, which would thus become load bearing. The fracture initiation stress of a polyblend should not therefore be substantially different from that of a glass.

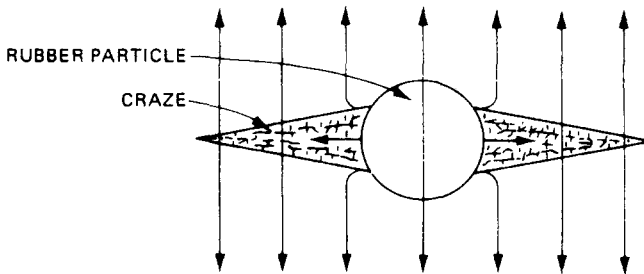


Figure 3.9. Rubber particle straddling craze perpendicular to stress is subjected to triaxial stresses and because of its high bulk modulus becomes load bearing. (After Bucknall¹³)

The rubber particles should not be so small that they are completely embedded in a craze. It is interesting to note that in high-impact polystyrene crazes tend to be about $2\ \mu\text{m}$ thick and the optimum particle sizes observed as a result of experience are quoted in the range $1\text{--}10\ \mu\text{m}$. For ABS the figures are about $0.5\ \mu\text{m}$ and $0.1\text{--}1.0\ \mu\text{m}$ respectively.

The presence of many crazes is considered to distribute stresses which would otherwise be concentrated at the tip of a few growing cracks. Additionally there is some evidence that when a propagating craze reaches a particle it often divides so that if there is a large number of particles per unit volume there is a high dissipation of energy.

3.6 SUMMARY

Polymers can exist in a number of states. They may be amorphous resins, rubbers or fluids or they can be crystalline structures. The molecular and the crystal structures can be monoaxially or biaxially oriented. Heterogeneous blends of polymers in different states of aggregation enable materials to be produced with combinations of properties not shown by single polymers.

The form which a polymer composition will take at any given temperature will depend on:

- (1) The glass transition temperature.
- (2) The ability of the polymer to crystallise.
- (3) The crystalline melting point.
- (4) Any orientation of molecules or crystal structures that may have been induced.
- (5) The type and extent of cross-linking (if any).
- (6) Whether or not polymers in different states of aggregation have been heterogeneously blended.

In the next chapter the structural features that control the first three of the above factors will be considered.

References

1. FRITH, E. M., AND TUCKETT, R. F., *Linear Polymers*, Longmans Green, London (1951)
2. SANDIFORD, D. J. H., *J. Appl. Chem.*, **8**, 186 (1958)
3. BRYDSON, J. A., Chapter 3 in *Polymer Science* (Ed. JENKINS, A. D.), North-Holland, Amsterdam (1972)
4. BOYER, R. F., *Rubb. Chem. Technol.*, **36**, 1303-1421 (1963)
5. SCHATZKI, T. F., *Polymer Preprints*, **6**(2), 646 (1965)
6. LADBURY, J. W., *Trans. Plastics Inst.*, **28**, 184 (1960)
7. BRYANT, W. M. D., *J. Polymer Sci.*, **2**, 547 (1947)
8. WOOD, L. A., *Recent Advances in Colloid Science*, Vol. 2, Interscience, New York, p. 58 (1946)
9. BRADFORD, E. B., and MCKEEVER, L. D., Chapter entitled 'Block Copolymers' in *Progress in Polymer Science* Vol. 3 (Ed. KENKINS, A. D.), Pergamon, Oxford (1971)
10. HOLDEN, G., BISHOP, E. T., and LEGGE, N. R., *J. Polymer Sci.*, Part C, **26**, 37 (1969)
11. MERZ, E. H., CLAVER, G. C., and BAER, M., *J. Polymer Sci.*, **22**, 325 (1956)
12. BRAGAW, C. G., Chapter in *Multicomponent Polymer Systems*, American Chemical Society, Washington (1971)
13. BUCKNALL, C. B., *Brit. Plastics*, **40** (11), 118 (1967); **40** (12), 84 (1967)
14. BUCKNALL, C. B., and SMITH, R. R., *Polymer*, **6**, 437 (1965)
15. KESKULA, H., Chapter entitled 'Rubber-modified Styrene Polymers' in *Polyblends and Composites* (Ed. BRUINS, P. F.), Interscience, New York (1970)

Bibliography

- BENTON, J., *Brit. Plastics*, **35**, 184, 251 (1962)
- BILLMEYER, F. W., *Textbook of Polymer Science*, Interscience, New York (1962)
- BOVEY, F. A. and WINSLOW, F. H. (Eds.), *Macromolecules—An introduction to polymer science*, Academic Press, New York (1979)
- BRUINS, P. F. (Ed.), *Polyblends and Composites*, Interscience, New York (1970)
- BUCKNALL, C. B., *Toughened Plastics*, Applied Science, London (1977)
- FRITH, E. M., and TUCKETT, R. F., *Linear Polymers*, Longmans Green, London (1951)
- GEIL, P. H., *Polymer Single Crystals*, Interscience, New York (1963)
- GORDON, M., *High Polymers*, Iliffe, London (1963)
- JENKINS, A. D. (Ed.), *Polymer Science*, North-Holland, Amsterdam (1972)
- MEARES, P., *Polymers: Structure and Bulk Properties*, Van Nostrand, London (1965)
- MILLER, M. L., *The Structure of Polymers*, Reinhold, New York (1966)
- NIELSEN, L. E., *Mechanical Properties of Polymers*, Reinhold, New York (1963)
- RODRIGUEZ, F., *Principles of Polymer Systems* (2nd Ed.), McGraw-Hill, New York (1983)
- SCHULTZ, J. M., *Polymer Materials Science*, Prentice Hall, New Jersey (1974)
- SHARPLES, A., *Introduction to Polymer Crystallisation*, Arnold, London (1966)
- SMITH, D. A. (Ed.), *Addition Polymers: Formation and Characterization*, Butterworths, London (1968)
- YOUNG, R. J., *Introduction to Polymers*, Chapman and Hall, London (1981) *Multicomponent Polymer Systems*, Advances in Chemistry Series No. 99, American Chemical Society, Washington (1971)

4

Relation of Structure to Thermal and Mechanical Properties

4.1 INTRODUCTION

It is sometimes said that three factors determine whether a polymer is glassy, rubbery or fibre-forming under a given set of conditions. These are the chain flexibility, the interchain attraction and the regularity of the polymer. The relationship has been expressed diagrammatically by Swallow¹ (*Figure 4.1*). The importance of these parameters arises from their influence on the glass transition temperature, the ability of a material to crystallise and, where relevant, the crystalline melting point. In this chapter specific influences which have a bearing on these last three properties will be discussed. At the end of the chapter there is a short discussion of structural features which determine certain selected properties.

4.2 FACTORS AFFECTING THE GLASS TRANSITION TEMPERATURE

There are a number of structural features which have a bearing on the value of the glass transition temperature. Since this temperature is that at which molecular rotation about single bonds becomes restricted, it is obvious that these features are ones which influence the ease of rotation. These can be divided into two groups:

- (1) Factors which affect the inherent or intrinsic mobility of a single chain considered on its own.
- (2) Those factors whose influence is felt because of their effect on the proximity and interaction of many polymer chains.

Before considering the special case of rotation about bonds in polymers it is useful to consider such rotations in simple molecules. Although reference is often made to the 'free rotation' about a single bond, in fact rotational energies of the order of 2 kcal/mole are required to overcome certain energy barriers in such simple hydrocarbons as ethane. During rotation of one part of a molecule about

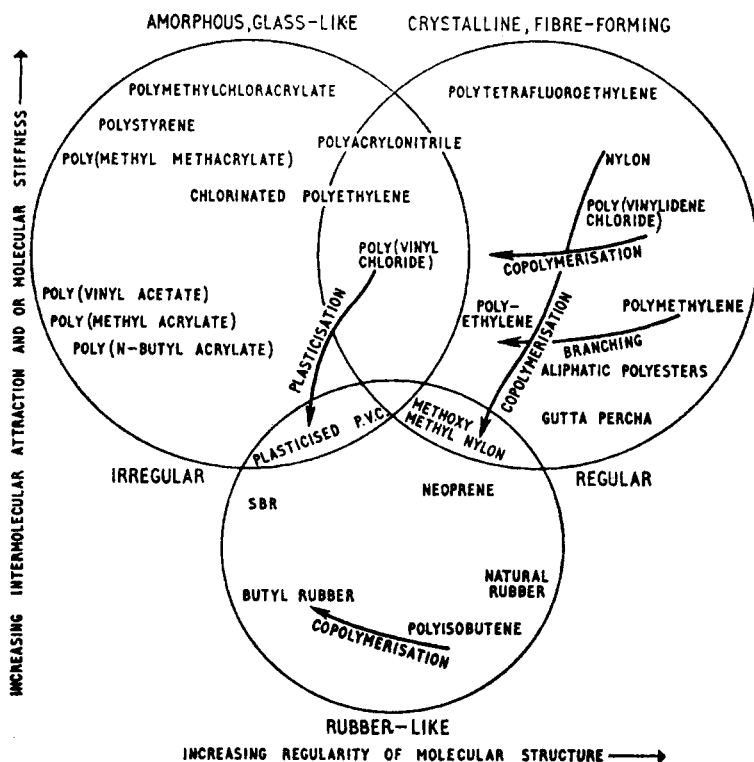


Figure 4.1. Effect of structure regularity, molecular stiffness and intermolecular attraction on polymer properties. (After Swallow¹)

another part the proximity of specific groups or atoms on one part to groups or atoms on the other part will vary. When the specific groups or atoms come close to those on the adjacent carbon atom there is usually a repulsion effect due to steric hindrance, the presence of dipole forces or because of the electronic structure. In some cases intramolecular hydrogen bonding may cause attraction rather than repulsion so that rotation away from this position may involve a large energy requirement. Examples of some of these effects are given in Figure 4.2.

Figure 4.3 depicts the change in height of rotational energy barriers with bond rotation of methylsuccinic acid. This shows quite clearly the repulsion effect which occurs when atoms or groups come into close proximity. This effect is particularly great where the polar carboxyl groups come close together. Such a position is less stable than others and is also the greatest barrier to rotation. The comparative stability of the staggered position is to be noted. A consequence of these rotational effects is that as the temperature is lowered certain conformations (the *trans* position in methylsuccinic acid) become more likely.

This effect is also observed with some polymers. The *trans* form of a hydrocarbon chain requires an energy about 0.8 kcal/mole less than the *gauche*. The *trans* form leads to an extended molecule and in hydrocarbons this becomes more favoured as the temperature is lowered. Linear polyethylenes take up this conformation in the crystalline state.

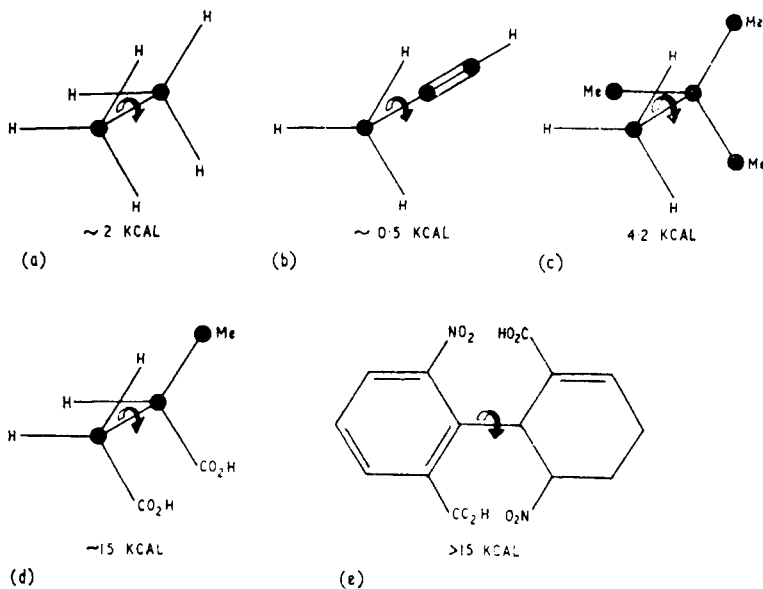


Figure 4.2. Rotational-energy barriers as a function of substitution. The small barrier (~ 2 kcal) in ethane (a) is lowered even further (~ 0.5 kcal) if three bonds are 'tied back' by replacing three hydrogen atoms of a methyl group by a triple-bonded carbon, as in methylacetylene (b). The barrier is raised (4.2 kcal) when methyl groups replace the smaller hydrogen atoms, as in neopentane (c). Dipole forces raise the barrier further (~ 15 kcal) in methylsuccinic acid (d) (cf. Figure 4.3). Steric hindrance is responsible for the high barrier (> 15 kcal) in the diphenyl derivative (e). (After Gordon²)

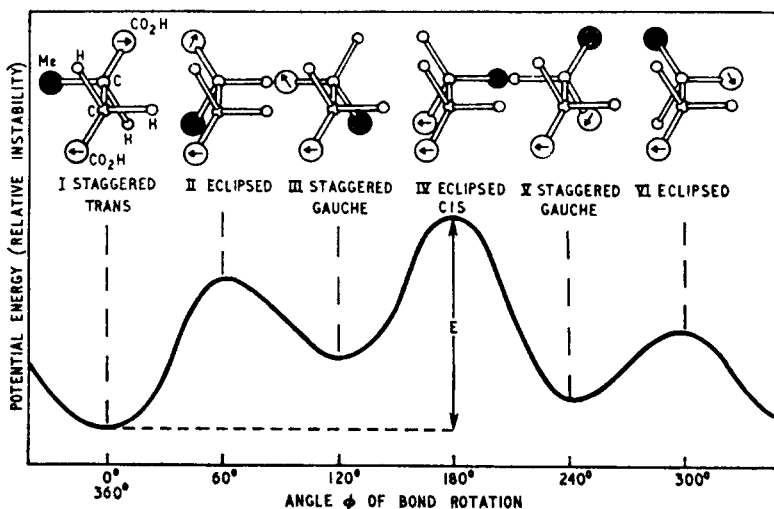


Figure 4.3. Energy versus bond rotation in methylsuccinic acid (schematic). The diagram shows the greater stability of staggered as compared with eclipsed forms, and the effect of size and dipole moment of substituents on the barriers. The slope of the curve at any point represents the force opposing rotation there. (E = energy of activation of rotation.) (After Gordon²)

From the preceding considerations it is appreciated that the intrinsic chain flexibility is determined by the nature of the chain backbone and by the nature of groups directly attached to the backbone.

It is generally considered that chains based on aliphatic C—C and C—O bonds are quite flexible. On the other hand the introduction of ring structures such as the *p*-phenylene group into the main chain has a marked stiffening effect. The glass transitions of poly(ethylene terephthalate) and the polycarbonate from bis-phenol A are much higher than those of their aliphatic counterparts because of the presence of such phenylene groups. Rotation about a single C—C bond is also impeded by the substitution of attached hydrogen atoms by methyl or other hydrocarbon groups. Polypropylene and the polymers of highly branched olefins have a higher glass transition than polyethylene for this reason. In the case of polymers of unbranched or lightly branched olefins other factors come into play.

The size of the group attached to the main chain carbon atom can influence the glass transition point. For example, in polytetrafluoroethylene, which differs from polyethylene in having fluorine instead of hydrogen atoms attached to the backbone, the size of the fluorine atoms requires the molecule to take up a twisted zigzag configuration with the fluorine atoms packed tightly around the chain. In this case steric factors affect the inherent flexibility of the chain.

Inclusion of double bonds will stiffen the chain at the point of inclusion but at the same time may increase the flexibility of adjacent bonds. The net effect may therefore be to reduce the glass transition temperature and this appears to occur in *cis*-1,4-polybutadiene when compared with polyethylene.

Segmental rotation is influenced by other polymer chains in the same region. Secondary bonding due to dipole forces, induction forces and dispersion forces or hydrogen bonding between chains can affect the mobility of a chain. The presence of polar groups or atoms such as chlorine will be a factor tending to raise the glass transition point. Thus the value for PVC is much higher than for polyethylene. It is interesting to note that two identical polar groups attached to the same chain atom may lead to a lower glass transition than in the case of polymers with one polar group. This is the case with poly(vinylidene chloride) as compared with poly(vinyl chloride). This has been attributed to the reduction in dipole moment as a result of the symmetry of substitution.

Hydrogen bonding has a similar effect to that of polar groups. Thus nylon 6, which differs from polyethylene by the presence of —CONH— groups, has a higher transition point than the polyolefin because of its ability to form hydrogen bonds. The forces of attraction, which cause a reduction of chain mobility, will also be affected by the chain separation. Thus the introduction of *n*-alkyl groups in separating the chains will decrease the interchain attraction, more than offsetting the effect of increasing the inherent chain stiffness. However, the presence of long side chains may cause entanglement and even permit some crystallisation. In some polymers, such as those of butadiene and the substituted butadienes, these effects cancel each other out. In the case of the methacrylates chain separation is more important than entanglement up to poly(*n*-dodecyl methacrylate), but with the higher substituted materials entanglement is the predominating influence causing an increase in the glass transition.

The molecular weight of a polymer will have some effect on the glass transition temperature. A low molecular weight polymer will have a greater number of 'chain ends' in a given volume than a high molecular weight polymer. The chain ends are less restrained and can become more active than segments in

the centre of a molecule and cause the polymer mass to expand. This gives the molecules greater mobility and they can be taken to a lower temperature before the thermal energy of the molecules is too low for the segments to rotate.

It is reasonable to assume that the glass transition temperature T_g drops linearly with increase in chain-end concentration, that is with an increase in the reciprocal of the molecular weight. This will give an equation of the form

$$T_g = T_g^\infty - K \left(\frac{1}{M_n} \right)$$

where T_g^∞ is the glass transition temperature of a sample containing molecules of infinite molecular weight, K is a positive constant and M_n is the number average molecular weight. Experimental data usually give a good fit to the above equation.

The glass transition temperature of a random copolymer usually falls between those of the corresponding homopolymers since the copolymers will tend to have intermediate chain stiffness and interchain attraction. Where these are the only important factors to be considered a linear relationship between T_g and copolymer composition is both reasonable to postulate and experimentally verifiable. One form of this relationship is given by the equation

$$C_2 = (T_g - T'_g) / [K(T''_g - T_g) + T_g - T'_g]$$

where C_2 is the weight fraction of the second component, T_g , T'_g and T''_g are the glass transition temperatures of the copolymer, the homopolymer of the first component and the homopolymer of the second component respectively. K is the ratio between the differences of the two expansion coefficients in the rubbery and the glassy state of the two homopolymers. Styrene-butadiene copolymers provide a good example of a system showing such a linear relationship.

It must be pointed out that deviations from such a simple relationship do occur. For example, since random copolymerisation tends to promote disorder, reduce molecular packing and also reduce the interchain forces of attraction, the T_g of copolymers is often lower than would be predicted by the linear relationship. Examples are also known where the T_g of the copolymer is higher than predicted. This could occur where hydrogen bonding or dipole attraction is possible between dissimilar comonomer residues in the chain but not between similar residues, i.e. special interchain forces exist with the copolymers.

With block copolymers two types of effect have been observed. In some instances a transition corresponding to each block is observable whilst in other cases a single transition is observed, usually close to that predicted by a linear relationship even where random copolymers show large deviations. This is because the blocks reduce both the contacts between dissimilar comonomer residues and also the disorder of the molecules which occurs in random copolymer systems.

The restricting influence of cross-linking on segmental mobility was pointed out in the previous chapter. The greater the degree of cross-linking the higher the transition temperature. *Table 4.1* shows how the transition temperature of natural rubber is related to the percentage of combined sulphur (a rough measure of the degree of cross-linking).³

On the other hand the addition of liquids to the polymer will cause separation of the chains and increase their general mobility. This is the effect of

Table 4.1 Dependence of the glass transition of rubber on the sulphur content

<i>Sulphur (%)</i>	$T_g(^{\circ}\text{C})$
0	-65
0.25	-64
10	-40
20	-24

plasticisation, which will cause a marked reduction in the transition temperature. The addition of about 40% of diethyl hexyl phthalate to PVC will reduce its glass transition temperature by about 100°C.

The factors which affect the glass transition are thus as follows:

- (1) Groups attached to the backbone which increase the energy required for rotation.
- (2) Rigid structures, e.g. phenylene groups, incorporated in the backbone of the molecule.
- (3) The packing of substituents around the main chain (c.f. PTFE with polyethylene).
- (4) Secondary bonding between chains, e.g. hydrogen bonding.
- (5) Primary bonding between chains, e.g. cross-linking.
- (6) Length of side chains.
- (7) Molecular weight.
- (8) Copolymerisation.
- (9) Plasticisation.

The glass transition temperatures of a number of polymers are given in *Table 4.2*.

4.3 FACTORS AFFECTING THE ABILITY TO CRYSTALLISE

In the case of an amorphous polymer the glass transition temperature will define whether or not a material is glass-like or rubbery at a given temperature. If, however, the polymer will crystallise, rubbery behaviour may be limited since the orderly arrangement of molecules in the crystalline structure by necessity limits the chain mobility. In these circumstances the transition temperature is of less consequence in assessing the physical properties of the polymer.

The ability of a material to crystallise is determined by the regularity of its molecular structure. A regular structure is potentially capable of crystallinity whilst an irregular structure will tend to give amorphous polymers. Structural irregularities can occur in the following ways:

- (1) By copolymerisation.
- (2) By introduction of groups in an irregular manner.
- (3) By chain branching.
- (4) By lack of stereoregularity.
- (5) By differences in geometrical isomerism.

Copolymerisation provides a very effective way of reducing the regularity and hence the ability to crystallise. Polyethylene is a crystalline material but with random ethylene-propylene copolymers crystallisation becomes a difficult process and a rubbery material results. The introduction of side groups in a random manner has a similar effect. If polyethylene is partially chlorinated, the regularity of the structure is reduced and a rubbery polymer will result. A chlorinated polyethylene which also contains a few sulphonyl chloride groups is a commercially available rubber (Hypalon). The treatment of poly(vinyl alcohol) with formaldehyde to give poly(vinyl formal) will also prevent crystallisation because of the structural irregularities produced (*Figure 4.4*).

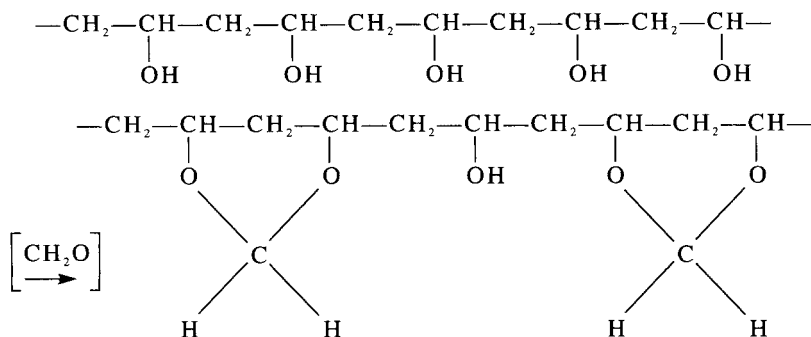


Figure 4.4

Branching can to some extent reduce the ability to crystallise. The frequent, but irregular, presence of side groups will interfere with the ability to pack. Branched polyethylenes, such as are made by high-pressure processes, are less crystalline and of lower density than less branched structures prepared using metal oxide catalysts. In extreme cases crystallisation could be almost completely inhibited. (Crystallisation in high-pressure polyethylenes is restricted more by the frequent short branches rather than by the occasional long branch.)

In recent years the significance of stereoregularity has become more appreciated. In vinyl compounds, for instance, different structures may arise for similar reasons that optical isomers are produced in simple organic chemicals. Covalent bonds linking one atom with others are not all in the same plane but form certain angles with each other. A carbon atom attached to four hydrogen atoms or to other carbon atoms has bonds subtended at angles of about 109 degrees. As conventionally represented on paper it would appear that linear polypropylene can only take one form (*Figure 4.5*). If, however, it is remembered that the actual molecule, even when fully extended, is not planar, then it will be seen that different forms can arise.

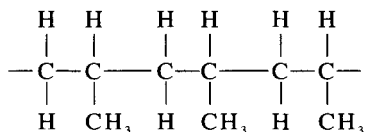


Figure 4.5

Table 4.2 Transitions in polymers and their probable origin

	$T_{\text{side chain}}$ (°C)	$T_{\text{cg type}}$ (°C)	T_{g} (°C)	T_{m} (°C)	Other (°C)	$\text{Features of interest affecting } T_{\text{g}}$
Poly(dimethyl siloxane)			-123	-85 to -65		Flexible backbone
<i>cis</i> -1,4-Polybutadiene			-107	-4		Flexibility enhanced by occasional C = C bond
<i>trans</i> -1,4-Polybutadiene			-107	+145		<i>cis-trans</i> effect
<i>cis</i> -1,4-Polyisoprene			-73	+25	+20	Stiffening effect of methyl group
<i>trans</i> -1,4-Polyisoprene			-53	+65	+56	<i>trans</i> -isomer
Polyethylene		-105	-20	+120	+80, +130	Flexible backbone
Polypropylene	-254		+5	+150	+60, -70	Stiffening effect of methyl group
Polybut-1-ene	-150	-123	-20	+20		Plasticising effect of alkyl side chain
Polyisobutylene			-73		+10	Symmetry
Polypent-1-ene			+24	+70		Plasticising effect of alkyl side group
Poly(3-methyl-but-1-ene)	-123	-123*	+60	+240		Branched side chain
Poly(4-methylpent-1-ene)	-248, -123	-123*	+55	+245		Branched side chain
Poly- <i>n</i> -heptylbutadiene			-83			Long side chain
Poly- <i>n</i> -decylbutadiene			-53			Interaction in long side chain
Polyoxymethylene		-70	-13	+160	+120	Flexible backbone
Polytetrafluoroethylene		-87	+115	+327	+19, +30	Stiff backbone
Polychlorotrifluoroethylene (PCTFE)		-20	+52	+221	+150	
Poly(vinyl alcohol)			+70	Decomp. below T_{m}		Polar interaction
Poly(vinyl acetate)			+30			Weak polar interaction
Poly(vinyl chloride)	-253	-25	+80			Polar interaction
Poly(vinylidene chloride)			-18	+190		Symmetry
Polyacrylonitrile			+80 to +104	Decomp.	+140	Polar interaction
Polystyrene (atactic)	-230	-110	+90 to +100	—	0 to +35, +166 to +190	Stiffening by benzene ring
Polystyrene (isotactic)			+100	+230		Regular structure
Poly(ethylene adipate)			-70			Flexible backbone
Poly(ethylene terephthalate)		-30	+67	+256		Stiffening by <i>p</i> -phenylene group
<i>Polymethacrylates:</i>						
Methyl (free radical)	-269, +20		+99		-100	Stiffening effect of methyl group

Table 4.2 Transitions in polymers and their probable origin (continued)

	<i>T</i> side chain (°C)	<i>T</i> _{cg} type (°C)	<i>T</i> _g (°C)	<i>T</i> _m (°C)	<i>Other</i> (°C)	<i>Features of interest affecting T_g</i>
Methyl (isotactic)			+45	+160		
Methyl (syndiotactic)			+115	>200		
Ethyl	-223, +50		+65			Side-chain plasticisation
Isopropyl	-150, +50		+81			Branched side chain
n-Butyl	-150		+20			Side-chain plasticisation
Isobutyl			+53			Branched side chain
n-Octyl			-20			Side-chain plasticisation
<i>Polyacrylates:</i>						
Methyl			0			Absence of α-CH ₃ , c.f. poly(methyl methacrylate)
Ethyl			-24			Side-chain plasticisation
t-Butyl			+40	+193		Side-chain branching
Isopropyl (isotactic)			-11	+162		Side-chain branching
Polycarbonate of bis-phenol A			+149	+225	-120	Stiffening by <i>p</i> -phenylene group
Polysulphone of bis-phenol A			+195		-100	Stiffening by <i>p</i> -phenylene group
Polysulphone of norcamphor			+250			Stiffening by norcamphor group
Polyacenaphthylene			+214			Steric hindrance
Poly- <i>N</i> -vinylcarbazole			+150	+320		Steric hindrance
Nylon 6			+50	+215		H-bonding
Nylon 66	-253	-120	+60	+264	-30	H-bonding
<i>Polyvinyl ethers:</i>						
Methyl			-31	+144		Flexible backbone
Ethyl				+86		Side-chain plasticisation
n-Propyl				+76		Side-chain plasticisation
n-Butyl				+64		Side-chain plasticisation
Isobutyl			-24	+165		Side-chain branching
t-Butyl				+240 to +260		Side-chain branching
Poly(vinyl cyclohexane)			+90	+372		Steric hindrance of side group
Poly(ethylene oxide)			-55	+66		Flexible backbone
Poly(propylene oxide)			-62	+65		Flexible backbone
Cellulose triacetate			+107	+300		Stiff backbone
Poly(methyl isopropenyl ketone)			+114	+243		Interchain attraction

*The transitions at -123°C in the methyl butene and methyl pentene polymers have been ascribed to both side-chain and main-chain mechanisms.

Reproduced, with minor revisions in the light of data now available, from chapter on 'The Glass Transition, Melting Point and Structure' by the author in *Polymer Science* edited by Professor A. D. Jenkins,⁴ with permission of North-Holland Publishing Company.

In *Figure 4.6* three idealised cases are given. *Figure 4.6 (a)* depicts an *isotactic* structure in which all of the methyl groups are on the same side of the main chain. An alternating system is shown in *Figure 4.6 (b)* which is known as a *syndiotactic* structure whilst *Figure 4.6 (c)* depicts a random system—known as an *atactic* structure. Thus the isotactic and syndiotactic structures are regular whilst the atactic is irregular. It is not possible to convert from one form to another simply by rotating the molecule about a chain C—C bond. This is easier to see using a molecular model rather than by looking at a formula written on a piece of paper. Since the structures are dissimilar, it is to be expected that the bulk properties of the polymer will differ. (In practice perfect isotactic and syndiotactic structures are not usually obtained and a polymer molecule may be part atactic and part isotactic or syndiotactic. Furthermore, in the mass, molecules of differing tacticity may exist. In the case of isotactic polypropylene in the crystalline state the molecules take up a helical arrangement which can either have a clockwise or anticlockwise twist.)

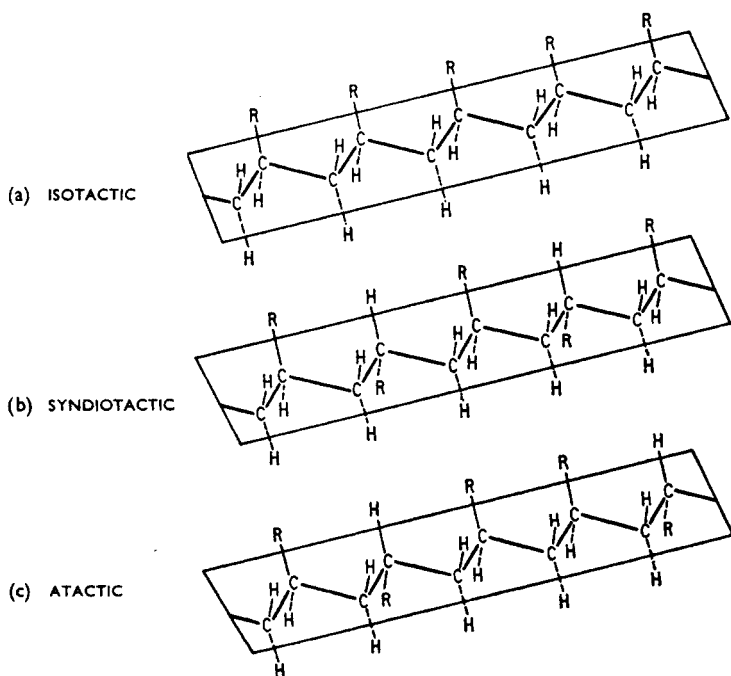


Figure 4.6. Relationship between isotactic, syndiotactic and atactic forms in head-to-tail vinyl polymers. (For simplicity of comparison the main chain in each case is shown stretched in the planar all-*trans* zigzag form)

The regular syndiotactic and isotactic structures are capable of crystallisation whereas the atactic polymer cannot normally do so. In the case of polypropylene the isotactic material is a crystalline fibre-forming material. It is also an important thermoplastic which can withstand boiling water for prolonged periods. Atactic polypropylene is a 'dead' amorphous material. Polystyrene as commonly encountered is atactic and glass-like but the syndiotactic material

introduced in the late 1990s is crystalline. The only occasions when an atactic polymer can crystallise are when the atoms or groups attached to the asymmetric carbon atom are of a similar size. For example, poly(vinyl alcohol) is atactic but as the hydroxy group is small enough for the polymer to pack into the same lattice as polyethylene a crystalline material results. (Most commercial grades of poly(vinyl alcohol) contain acetate groups so that crystallinity in these materials is somewhat limited.)

Related to stereoregularity is the possibility of *cis*, *trans* isomerism. The molecule of natural rubber is a *cis*-1,4-polyisoprene whilst that of gutta percha is the *trans* isomer.

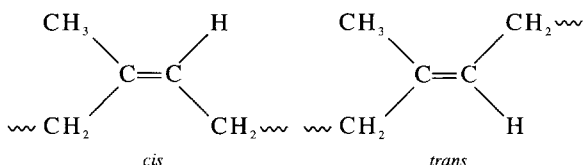


Figure 4.7

These different forms (Figure 4.7) take up different crystalline structures and consequently the bulk properties of the polymer differ. At room temperature gutta percha is a stiff leathery material.

A further source of irregularity can arise from the mode of polymerisation; radicals, or ions, can in theory add to a monomer in either a head-to-tail (a) or head-to-head (b) fashion (Figure 4.8).

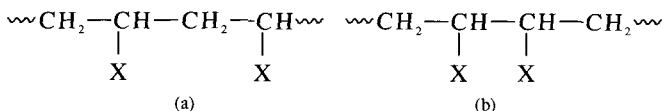


Figure 4.8

It is an observed fact that with most synthetic polymers the head-to-tail structure is formed. In the case of diene polymers differences may arise in the point of addition. Reaction can take place at the 1 and 4 positions, the 1 and 2 positions or the 3 and 4 positions to give the structures indicated in Figure 4.9.

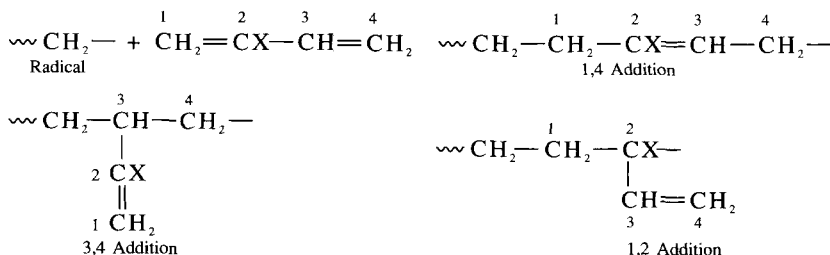


Figure 4.9

The presence of pendant reactive vinyl groups through 1,2 and 3,4 addition provides a site for branching and cross-linking since these may be involved in other chain reactions. Because of this a 1,4 polymer is generally to be desired.

4.4 FACTORS AFFECTING THE CRYSTALLINE MELTING POINT

To a large extent the factors which determine the position of the glass transition temperature of a polymer (chain stiffness and intermolecular forces) also determine the melting point of a crystalline polymer. In *Figure 4.10* a rough correlation is seen between the glass transition and melting points of a number of crystalline polymers. The glass transition temperature of many polymers is about two-thirds that of the crystalline melting point when measured in K. An important exception to this occurs with copolymers.

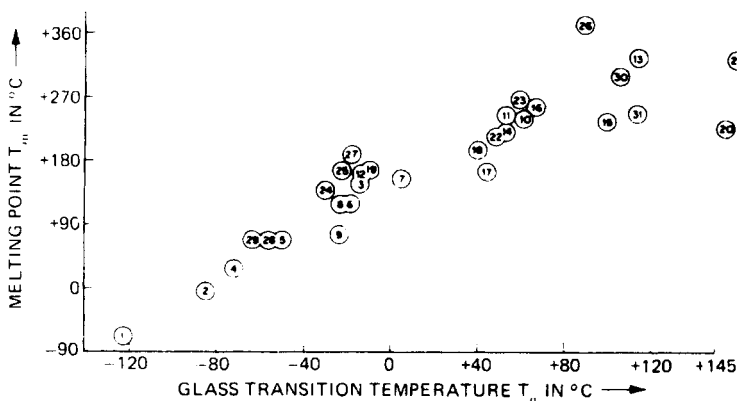
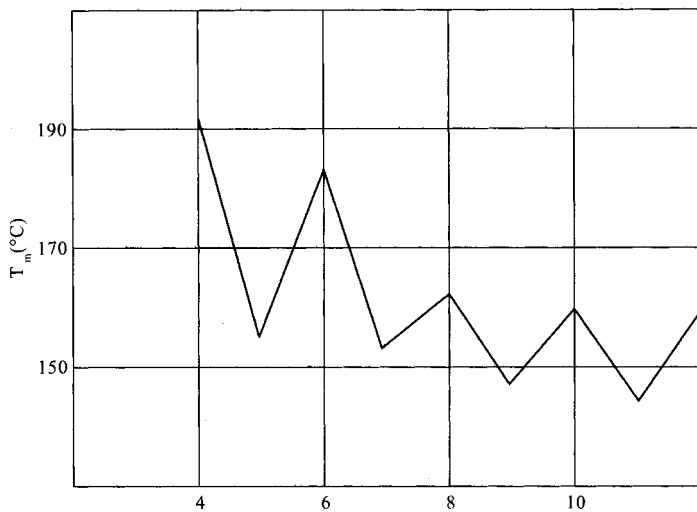


Figure 4.10. Relationship between glass transition temperature and melting point. (Reproduced by permission of North-Holland Publishing Company⁴)

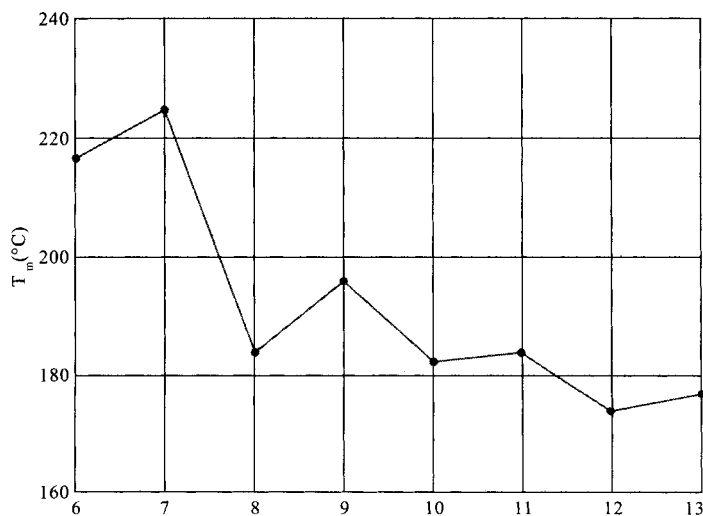
- | | |
|-------------------------------------|--|
| (1) Poly(dimethyl siloxane) | (17) Isotactic poly(methyl methacrylate) |
| (2) <i>cis</i> -1,4-Polybutadiene | (18) Poly(<i>t</i> -butyl acrylate) |
| (3) <i>trans</i> -1,4-Polybutadiene | (19) Isotactic poly(isopropyl acrylate) |
| (4) <i>cis</i> -1,4-Polyisoprene | (20) Bis-phenol polycarbonate |
| (5) <i>trans</i> -1,4-Polyisoprene | (21) Poly(vinylcarbazole) |
| (6) Polyethylene | (22) Nylon 6 |
| (7) Polypropylene | (23) Nylon 66 |
| (8) Polybut-1-ene | (24) Poly(vinyl methyl ether) |
| (9) Polypent-1-ene | (25) Poly(vinyl isobutyl ether) |
| (10) Poly-3-methylbut-1-ene | (26) Poly(vinyl cyclohexanone) |
| (11) Poly-4-methylpent-1-ene | (27) Poly(vinylidene chloride) |
| (12) Polyoxymethylene | (28) Poly(ethylene oxide) |
| (13) Polytetrafluoroethylene | (29) Poly(propylene oxide) |
| (14) Polychlorotrifluoroethylene | (30) Cellulose triacetate |
| (15) Isotactic polystyrene | (31) Poly(methyl isopropenyl ketone) |
| (16) Poly(ethylene terephthalate) | |

An interesting second-order effect on the melting point occurs with condensation and rearrangement polymers where there are repeating segments of methylene groups in the chain. While there is a tendency for the melting point to decrease with the number of methylene groups in the repeat unit, i.e. with

decrease in the concentration of polar (e.g. ester or amide) linkages it is commonly found that where there is an even number of methylene groups in the segment the melting point is higher than with adjacent polymers in the series with odd numbers of methylene groups. This is illustrated in *Figure 4.11(a)* for polyurethanes of general formula $-(\text{CH}_2)_4\text{OOCNH}(\text{CH}_2)_n\text{NHCOO}-$ and in *Figure 4.11(b)* for polyamides of general formula $-(\text{CH}_2)_n\text{CONH}-$. The effect is further illustrated in *Figure 18.10* (for polyamides) and *Figure 25.14* for polyesters.



(a) Number of carbon atoms in polyurethane



(b) Number of carbon atoms in polyamide

Figure 4.11 Zig-zag effect on melting points with increasing number of carbon atoms in (a) polyurethanes of type $-(\text{CH}_2)_4\text{OOCNH}(\text{CH}_2)_n\text{NHCOO}-$ and (b) polyamides of type $-(\text{CH}_2)_n\text{CONH}-$

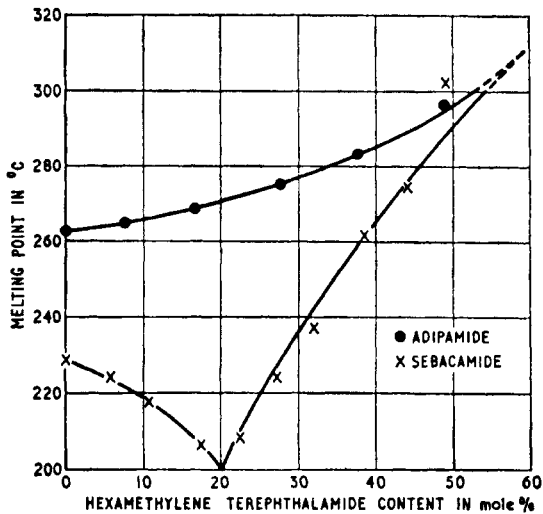


Figure 4.12. Melting points of copolymers of hexamethyleneadipamide and -terephthalamide, and of hexamethylene-sebacamide and -terephthalamide. (After Edgar and Hill⁵)

Whereas the glass transition of a copolymer is usually intermediate between those of the corresponding homopolymers this is not commonly the case with the melting points. Figure 4.12 shows the effect of copolymerising hexamethylene-sebacamide with hexamethyleneterephthalamide. Only when the monomer units are isomorphous, so that the molecules can take up the same structure, is there a linear relationship between melting point and composition (as with hexamethyleneadipamide and hexamethyleneterephthalamide).

Further information on the effect of polymer structure on melting points has been obtained by considering the heats and entropies of fusion. The relationship between free energy change ΔF with change in heat content ΔH and entropy change ΔS at constant temperature is given by the equation

$$\Delta F = \Delta H - T\Delta S$$

In thermodynamic language it is said that a reaction will occur if there is a decrease in the free energy, i.e. ΔF is negative. Since at the melting point melting and crystallising processes are balanced ΔF is zero and the expression may be written

$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

Where T_m is the melting point
 ΔH_m the heat of fusion
 ΔS_m the entropy of fusion

The entropy term is a measure of the degree of freedom of the molecules and thus a measure of its flexibility. Measurement of the heats and entropies of fusion has provided interesting information on the relative importance of various factors

influencing the melting point of specific polymers. The linear aliphatic polyesters have low melting points and this has been attributed to the high flexibility of the C—O bond. This would suggest a high entropy of fusion but in fact it is observed that both the heat and entropy terms are lower than in the case of polyethylene. These observations remain to be fully explained.

4.5 SOME INDIVIDUAL PROPERTIES

By a knowledge of the glass transition, the ability to crystallise and, where relevant, the crystalline melting point general statements may be made regarding the properties of a given polymer at a specified temperature. From this information it is possible to say that the material is either a rubber, a glass-like resin, a melt, a hard crystalline solid (below T_g or with a high degree of crystallinity) or a flexible crystalline solid (polymer above T_g and with a moderate low degree of crystallinity). Each class of materials has characteristically different properties. In the case of rubbers and glass-like amorphous resins T_g will indicate the range of minimum and maximum service temperatures respectively. A polymer with T_g close to room temperature might be expected to have only a limited value as its properties would be liable to large changes with changes in ambient temperature. Paradoxically many plasticised PVC compounds are in such a position and yet they form one of the most important classes of plastics materials.

In the case of a crystalline polymer the maximum service temperature will be largely dependent on the crystalline melting point. When the polymer possesses a low degree of crystallinity the glass transition temperature will remain of paramount importance. This is the case with unplasticised PVC and the polycarbonate of bis-phenol A.

4.5.1 Melt Viscosity

The melt viscosity of a polymer at a given temperature is a measure of the rate at which chains can move relative to each other. This will be controlled by the ease of rotation about the backbone bonds, i.e. the chain flexibility, and on the degree of entanglement. Because of their low chain flexibility, polymers such as polytetrafluoroethylene, the aromatic polyimides, the aromatic polycarbonates and to a less extent poly(vinyl chloride) and poly(methyl methacrylate) are highly viscous in their melting range as compared with polyethylene and polystyrene.

For a specific polymer the melt viscosity is considerably dependent on the (weight average) molecular weight. The higher the molecular weight the greater the entanglements and the greater the melt viscosity. Natural rubber and certain poly(methyl methacrylate) products (e.g. Perspex), which have molecular weights of the order of 10^6 , cannot be melt processed until the chains have been broken down into smaller units by mastication processes. Chain branching also has an effect. In the case of polyethylene and the silicones the greater the branching, at constant weight average molecular weight, the lower the melt viscosity. However, in poly(vinyl acetate) the melt viscosity increases with an increase in branching. It has been suggested that the branch length may be the controlling influence in this. Factors affecting the viscous flow properties of polymers are discussed more fully in Chapter 8.

4.5.2 Yield Strength and Modulus

On comparison of the yield strengths and elastic moduli of amorphous polymers well below their glass transition temperature it is observed that the differences between polymers are quite small. Yield strengths are of the order of 8000 lbf/in² (55 MPa) and tension modulus values are of the order of 500 000 lbf/in² (3450 MPa). In the molecular weight range in which these materials are used differences in molecular weight have little effect.

In the case of commercial crystalline polymers wider differences are to be noted. Many polyethylenes have a yield strength below 2000 lbf/in² (14 MPa) whilst the nylons may have a value of 12 000 lbf/in² (83 MPa). In these polymers the intermolecular attraction, the molecular weight and the type and amount of crystalline structure all influence the mechanical properties.

4.5.3 Density

This, the mass per unit volume, is a function of the weight of individual molecules and the way they pack. The hydrocarbons do not possess 'heavy' atoms and therefore the mass of the molecule per unit volume is rather low. Amorphous hydrocarbon polymers generally have specific gravities of 0.86–1.05. Where large atoms are present, e.g. chlorine atoms, the mass per unit volume is higher and so PVC, a substantially amorphous polymer, has a specific gravity of about 1.4.

If a polymer can crystallise then molecular packing is much more efficient and higher densities can be achieved. The high densities of PTFE (about 2.2) and poly(vinylidene chloride) (about 1.7) are partially attributable to this fact. Polyethylenes made by different processes often differ in the degree of branching and thus can crystallise or pack to varying events. For this reason polyethylenes produced by a high-pressure process have a lower density than those produced using supported metal oxide catalysts. The amorphous ethylene-propylene rubbers have lower densities than either polyethylene or isotactic polypropylene, both of which are capable of crystallising.

The conformation adopted by a molecule in the crystalline structure will also affect the density. Whereas polyethylene adopts a planar zigzag conformation, because of steric factors a polypropylene molecule adopts a helical conformation in the crystalline zone. This requires somewhat more space and isotactic polypropylene has a lower density than polyethylene.

4.5.4 Impact Strength

Familiarity with a given plastics material under normal conditions of use leads to it being considered as either a brittle or a tough material. Thus polystyrene, poly(methyl methacrylate) and unmodified unplasticised PVC are normally rated as brittle, breaking with a sharp fracture, whereas low-density polyethylene and plasticised PVC are considered to be tough. Whether a material exhibits brittle fracture or appears tough depends on the temperature and the rate of striking, that is it is a function of the rate of deformation. One object of research into the physical properties of plastics material is to determine the locations of tough-brittle transitions for commercial polymers. As with other physical properties the position of the glass transition temperature and the facility with which crystallisation can take place are fundamental to the impact strength of a

material. Well below the glass transition temperature amorphous polymers break with a brittle fracture but they become tougher as the glass transition temperature is approached. A rubbery state will develop above the glass transition and the term impact strength will cease to have significance. In the case of crystalline materials the toughness will depend on the degree of crystallinity; large degrees of crystallinity will lead to inflexible masses with only moderate impact strengths. The size of the crystalline structure formed will also be a significant factor, large spherulitic structures leading to masses with low impact strength. As indicated in the previous chapter spherulitic size may be controlled by varying the ratio of nucleation to growth rates.

The valuable characteristics of polyblends, two-phase mixtures of polymers in different states of aggregation, were also discussed in the previous chapter. This technique has been widely used to improve the toughness of rigid amorphous polymers such as PVC, polystyrene, and styrene-acrylonitrile copolymers.

References

1. SWALLOW, J. C., *J. Roy. Soc. Arts*, **99**, 355 (1951)
2. GORDON, M., *High Polymers*, Iliffe, London (1963)
3. JENCKEL, E., and UEBERREITER, K., *Z. Phys. Chems.*, **A182**, 361 (1939)
4. BRYDSON, J. A., Chapter entitled 'Glass Transition, Melting Point and Structure' in *Polymer Science* (Ed. JENKINS, A. D.), North-Holland, Amsterdam (1972)
5. EDGAR, O. B., and HILL, R., *J. Polymer Sci.*, **8**, 1 (1952)

Bibliography

- BILLMEYER, F. W., *Textbook of Polymer Science*, Interscience, New York (1962)
- BUECHE, F., *Physical Properties of Polymers*, Interscience, New York (1962)
- GORDON, M., *High Polymers*, Iliffe, London (1963)
- HAWARD, R. N., (Ed.), *The Physics of Glassy Polymers*, Applied Science, London (1973)
- JENKINS, A. D., (Ed.), *Polymer Science*, North-Holland, Amsterdam (1972)
- MEARES, P., *Polymers: Structure and Bulk Properties*, Van Nostrand, London (1965)
- MILLER, M. L., *The Structure of Polymers*, Reinhold, New York (1966)
- RITCHIE, P. D., (Ed.), *Physics of Plastics*, Iliffe, London (1965)
- TOBOLSKY, A. V., *Properties and Structure of Polymers*, John Wiley, New York (1960)

5

Relation of Structure to Chemical Properties

5.1 INTRODUCTION

It is sometimes stated that a given material has 'a good chemical resistance', or alternatively the material may be stated to be poor or excellent in this respect. Such an all-embracing statement can be little more than a rough generalisation, particularly since there are many facets to the behaviour of polymers in chemical environments.

There are a number of properties of a polymer about which information is required before detailed statements can be made about its chemical properties. The most important of these are:

- (1) The solubility characteristics.
- (2) The effect of specific chemicals on molecular structure, particularly in so far as they lead to degradation and cross-linking reactions.
- (3) The effect of specific chemicals and environments on polymer properties at elevated temperatures.
- (4) The effect of high-energy irradiation.
- (5) The aging and weathering of the material.
- (6) Permeability and diffusion characteristics.
- (7) Toxicity.

Before dealing with each of these aspects, it is useful to consider, very briefly, the types of bonds which hold atoms and molecules together.

5.2 CHEMICAL BONDS

The atoms of a molecule are held together by primary bonds. The attractive forces which act between molecules are usually referred to as secondary bonds, secondary valence forces, intermolecular forces or van der Waals forces.

Primary bond formation takes place by various interactions between electrons in the outermost shell of two atoms resulting in the production of a more stable

state. The three main basic types of primary bond are ionic, covalent and co-ordinate.

An *ionic bond* is formed by the donation of an electron by one atom to another so that in each there is a stable number of electrons in the outermost shell (eight in the case of most atoms). An example is the reaction of sodium and chlorine (Figure 5.1).



Figure 5.1

The stable sodium ion has a positive charge because it is short of one electron and the chlorine atom is negatively charged for the converse reason. Ionic bonds are seldom found in polymers of current interest as plastics materials although the ionic bond is important in ion-exchange resins and in the 'ionomers' (see Chapter 11).

The most important interatomic bond in polymers, and indeed in organic chemistry, is the *covalent bond*. This is formed by the sharing of one or more pairs of electrons between two atoms. An example is the bonding of carbon and hydrogen to form methane (Figure 5.2).

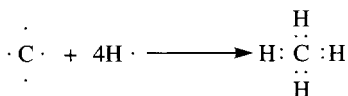


Figure 5.2

In the case of carbon the stable number of electrons for the outer shell is eight and for hydrogen, two. Thus all the atoms possess or share the number of electrons required for stability. Where a pair of electrons is shared between two atoms, it is stated that the atoms are bound by a single bond. If there are two pairs a double bond is formed and if there are three pairs a triple bond.

The third main type of bond is the *co-ordinate bond*, in which both of the shared electrons come from one atom. Examples of interest in polymer science are the addition compounds of boron trifluoride (Figure 5.3).

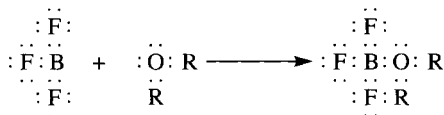


Figure 5.3

In the covalent bond, the primary bond of greatest importance in high polymers, the electron pair is seldom equally shared between the two atoms. Thus one end of the bond has a small negative charge and the other end has a slight positive charge. Such a bond is said to be polar and the strength and direction of the polarity is determined by the atoms forming the bond.

An estimate of the polarity of a bond between two atoms may be obtained by reference to the electronegativity scale. The electronegativity values of some common elements are given in *Table 5.1*. The higher the value the greater the electronegativity.

Table 5.1 Electronegativity values of some common elements

<i>Element</i>	<i>Electronegativity</i>	<i>Element</i>	<i>Electronegativity</i>
Caesium	0.7	Iodine	2.4
Potassium	0.8	Carbon	2.5
Sodium	0.9	Sulphur	2.5
Lithium	1.0	Bromine	2.8
Aluminium	1.5	Nitrogen	3.0
Silicon	1.8	Chlorine	3.0
Hydrogen	2.1	Oxygen	3.5
Phosphorus	2.1	Fluorine	4.0

The greater the difference in the electronegativity values of the atoms forming the bond the greater the polarity of the bond. Where the electronegativity difference is greater than 2, electrovalent bonds are commonly formed; where it is less than 2 the bond is usually covalent but it may also be polar. Thus a carbon-fluorine bond will be more polar than a carbon-hydrogen bond. The electronegativity difference is approximately equal to the square root of the ionic resonance energy in electron volts (eV).

As a result of many observations on the energetics of the formation and dissociation of molecules it has been found possible to give typical bond energies and bond lengths to a number of bonds. Some of these are given in *Table 5.2*.

Although the primary bonds are important when considering the chemical reactivity and thermal stability of polymers, it is the secondary bonds which are

Table 5.2 Typical bond lengths and dissociation energies for some selected primary bonds

<i>Bond</i>	<i>Bond length R</i>	<i>Dissociation energy (kcal/mole)</i>
O—O	1.32	35
Si—Si	2.35	42.5
S—S	1.9–2.1	64
C—N	1.47	73
C—Cl	1.77	81
C—C	1.54	83
C—O	1.46	86
N—H	1.01	93
C—H	1.10	99
C—F	1.32–1.39	103–123
O—H	0.96	111
C=C	1.34	146
C=O	1.21	179
C≡N	1.15	213

of dominant importance in determining the solubility of polymers. Although some of these secondary bonds act intramolecularly, it is the intermolecular forces which are of greatest importance. The intermolecular forces can be of four types: dipole forces, induction forces, dispersion forces and the hydrogen bond.

Because of the polarity of many covalent bonds, different parts of a molecule may carry equal and opposite charges. At molecular distances a charged grouping of one polarity can attract a group of the opposite polarity on a neighbouring molecule. The dipole interaction leading to *dipole forces* between two polar molecules is shown in *Figure 5.4*. The extent of mutual dipole alignment will be a predominant factor in determining the intermolecular attraction. Since this alignment is opposed by thermal motion, dipole forces are critically dependent on temperature.



Figure 5.4

A polar molecule can also induce a dipole on a neighbouring molecule that possesses no permanent dipole. The resultant intermolecular attraction between the permanent and the induced dipole is spoken of as the *induction force*. Its magnitude is small and independent of temperature.

Although there are many molecules which appear to be non-polar, i.e. the centres of positive and negative charges appear coincident, all molecules, even the inert gases, have time-varying dipole moments which will depend on the position of the electrons at any given instant. These varying dipole moments average out to zero but they can lead to attractive forces between molecules. These are referred to as *dispersion forces* and they represent the bulk of the intermolecular forces which are present in the absence of strong permanent dipoles. The magnitudes of these three intermolecular forces in a few selected molecules are given in *Table 5.3*.

A special case is that of *hydrogen bonding* where the hydrogen atom attached to a proton donor group (e.g. carboxyl, hydroxyl, amine or amide group) is shared with a basic, proton-accepting group (e.g. the oxygen in a carboxyl, ether or hydroxyl group or the nitrogen atom in amines or amides).

Table 5.3 Magnitude of various intermolecular forces in some simple molecules

Molecule	Intermolecular energy (kcal/mole)			
	Dipole	Induction	Dispersion	Total
A	0	0	2.03	2.03
CO	0.0001	0.0002	2.09	2.09
HI	0.006	0.03	6.18	6.21
HCl	0.79	0.24	4.02	5.05
NH ₃	3.18	0.37	3.52	7.07
H ₂ O	8.69	0.46	2.15	11.30

Intermolecular forces are generally less than 10 kcal/mole. In polymers, in the absence of hydrogen bonding, the intermolecular force is primarily due to dispersion effects.

5.3 POLYMER SOLUBILITY

A chemical will be a solvent for another material if the molecules of the two materials are compatible, i.e. they can co-exist on the molecular scale and there is no tendency to separate. This statement does not indicate the speed at which solution may take place since this will depend on additional considerations such as the molecular size of the potential solvent and the temperature. Molecules of two different species will be able to co-exist if the force of attraction between different molecules is not less than the forces of attraction between two like molecules of either species. If the average force of attraction between dissimilar molecules A and B is F_{AB} and that between similar molecules of type B F_{BB} and between similar molecules of type A F_{AA} then for compatibility $F_{AB} \geq F_{BB}$ and $F_{AB} \geq F_{AA}$. This is shown schematically in *Figure 5.5* (a).

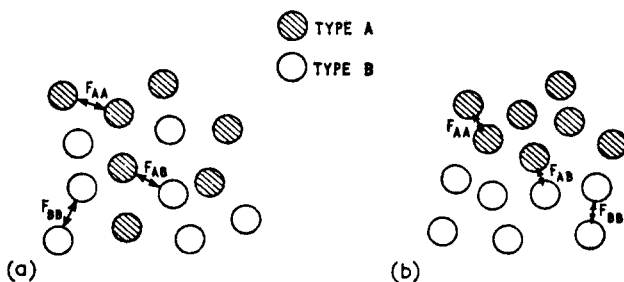


Figure 5.5. Schematic representation of compatible and incompatible systems. (a) $F_{AB} \geq F_{AA}$; $F_{AB} \geq F_{BB}$. Mixture compatible. (b) F_{AA} or $F_{BB} > F_{AB}$. Molecules separate

If either F_{AA} or F_{BB} is greater than F_{AB} the molecules with the highest intermolecular attraction will tend to congregate or cohere and they will expel the dissimilar molecule with the result that two phases will be formed. These conditions are shown in *Figure 5.5* (b).

It now becomes necessary to find some suitable measure of the forces of attraction holding molecules together. If we first consider like molecules we might expect the latent heat of vaporisation L to provide a useful basis, but this would exceed the value of interest to us by an amount corresponding to the mechanical work done on evaporation, an amount approximating to RT where R is the gas constant and T the absolute temperature. The value of $L - RT$, the energy of vaporisation, will also clearly depend on the molecular size, a parameter which would not be expected to have large effect on the forces of attraction between two dissimilar molecules. More relevant will be the terms $(L - RT)/M$ (a measure of the energy of vaporisation per unit weight) and

$$\frac{L - RT}{M/D}$$

the energy of vaporisation per molar volume (where M is the molecular weight). This latter term is known as the *cohesive energy density* and has often been expressed in units of cal/cm^3 . However, these units are contrary to the SI system where the units will be expressed as MPa. More commonly encountered in qualitative studies is the square root of the cohesive energy density, which is known as the solubility parameter and given the symbol δ , i.e.

$$\delta = \left(\frac{L - RT}{M/D} \right)^{1/2} \quad (\text{cal/cm}^3)^{1/2} \text{ or MPa}^{1/2}$$

The solubility parameter is thus an experimentally determinable property although special methods are necessary with polymers, which cannot normally be vaporised without decomposition. Such methods are discussed in Section 5.3.3.

It is the aim of this part of the chapter to show how certain predictions may be made about the solubility of a given material such as a polymer in any given solvent. We have seen that the solubility parameter has given us a measure of F_{AA} and F_{BB} but the magnitude of F_{AB} will have to be considered separately for the following systems:

- (1) Amorphous non-polar polymers and amorphous non-polar solvents.
- (2) Crystalline non-polar polymers and amorphous solvents.
- (3) Amorphous non-polar polymers and crystalline solvents.
- (4) Amorphous polar polymers and solvents.
- (5) Crystalline polar polymers and solvents.
- (6) Vulcanised rubber and thermosetting plastics.

Amorphous non-polar polymers and amorphous non-polar solvents

It is assumed in these circumstances, by analogy with gravitational and electrostatic attraction, that F_{AB} will be equal to the geometric mean of F_{AA} and F_{BB} . If by arbitrary definition we take $F_{AA} > F_{AB}$ then

$$F_{AA} > F_{AB} > F_{BB}$$

Since we have already seen that solution will only occur when

$$F_{AB} \geq F_{AA} \text{ and } F_{AB} \geq F_{BB}$$

then compatibility between amorphous non-polar polymers and solvents can only occur when

$$F_{AA} \cong F_{AB} \cong F_{BB}$$

that is, when polymer and solvent have similar solubility parameters (in practice within about $2 \text{ MPa}^{1/2}$).

Tables 5.4 and 5.5 predict that unvulcanised natural rubber ($\delta = 16.5$) will be dissolved in toluene ($\delta = 18.2$) and in carbon tetrachloride ($\delta = 17.5$) but not in ethanol ($\delta = 26.0$), all values being in units of $\text{MPa}^{1/2}$. This is found to be true. Similarly it is found that there is a wide range of solvents for polystyrene in the solubility parameter range $17.2\text{--}19.7 \text{ MPa}^{1/2}$.

Table 5.4 Solubility parameters of polymers

<i>Polymer</i>	δ	
	MPa ^{1/2}	(cal/cm ³) ^{1/2}
Polytetrafluoroethylene	12.6	6.2
Polychlorotrifluoroethylene	14.7	7.2
Polydimethylsiloxane	14.9	7.3
Ethylene-propylene rubber	16.1	7.9
Polyisobutylene	16.1	7.9
Polyethylene	16.3	8.0
Polypropylene	16.3	8.0
Polyisoprene (natural rubber)	16.5	8.1
Polybutadiene	17.1	8.4
Styrene-butadiene rubber	17.1	8.4
Poly(t-butyl methacrylate)	16.9	8.3
Poly(n-hexyl methacrylate)	17.6	8.6
Poly(n-butyl methacrylate)	17.8	8.7
Poly(butyl acrylate)	18.0	8.8
Poly(ethyl methacrylate)	18.3	9.0
Polymethylphenyl siloxane	18.3	9.0
Poly(ethyl acrylate)	18.7	9.2
Polysulphide rubber	18.3-19.2	9.0-9.4
Polystyrene	18.7	9.2
Polychloroprene rubber	18.7-19.2	9.2-9.4
Poly(methyl methacrylate)	18.7	9.2
Poly(vinyl acetate)	19.2	9.4
Poly(vinyl chloride)	19.4	9.5
Bis-phenol A polycarbonate	19.4	9.5
Poly(vinylidene chloride)	20.0-25.0	9.8-12.2
Ethylcellulose	17.3-21.0	8.5-10.3
Cellulose di(nitrate)	21.6	10.55
Poly(ethylene terephthalate)	21.8	10.7
Acetal resins	22.6	11.1
Cellulose diacetate	23.2	11.35
Nylon 66	27.8	13.6
Poly(methyl α -cyanoacrylate)	28.7	14.1
Polyacrylonitrile	28.7	14.1

Because of difficulties in their measurement, published figures for a given polymer can range up to 3% on either side of the average figure quoted. More comprehensive data are given in reference 7.

Table 5.5 Solubility parameters and partial polarities (P) of some common solvents

Polymer	δ		P
	$\text{MPa}^{1/2}$	$(\text{cal/cm}^3)^{1/2}$	
Neo-pentane	12.8	6.3	0
Isobutylene	13.7	6.7	0
n-Hexane	14.9	7.3	0
Diethyl ether	15.1	7.4	0.3
n-Octane	15.5	7.6	0
Methylcyclohexane	15.9	7.8	0
Ethyl isobutyrate	16.1	7.9	—
Di-isopropyl ketone	16.3	8.0	0.3
Methyl amylacetate	16.3	8.0	—
Turpentine	16.5	8.1	0
Cyclohexane	16.7	8.2	0
2,2-Dichloropropane	16.7	8.2	—
sec-Amyl acetate	16.9	8.3	—
Dipentene	17.3	8.5	0
Amyl acetate	17.3	8.5	0.07
Methyl n-butyl ketone	17.6	8.6	0.35
Pine oil	17.6	8.6	—
Carbon tetrachloride	17.6	8.6	0
Methyl n-propyl ketone	17.8	8.7	0.4
Piperidine	17.8	8.7	—
Xylene	18.0	8.8	0
Dimethyl ether	18.0	8.8	—
Toluene	18.2	8.9	0
Butyl cellosolve	18.2	8.9	—
1,2-Dichloropropane	18.3	9.0	—
Mesityl oxide	18.3	9.0	—
Isophorone	18.6	9.1	—
Ethyl acetate	18.6	9.1	0.17
Benzene	18.7	9.2	0
Diacetone alcohol	18.7	9.2	—
Chloroform	19.0	9.3	0.02
Trichloroethylene	19.0	9.3	0
Tetrachloroethylene	19.2	9.4	0.01
Tetralin	19.4	9.5	—
Carbitol	19.6	9.6	—
Methyl chloride	19.8	9.7	—
Methylene dichloride	19.8	9.7	—
Ethylene dichloride	20.0	9.8	0
Cyclohexanone	20.2	9.9	—
Cellosolve	20.2	9.9	—
Dioxane	20.2	9.9	0.01
Carbon disulphide	20.4	10.0	0
Acetone	20.4	10.0	0.69
n-Octanol	21.0	10.3	0.04
Butyronitrile	21.4	10.5	0.72
n-Hexanol	21.8	10.7	0.06

Table 5.5 Continued

<i>Polymer</i>	δ		<i>P</i>
	MPa ^{1/2}	(cal/cm ³) ^{1/2}	
<i>sec</i> -Butanol	22.0	10.8	0.11
Pyridine	22.2	10.9	0.17
Nitroethane	22.6	11.1	0.71
<i>n</i> -Butanol	23.2	11.4	0.10
Cyclohexanol	23.2	11.4	0.08
Isopropanol	23.4	11.5	—
<i>n</i> -Propanol	24.2	11.9	0.15
Dimethylformamide	24.7	12.1	0.77
Hydrogen cyanide	24.7	12.1	—
Acetic acid	25.7	12.6	0.30
Ethanol	26.0	12.7	0.27
Cresol	27.1	13.3	—
Formic acid	27.6	13.5	—
Methanol	29.6	14.5	0.39
Phenol	29.6	14.5	0.06
Glycerol	33.6	16.5	0.47
Water	47.7	23.4	0.82

A comprehensive list of solubility parameters is given in reference 7.

These tables are of greatest use with non-polar materials with values of δ less than 19.4 MPa^{1/2} and where the polymers are amorphous. It will now be necessary to discuss other systems.

Crystalline non-polar polymers and amorphous solvents

Most polymers of regular structure will crystallise if cooled below a certain temperature, the melting point T_m . This is in accord with the thermodynamic law (see Section 5.3.4) that a process will only occur if there is a decrease in free energy F in going from one state to another. This free energy change ΔF is related to the heat of melting ΔH , the temperature T and the entropy change ΔS by the equation

$$\Delta F = \Delta H - T\Delta S$$

Since on crystallising the ΔH is negative, the free energy change ΔF is also negative. The process will reverse, i.e. melting will occur, only when $T\Delta S$ becomes equal to ΔH . Immersing the crystalline polymer in a liquid of similar solubility parameter at temperatures well below T_m will do little to change the balance although the entropy term ΔS would increase slightly owing to an increase in molecular disorder on dissolution.

There are thus no solvents at room temperature for polyethylene, polypropylene, poly-4 methylpent-1-ene, polyacetals and polytetrafluoroethylene. However, as the temperature is raised and approaches T_m the $T\Delta S$ term becomes greater than ΔH and appropriate solvents become effective. Swelling will, however, occur in the amorphous zones of the polymer in the presence of solvents of similar solubility parameter, even at temperatures well below T_m .

Amorphous non-polar polymers and crystallising solvents

This situation is identical to the previous one and occurs for example when paraffin wax is mixed into rubber above the melting point of the wax. On cooling, the wax starts to crystallise, some of it forming a bloom on the rubber surface. Such a bloom assists in protecting a diene rubber from ozone attack.

Amorphous polar polymers and solvents

As already mentioned molecules cohere because of the presence of one or more of four types of forces, namely dispersion, dipole, induction and hydrogen bonding forces. In the case of aliphatic hydrocarbons the dispersion forces predominate. Many polymers and solvents, however, are said to be polar because they contain dipoles and these can enhance the total intermolecular attraction. It is generally considered that for solubility in such cases both the solubility parameter and the degree of polarity should match. This latter quality is usually expressed in terms of *partial polarity* which expresses the fraction of total forces due to the dipole bonds. Some figures for partial polarities of solvents are given in *Table 5.5* but there is a serious lack of quantitative data on polymer partial polarities. At the present time a comparison of polarities has to be made on a commonsense rather than a quantitative approach.

An alternative approach, due to Hansen, is to partition the solubility parameter into three components, δ_d , δ_p , and δ_h , due to contributions from dispersion forces, dipole-dipole forces and hydrogen bonding forces respectively. The three components may be represented by co-ordinates in three-dimensional space. Partitioning can, at least in theory, be carried out for the solubility parameters of both solvents and polymers. It may be argued that for each polymer there is a characteristic radius originating from its point in space which encloses the points for all liquids that are solvents for the polymer. As a very rough guide this radius is about 2 SI units. Whilst data for many solvents have been presented there is only limited information on polymers. Values for some solvents and polymers are given in *Table 5.6*.

Table 5.6 Partitioned values of the solubility parameter (after Hansen¹)

	δ_d (cal/cm ³) ^{1/2}	δ_p (cal/cm ³) ^{1/2}	δ_h (cal/cm ³) ^{1/2}	δ (cal/cm ³) ^{1/2}
Hexane	8.18	0	0	8.18
Benzene	8.95	0.5	1.0	9.15
Tetrahydrofuran	8.22	2.8	3.9	9.52
Acetone	7.58	5.1	3.4	9.77
Dioxane	9.30	0.9	3.6	10.00
Dimethylformamide	8.52	6.7	5.5	12.14
Methanol	7.42	6.0	10.9	14.28
Ethylene glycol	8.25	5.4	12.7	16.30
Water	6.00	15.3	16.7	23.50
Polyethylene	8.1	0	0	8.1
Polystyrene	8.95	0.5	1.6	9.11
Poly(methyl methacrylate)	7.69	4.0	3.3	9.28

1. $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$

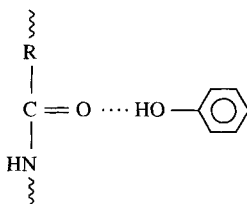
2. Data sources for *Tables 5.5* and *5.6* were different. That the data do not always coincide is an indication of their imprecision.

Crystalline polar polymers and solvents

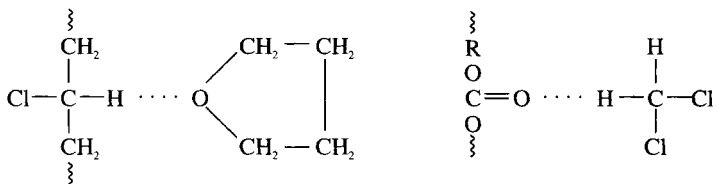
It has already been pointed out that crystalline non-polar polymers do not normally have solvents well below their crystalline melting point and the same comment can apply to a large number of polar crystalline polymers.

It has, however, been possible to find solvents for some polar crystalline polymers such as the nylons, poly(vinyl chloride) and the polycarbonates. This is because of specific interactions between polymer and solvent that may often occur, for instance by hydrogen bonding.

For example, nylon 66 will dissolve in formic acid, glacial acetic acid, phenol and cresol, four solvents which not only have similar solubility parameters but also are capable of acting as proton donors whilst the carbonyl groups on the nylon act as proton acceptors (*Figure 5.6*).

*Figure 5.6*

A more interesting example is given with PVC and the polycarbonate of bisphenol A, both slightly crystalline polymers. It is noticed here that whilst methylene dichloride is a good solvent and tetrahydrofuran a poor solvent for the polycarbonate the reverse is true for PVC yet all four materials have similar solubility parameters. It would seem that the explanation is that a form of hydrogen bonding occurs between the polycarbonate and methylene dichloride and between PVC and tetrahydrofuran (*Figure 5.7*). In other words there is a specific interaction between each solvent pair.

*Figure 5.7*

Many studies have been made to try to assess the propensity to hydrogen bonding of chemical structures. As a result the following broad generalisations may be made:

- (1) *Proton donors* include highly halogenated compounds such as chloroform and pentachlorethane. Less halogenated materials are weaker donors.
- (2) *Polar acceptors* include, in roughly descending order of strength, amines, ethers, ketones, aldehydes and esters (with aromatic materials usually being more powerful than aliphatics).

- (3) Some materials such as water, alcohols, carboxylic acids and primary and secondary amines may be able to act simultaneously as proton donors and acceptors. Cellulose and poly(vinyl alcohol) are two polymers which also function in this way.
- (4) A number of solvents such as the hydrocarbons, carbon disulphide and carbon tetrachloride are quite incapable of forming hydrogen bonds.

Vulcanised rubber and thermosetting plastics

The conventionally covalently cross-linked rubbers and plastics cannot dissolve without chemical change. They will, however, swell in solvents of similar solubility parameter, the degree of swelling decreasing with increase in cross-link density. The solution properties of the thermoelastomers which are two-phase materials are much more complex, depending on whether or not the rubber phase and the resin domains are dissolved by the solvent.

5.3.1 Plasticisers

It has been found that the addition of certain liquids (and in rare instances solids) to a polymer will give a non-tacky product with a lower processing temperature and which is softer and more flexible than the polymer alone. As an example the addition of 70 parts of di-iso-octyl phthalate to 100 parts of PVC will convert the polymer from a hard rigid solid at room temperature to a rubber-like material. Such liquids, which are referred to as plasticisers, are simply high boiling solvents for the polymer. Because it is important that such plasticisers should be non-volatile they have a molecular weight of at least 300. Hence because of their size they dissolve into the polymer only at a very slow rate at room temperature. For this reason they are blended (fluxed, gelled) with the polymer at elevated temperatures or in the presence of volatile solvents (the latter being removed at some subsequent stage of the operation).

For a material to act as a plasticiser it must conform to the following requirements:

- (1) It should have a molecular weight of at least 300.
- (2) It should have a similar solubility parameter to that of the polymer.
- (3) If the polymer has any tendency to crystallise, it should be capable of some specific interaction with the polymer.
- (4) It should not be a crystalline solid at the ambient temperature unless it is capable of specific interaction with the polymer.

The solubility parameters of a number of commercial plasticisers are given in *Table 5.7*

From *Table 5.7* it will be seen that plasticisers for PVC such as the octyl phthalates, tritoyl phosphate and dioctyl sebacate have solubility parameters within 1 cgs unit of that of the polymer. Dimethyl phthalate and the paraffinic oils which are not PVC plasticisers fall outside the range. It will be noted that tritoyl phosphate which gels the most rapidly with PVC has the closest solubility parameter to the polymer. The sebacates which gel more slowly but give products which are flexible at lower temperatures than corresponding formulations from tritoyl phosphate have a lower solubility parameter. It is, however, likely that any difference in the effects of phthalate, phosphate and sebacate plasticisers in

Table 5.7 Solubility parameters for some common plasticisers

Plasticiser	δ	
	$(\text{cal}/\text{cm}^3)^{1/2}$	$\text{MPa}^{1/2}$
Paraffinic oils	7.5 approx.	15.3 approx.
Aromatic oils	8.0 approx.	16.4 approx.
Camphor	7.5	15.3
Di-iso-octyl adipate	8.7	17.8
Di-octyl sebacate	8.7	17.8
Di-isodecyl phthalate	8.8	18.0
Dibutyl sebacate	8.9	18.2
Di-(2-ethylhexyl) phthalate	8.9	18.2
Di-iso-octyl phthalate	8.9	18.2
Di-2-butoxyethyl phthalate	9.3	18.9
Dibutyl phthalate	9.4	19.2
Triphenyl phosphate	9.8	20.0
Tritolyl phosphate	9.8	20.0
Trixylyl phosphate	9.9	20.2
Dibenzyl ether	10.0	20.4
Triacetin	10.0	20.4
Dimethyl phthalate	10.5	21.4
Santicizer 8	11.0 approx.	22.4

Data obtained by Small's method² except for that of Santicizer 8 which was estimated from boiling point measurements.

PVC is due more to differences in hydrogen bonding or some other specific interaction. It has been shown by Small² that the interaction of plasticiser and PVC is greatest with the phosphate and lowest with the sebacate.

Comparison of *Table 5.4* and *5.7* allows the prediction that aromatic oils will be plasticisers for natural rubber, that dibutyl phthalate will plasticise poly(methyl methacrylate), that tritolyl phosphate will plasticise nitrile rubbers, that dibenzyl ether will plasticise poly(vinylidene chloride) and that dimethyl phthalate will plasticise cellulose diacetate. These predictions are found to be correct. What is not predictable is that camphor should be an effective plasticiser for cellulose nitrate. It would seem that this crystalline material, which has to be dispersed into the polymer with the aid of liquids such as ethyl alcohol, is only compatible with the polymer because of some specific interaction between the carbonyl group present in the camphor with some group in the cellulose nitrate.

The above treatment has considered plasticisers as a special sort of solvent and has enabled broad predictions to be made about which plasticisers will be compatible with which polymer. It has not, however, explained the mechanism by which plasticisers become effective.

Before providing such an explanation it should first be noted that progressive addition of a plasticiser causes a reduction in the glass transition temperature of the polymer-plasticiser blend which eventually will be rubbery at room temperature. This suggests that plasticiser molecules insert themselves between polymer molecules, reducing but not eliminating polymer-polymer contacts and generating additional free volume. With traditional hydrocarbon softeners as used in diene rubbers this is probably almost all that happens. However, in the

case of polar polymers such as PVC some interaction between polymers and plasticisers occurs, offsetting the spacing effect. This interaction may be momentary or permanent but at any one time and temperature an equilibrium number of links between polymer and plasticisers still exist. One plasticiser molecule may form links with two polymer molecules and act as a sort of cross-link. The greater the interaction, the more the spacing effect will be offset. Whilst some authors have suggested dipole and induction force interactions, Small² has convincingly argued the case for hydrogen bonding as the main cause of interaction. Both polar and H-bonding theories help to explain the fact that tritolyl phosphate (highly polar and a strong proton acceptor) gels more rapidly with PVC but has less effect on lowering T_g and hardness than dioctyl sebacate (weakly polar and a weak proton acceptor). Di-iso-octyl phthalate (moderately polar and a moderate proton acceptor) not surprisingly has intermediate effects.

There is no reason why interaction should not more than offset the spacing effect and this is consistent with descriptions of antiplasticisation which have recently found their way into a number of research publications.

5.3.2 Extenders

In the formulation of PVC compounds it is not uncommon to replace some of the plasticiser with an extender, a material that is not in itself a plasticiser but which can be tolerated up to a given concentration by a polymer-true plasticiser system. These materials, such as chlorinated waxes and refinery oils, are generally of lower solubility parameter than the true plasticisers and they do not appear to interact with the polymer. However, where the solubility parameter of a mixture of plasticiser and extender is within unity of that of the polymer the mixture of three components will be compatible. It may be shown that

$$\delta_{\text{mixture}} = X_1 \delta_1 + X_2 \delta_2$$

where δ_1 and δ_2 are the solubility parameters of two liquids
 X_1 and X_2 are their mole fractions in the mixture.

Because the solubility parameter of tritolyl phosphate is higher than that of dioctyl sebacate, PVC-tritolyl phosphate blends can tolerate more of a low solubility parameter extender than can a corresponding sebacate formulation.

5.3.3 Determination of Solubility Parameter

Since a knowledge of a solubility parameter of polymers and liquids is of value in assessing solubility and solvent power it is important that this may be easily assessed. A number of methods have been reviewed by Burrell³ and of these two are of particular use.

From heat of vaporisation data

It has already been stated that

$$\delta = \left(\frac{\Delta E}{V} \right)^{1/2} = \left(\frac{\Delta H - RT}{M/D} \right)^{1/2}$$

Where δ is the solubility parameter

ΔE the energy of vaporisation

V the molar volume

ΔH the latent heat of vaporisation

R the gas constant

T the temperature

M the molecular weight

D the density.

At 25°C, a common ambient temperature,

$$\Delta E_{25} = \Delta H_{25} - 592, \text{ in cgs units.}$$

Unfortunately values of ΔH at such low temperatures are not readily available and they have to be computed by means of the Clausius–Clapeyron equation or from the equation given by Hildebrand and Scott⁴

$$\Delta H_{25} = 23.7T_b + 0.020T_b^2 - 2950$$

where T_b is the boiling point.*

From this equation a useful curve relating ΔE and T_b has been compiled and from this the solubility parameter may easily be assessed (*Figure 5.8*).

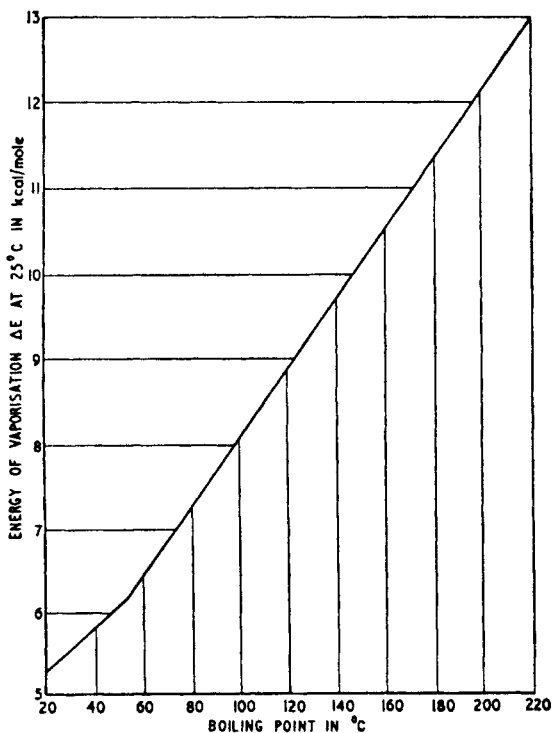


Figure 5.8. Relationship between ΔE and boiling point for use in calculating solubility parameters. (After Burrell³)

* The Hildebrand equation and *Figure 5.8*, which is derived from it, yield values of ΔH_{25} in terms of units of cal/g. The SI units of J/g are obtained by multiplying by a factor of 4.1855.

From structural formulae

The solubility parameter of high polymers cannot be obtained from latent heat of vaporisation data since such polymers cannot be vaporised without decomposition (there may be some exceptions to this generalisation for lower molecular weight materials and at very low pressures). It is therefore convenient to define the solubility parameter of a polymer 'as the same as that of a solvent in which the polymer will mix in all proportions without heat effect, volume change or without any reaction or specific association'. It is possible to estimate the value of δ for a given polymer by immersing samples in a range of solvents of known δ and noting the δ value of best solvents. In the case of cross-linked polymers the δ value can be obtained by finding the solvent which causes the greatest equilibrium swelling. Such a method is time-consuming so that the additive method of Small² becomes of considerable value. By considering a number of simple molecules Small was able to compile a list of molar attraction constants G for the various parts of a molecule. By adding the molar attraction constants it was found possible to calculate δ by the relationship

$$\delta = \frac{D \sum G}{M}$$

where D is the density

M is the molecular weight.

When applied to polymers it was found that good agreement was obtained with results obtained by immersion techniques except where hydrogen bonding was significant. The method is thus not suitable for alcohols, amines, carboxylic acids or other strongly hydrogen bonded compounds except where these form only a small part of the molecule. Where hydrogen bonding is insignificant, accuracy to the first decimal place is claimed. The δ values given in *Table 5.7* were computed by the author according to Small's method. The values in *Tables 5.4* and *5.5* were obtained either by computation or from a diversity of sources.

Some molar attraction constants compiled by Small are given in *Table 5.8*.

As an example of the use of Small's table the solubility parameter of poly(methyl methacrylate) may be computed as follows:

The formula for the polymer is shown in *Figure 5.9*.

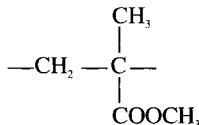


Figure 5.9

Small's formula is $\delta = D \sum G / M$ and the value of $\sum G / M$ will be the same for the repeating unit as for the polymer.*

* Small's method and constants yield values of δ in units of $(\text{cal}/\text{cm}^3)^{1/2}$. The SI value may be obtained by multiplying by 2.04.

Table 5.8 Molar attraction constants² at 25°C

Group	Molar attraction constant <i>G</i>
—CH ₃	214
—CH ₂ — (single bonded)	133
—CH<	28
$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array}$	-93
CH ₂ =	190
—CH= (double bonded)	111
>C=	19
CH≡C—	285
—C≡C—	222
Phenyl	735
Phenylene (<i>o,m,p</i>)	658
Naphthyl	1146
Ring (5-membered)	105–115
Ring (6-membered)	95–105
Conjugation	20–30
H	80–100
O (ethers)	70
CO (ketones)	275
COO (esters)	310
CN	410
Cl single	270
Cl twinned as in >CCl ₂	260
Cl triple as in —CCl ₃	250
Br single	340
I single:	425
CF ₂ } in fluorocarbons only	150
CF ₃ }	274
S sulphides	225
SH thiols	315
ONO ₂ nitrates	~440
NO ₂ (aliphatic)	~440
PO ₄ (organic)	~500
†Si (in silicones)	~ 38

† Estimated by H. Burrell.

Now M (for repeating unit) = 100 D = 1.182 CH₃ at 214 4281 CH₂ at 133 133

1 COO at 310 310

$$1 \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{ at } -93-93$$
 $\Sigma G = 778$

$$\delta = \frac{D\Sigma G}{M} = \frac{1.18 \times 778}{100} = 9.2 \text{ (cal/cm}^3\text{)}^{1/2} = 18.7 \text{ MPa}^{1/2}$$

In the case of crystalline polymers better results are obtained using an 'amorphous density' which can be extrapolated from data above the melting point, or from other sources. In the case of polyethylene the apparent amorphous density is in the range 0.84–0.86 at 25°C. This gives a calculated value of about 8.1 for the solubility parameter which is still slightly higher than observed values obtained by swelling experiments.

5.3.4 Thermodynamics and Solubility

The first law of thermodynamics expresses the general principle of energy conservation. It may be stated as follows: 'In an energetically isolated system the total energy remains constant during any change which may occur in it.' Energy is the capacity to do work and units of energy are the product of an intensity factor and a capacity factor. Thus the unit of mechanical energy (joule) is the product of the unit of force (newton) and the unit of distance (metre). Force is the intensity factor and distance the capacity factor. Similarly the unit of electrical energy (joule) is the product of an intensity factor (the potential measured in volts) and a capacity factor (the quantity of electricity measured in coulombs). Heat energy may, in the same way, be considered as the product of temperature (the intensity factor) and the quantity of heat, which is known as the entropy (the capacity factor).

It follows directly from the first law of thermodynamics that if a quantity of heat Q is absorbed by a body then part of that heat will do work W and part will be accounted for by a rise in the internal energy ΔE of that body, i.e.

$$Q = \Delta E + W$$

$$W = Q - \Delta E$$

This expression states that there will be energy free to do work when Q exceeds ΔE . Expressed in another way work can be done, that is an action can proceed, if $\Delta E - Q$ is negative. If the difference between ΔE and Q is given the symbol ΔA , then it can be said that a reaction will proceed if the value of ΔA is negative. Since the heat term is the product of temperature T and change of entropy ΔS , for reactions at constant temperature then

$$\Delta A = \Delta E - T\Delta S \quad (5.1)$$

ΔA is sometimes referred to as the change in work function. This equation simply states that energy will be available to do work only when the heat absorbed exceeds the increase in internal energy. For processes at constant temperature and pressure there will be a rise in the 'heat content' (enthalpy) due both to a rise in the internal energy and to work done on expansion. This can be expressed as

$$\Delta H = \Delta E + P\Delta V \quad (5.2)$$

when ΔH is known as the change in enthalpy and ΔV the change in volume of the system under a constant pressure P .

Combining equations (5.1) and (5.2) gives

$$\Delta A + P\Delta V = \Delta H - T\Delta S$$

or

$$\Delta F = \Delta H - T\Delta S \quad (5.3)$$

This is the so-called free energy equation where ΔF (equal to $\Delta A + P\Delta V$) is known as the free energy.

It has already been shown that a measure of the total work available is given by the magnitude of $-\Delta A$. Since some of the work may be absorbed in expansion ($P\Delta V$) the magnitude of $-\Delta F$ gives an estimate of the net work or free energy available.

Put in another way, since in equation (5.3) we have in effect only added $P\Delta V$ to each side of equation (5.1) it follows that energy will only be available to do work when the heat absorbed ($T\Delta S$) exceeds the change in enthalpy, i.e. when ΔF has a negative value.

The free energy equation is very useful and has already been mentioned in the previous chapter in connection with melting points. If applied to the mixing of molecules the equation indicates that mixing will occur if $T\Delta S$ is greater than ΔH . Therefore

- (1) The higher the temperature the greater the likelihood of mixing (an observed fact).
- (2) The greater the increase in entropy the greater the likelihood of mixing.
- (3) The less the heat of mixing the greater the likelihood of mixing.

Now it may be shown that entropy is a measure of disorder or the degree of freedom of a molecule. When mixing takes place it is to be expected that separation of polymer molecules by solvent will facilitate the movement of the polymer molecules and thus increase their degree of freedom and their degree of disorder. This means that such a mixing process is bound to cause an increase in entropy. A consequence of this is that as ΔS will always be positive during mixing, the term $T\Delta S$ will be positive and therefore solution will occur if ΔH , the heat of mixing is zero or at least less than $T\Delta S$.

It has been shown by Hildebrand and Scott⁴ that, in the absence of specific interaction

$$\Delta H = V_m \left[\left(\frac{\Delta X_1}{V_1} \right)^{1/2} - \left(\frac{\Delta X_2}{V_2} \right)^{1/2} \right]^2 a_1 a_2$$

where V_m is the total volume of the mixture
 ΔX is the energy of vaporisation
 V the molar volume of each compound
 a the volume fraction of each compound.

Since we have defined the expression $(\Delta X/V)^{1/2}$ as the solubility parameter δ , the above equation may be written

$$\Delta H = V_m (\delta_1 - \delta_2) a_1 a_2$$

If δ_1 and δ_2 are identical then ΔH will be zero and so ΔF is bound to be negative and the compounds will mix. Thus the intuitive arguments put forward in Section 5.3 concerning the solubility of amorphous polymers can be seen to be consistent with thermodynamical treatment. The above discussion is, at best, an oversimplification of thermodynamics, particularly as applied to solubility. Further information may be obtained from a number of authoritative sources.⁴⁻⁶

5.4 CHEMICAL REACTIVITY

The chemical resistance of a plastics material is as good as its weakest point. If it is intended that a plastics material is to be used in the presence of a certain chemical then each ingredient must be unaffected by the chemical. In the case of a polymer molecule, its chemical reactivity will be determined by the nature of chemical groups present. However, by its very nature there are aspects of chemical reactivity which find no parallel in the chemistry of small molecules and these will be considered in due course.

In commercial plastics materials there are a comparatively limited number of chemical structures to be found and it is possible to make some general observations about chemical reactivity in the following tabulated list of examples:

- (1) Polyolefins such as polyethylene and polypropylene contain only C—C and C—H bonds and may be considered as high molecular weight paraffins. Like the simpler paraffins they are somewhat inert and their major chemical reaction is substitution, e.g. halogenation. In addition the branched polyethylenes and the higher polyolefins contain tertiary carbon atoms which are reactive sites for oxidation. Because of this it is necessary to add antioxidants to stabilise the polymers against oxidation. Some polyolefins may be cross-linked by peroxides.
- (2) Polytetrafluoroethylene contains only C—C and C—F bonds. These are both very stable and the polymer is exceptionally inert. A number of other fluorine-containing polymers are available which may contain in addition C—H and C—Cl bonds. These are somewhat more reactive and those containing C—H bonds may be cross-linked by peroxides and certain diamines and di-isocyanates.
- (3) Many polymers, such as the diene rubbers, contain double bonds. These will react with many agents such as oxygen, ozone, hydrogen halides and halogens. Ozone, and in some instances oxygen, will lead to scission of the main chain at the site of the double bond and this will have a catastrophic effect on the molecular weight. The rupture of one such bond per chain will halve the number average molecular weight.
- (4) Ester, amide and carbonate groups are susceptible to hydrolysis. When such groups are found in the main chain, their hydrolysis will also result in a reduction of molecular weight. Where hydrolysis occurs in a side chain the effect on molecular weight is usually insignificant. The presence of benzene rings adjacent to these groups may offer some protection against hydrolysis except where organophilic hydrolysing agents are employed.
- (5) Hydroxyl groups are extremely reactive. These occur attached to the backbone of the cellulose molecule and poly(vinyl alcohol). Chemically modified forms of these materials are dealt with in the appropriate chapters.
- (6) Benzene rings in both the skeleton structure and on the side groups can be subjected to substitution reactions. Such reactions do not normally cause great changes in the fundamental nature of the polymer, for example they seldom lead to chain scission or cross-linking.

Polymer reactivity differs from the reactivity of simple molecules in two special respects. The first of these is due to the fact that a number of weak links

exist in the chains of many polymer species. These can form the site for chain scission or of some other chemical reaction. The second reason for differences between polymers and small molecules is due to the fact that reactive groups occur repeatedly along a chain. These adjacent groups can react with one another to form ring products such as poly(vinyl acetal) (Chapter 14) and cyclised rubbers (Chapter 30). Further one-step reactions which take place in simple molecules can sometimes be replaced by chain reactions in polymers such as the 'zipper' reactions which cause the depolymerisation of polyacetals and poly(methyl methacrylate).

5.5 EFFECTS OF THERMAL, PHOTOCHEMICAL AND HIGH-ENERGY RADIATION

Plastics materials are affected to varying extents by exposure to thermal, photochemical and high-energy radiation. These forms of energy may cause such effects as cross-linking, chain scission, modifications to chain structure and modifications to the side group of the polymer, and they may also involve chemical changes in the other ingredients present.

In the absence of other active substances, e.g. oxygen, the heat stability is related to the bond energy of the chemical linkages present. *Table 5.2* gives typical values of bond dissociation energies and from them it is possible to make some assessment of the potential thermal stability of a polymer. In practice there is some interaction between various linkages and so the assessment can only be considered as a guide. *Table 5.9* shows the value for $T_{1/2}$ (the temperature at which a polymer loses half its weight *in vacuo* at 30 minutes preceded by 5 minutes preheating at that temperature) and K_{350} the rate constant (in %/min) for degradation at 350°C.

The high stability of PTFE is due to the fact that only C—C and C—F bonds are present, both of which are very stable. It would also appear that the C—F bonds have a shielding effect on the C—C bonds. Poly-*p*-xylene contains only the benzene ring structure (very stable thermally) and C—C and C—H bonds and these are also stable. Polymethylene, which contains only the repeating methylene groups, and hence only C—C and C—H bonds, is only slightly less stable. Polypropylene has a somewhat lower value than polymethylene since the stability of the C—H at a tertiary carbon position is somewhat lower than that at a secondary carbon atom. The lower stability of PVC is partly explained by the lower dissociation energy of the C—Cl bond but also because of weak points which act as a site for chain reactions. The rather high thermal degradation rate of poly(methyl methacrylate) can be explained in the same way. Oxygen-oxygen and silicon-silicon bonds have a low dissociation energy and do not occur in polymers except possibly at weak points in some chains.

There is much evidence that weak links are present in the chains of most polymer species. These weak points may be at a terminal position and arise from the specific mechanism of chain termination or may be non-terminal and arise from a momentary aberration in the *modus operandi* of the polymerisation reaction. Because of these weak points it is found that polyethylene, polytetrafluoroethylene and poly(vinyl chloride), to take just three well-known examples, have a much lower resistance to thermal degradation than low molecular weight analogues. For similar reasons polyacrylonitrile and natural rubber may degrade whilst being dissolved in suitable solvents.

Table 5.9 Thermal degradation of selected polymers (Ref. 7)

Polymer	T_h (°C)	K_{350} (%/min)
PTFE	509	0.0000052
Poly- <i>p</i> -xylene	432	0.002
Polymethylene	414	0.004
Polypropylene	387	0.069
Poly(methyl methacrylate)	327	5.2
Poly(vinyl chloride)	260	170

Weak links, particularly terminal weak links, can be the site of initiation of a chain ‘unzipping’ reaction.^{8,9} A monomer or other simple molecule may be abstracted from the end of the chain in such a way that the new chain end is also unstable. The reaction repeats itself and the polymer depolymerises or otherwise degrades. This phenomenon occurs to a serious extent with polyacetals, poly(methyl methacrylate) and, it is believed, with PVC.

There are four ways in which these unzipping reactions may be moderated:

- (1) By preventing the initial formation of weak links. These will involve, amongst other things, the use of rigorously purified monomer.
- (2) By deactivating the active weak link. For example, commercial polyacetal (polyformaldehyde) resins have their chain ends capped by a stable grouping. (This will, however, be of little use where the initiation of chain degradation is not at the terminal group.)
- (3) By copolymerising with a small amount of second monomer which acts as an obstruction to the unzipping reaction, in the event of this being allowed to start. On the industrial scale methyl methacrylate is sometimes copolymerised with a small amount of ethyl acrylate, and formaldehyde copolymerised with ethylene oxide or 1,3-dioxolane for this very reason.
- (4) By the use of certain additives which divert or moderate the degradation reaction. A wide range of antioxidants and stabilisers function by this mechanism (see Chapter 7).

The problems of assessment of long-term heat resistance are discussed further in Chapter 9.

Most polymers are affected by exposure to light, particularly sunlight. This is the result of the absorption of radiant light energy by chemical structures. The lower the wavelength the higher the energy. Fortunately for most purposes, most of the light waves shorter than 300 nm are destroyed or absorbed before they reach the surface of the earth and for non-astronautical applications these short waves may be ignored and most damage appears to be done by rays of wavelength in the range 300–400 nm. At 350 nm the light energy has been computed to be equal to 82 kcal/mole and it will be seen from *Table 5.2* that this is greater than the dissociation energy of many bonds. Whether or not damage is done to a polymer also depends on the absorption frequency of a bond. A C—C bond absorbs at 195 nm and at 230–250 nm and aldehyde and ketone carbonyl bonds at 187 nm and 280–320 nm. Of these bonds it would be expected that only the carbonyl bond would cause much trouble under normal terrestrial conditions.

PTFE and other fluorocarbon polymers would be expected to have good light stability because the linkages present normally have bond energies exceeding the light energy. Polyethylene and PVC would also be expected to have good light stability because the linkages present do not absorb light at the damaging wavelength present on the earth's surface. Unfortunately carbonyl and other groups which are present in processed polymer may prove to be a site for photochemical action and these two polymers have only limited light stability. Antioxidants in polyethylene, used to improve heat stability, may in some instances prove to be a site at which a photochemical reaction can be initiated. To some extent the light stability of a polymer may be improved by incorporating an additive that preferentially absorbs energy, at wavelengths that damage the polymer linkage. It follows that an ultraviolet light absorber that is effective in one polymer may not be effective in another polymer. Common ultraviolet absorbers include certain salicylic esters such as phenyl salicylate, benzotriazole and benzophenones. Carbon black is found to be particularly effective in polyethylene and acetal resins. In the case of polyethylene it will reduce the efficiency of amine antioxidants.

In analogy with thermal and light radiations, high-energy radiation may also lead to scission and cross-linking. The relative stabilities of various polymer structures are shown in *Figure 5.10*¹⁰. Whilst some materials cross-link others degrade (i.e. are liable to chain scission). *Table 5.10* lists some polymers that cross-link and some that degrade. It is of interest to note that whereas most polymers of monosubstituted ethylene cross-link, most polymers of disubstituted ethylenes degrade. Exceptions are polypropylene, which degrades, and PVC, which either degrades or cross-links according to the conditions. Also of interest is the different behaviour of both PTFE and poly(methyl methacrylate) when subjected to different types of radiation. Although both polymers have a good stability to ultraviolet light they are both easily degraded by high-energy radiation.

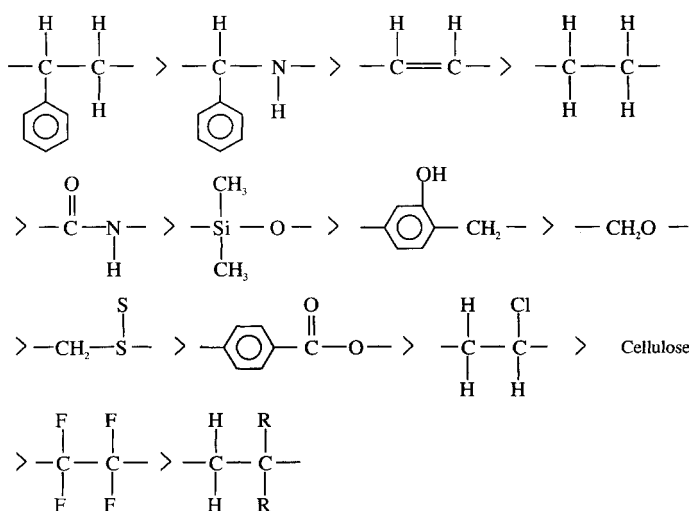


Figure 5.10 Relative stabilities of various polymers to exposure by high-energy sources. (After Ballantine¹⁰)

Table 5.10 Behaviour of polymers subjected to high-energy radiation¹¹

<i>Polymers that cross-link</i>	<i>Polymers that degrade</i>
Polyethylene	Polyisobutylene
Poly(acrylic acid)	Poly- α -methylstyrene
Poly(methyl acrylate)	Poly(methyl methacrylate)
Polyacrylamide	Poly(methacrylic acid)
Natural rubber	Poly(vinylidene chloride)
Polychloroprene	Polychlorotrifluoroethylene
Polydimethylsiloxanes	Cellulose
Styrene-acrylonitrile copolymers	PTFE
	Polypropylene

5.6 AGING AND WEATHERING

From the foregoing sections it will be realised that the aging and weathering behaviour of a plastics material will be dependent on many factors. The following agencies may cause a change in the properties of a polymer:

- (1) Chemical environments, which may include atmospheric oxygen, acidic fumes and water.
- (2) Heat.
- (3) Ultraviolet light.
- (4) High-energy radiation.

In a commercial plastics material there are also normally a number of other ingredients present and these may also be affected by the above agencies. Furthermore they may interact with each other and with the polymer so that the effects of the above agencies may be more, or may be less, drastic. Since different polymers and additives respond in different ways to the influence of chemicals and radiant energy, weathering behaviour can be very specific.

A serious current problem for the plastics technologist is to be able to predict the aging and weathering behaviour of a polymer over a prolonged period of time, often 20 years or more. For this reason it is desirable that some reliable accelerated weathering test should exist. Unfortunately, accelerated tests have up until now achieved only very limited success. One reason is that when more than one deteriorating agency is present, the overall effect may be quite different from the sum of the individual effects of these agencies. The effects of heat and light, or oxygen and light, in combination may be quite serious whereas individually their effect on a polymer may have been negligible. It is also difficult to know how to accelerate a reaction. Simply to carry out a test at higher temperature may be quite misleading since the temperature dependencies of various reactions differ. In an accelerated light aging test it is more desirable to subject the sample to the same light distribution as 'average daylight' but at greater intensity. It is, however, difficult to obtain light sources which mimic the energy distribution. Although some sources have been found that correspond well initially, they often deteriorate quickly after some hours of use and become unreliable. Exposure to sources such as daylight, carbon arc lamps and xenon lamps can have quite different effects on plastics materials.

5.7 DIFFUSION AND PERMEABILITY

There are many instances where the diffusion of small molecules into, out of and through a plastics material are of importance in the processing and usage of the latter. The solution of polymer in a solvent involves the diffusion of solvent into the polymer so that the polymer mass swells and eventually disintegrates. The gelation of PVC with a plasticiser such as tritolyl phosphate occurs through diffusion of plasticiser into the polymer mass. Cellulose acetate film is produced by casting from solution and diffusion processes are involved in the removal of solvent. The ease with which gases and vapours permeate through a polymer is of importance in packaging applications. For example in the packaging of fruit the packaging film should permit diffusion of carbon dioxide through the film but restrain, as far as possible, the passage of oxygen. Low air permeability is an essential requirement of an inner tube and a tubeless tyre and, in a somewhat less serious vein, a child's balloon. Lubricants in many plastics compositions are chosen because of their incompatibility with the base polymers and they are required to diffuse out of the compound during processing and lubricate the interface of the compound and the metal surfaces of the processing equipment (e.g. mould surfaces and mill roll surfaces). From the above examples it can be seen that a high diffusion and permeability is sometimes desirable but at other times undesirable.

Diffusion occurs as a result of natural processes that tend to equal out the concentration of a given species of particle (in the case under discussion, a molecule) in a given environment. The diffusion coefficient of one material through another (D) is defined by the equation

$$F = -D \frac{\partial c}{\partial x}$$

where F is the weight of the diffusing material crossing unit area of the other material per unit time, and the differential is the concentration gradient in weight per ml per cm at right angles to the unit area considered.

Diffusion through a polymer occurs by the small molecules passing through voids and other gaps between the polymer molecules. The diffusion rate will therefore depend to a large extent on the size of the small molecules and the size of the gaps. An example of the effect of molecular size is the difference in the effects of tetrahydrofuran and di-iso-octyl phthalate on PVC. Both have similar solubility parameters but whereas tetrahydrofuran will diffuse sufficiently rapidly at room temperature to dissolve the polymer in a few hours the diffusion rate of the phthalate is so slow as to be almost insignificant at room temperature. (In PVC pastes, which are suspensions of polymer particles in plasticisers, the high interfacial areas allow sufficient diffusion for measurable absorption of plasticisers, resulting in a rise of the paste viscosity.) The size of the gaps in the polymer will depend to a large extent on the physical state of the polymer, that is whether it is glassy, rubbery or crystalline. In the case of amorphous polymers above the glass transition temperature, i.e. in the rubbery state, molecular segments have considerable mobility and there is an appreciable 'free volume' in the mass of polymer. In addition, because of the segment mobility there is a high likelihood that a molecular segment will at some stage move out of the way of a diffusing small molecule and so diffusion rates are higher in rubbers than in other types of polymer.

Table 5.11 Permeability data for various polymers values for $P \times 10^{10} \text{ cm}^3 \text{ s}^{-1} \text{ mm cm}^{-2} \text{ cmHg}^{-1}$

Polymer	Permeability			90% R.H. H ₂ O (25°C)	Ratios to N ₂ perm. = G value			Nature of polymer
	N ₂ (30°C)	O ₂ (30°C)	CO ₂ (30°C)		P _{O₂}/P_{N₂}}	P _{CO₂}/P_{N₂}}	P _{H₂O}/P_{N₂}}	
Poly(vinylidene chloride)	0.0094	0.053	0.29	14	5.6	31	1400	crystalline
PCTFE	0.03	0.10	0.72	2.9	3.3	24	97	crystalline
Poly(ethylene terephthalate)	0.05	0.22	1.53	1300	4.4	31	26 000	crystalline
Rubber hydrochloride (Pliofilm ND)	0.08	0.30	1.7	240	3.8	21	3000	crystalline
Nylon 6	0.10	0.38	1.6	7000	3.8	16	70 000	crystalline
PVC (unplasticised)	0.40	1.20	10	1560	3.0	25	3900	slight crystalline
Cellulose acetate	2.8	7.8	68	75 000	2.8	24	2680	glassy
Polyethylene ($d = 0.954-0.960$)	2.7	10.6	35	130	3.9	13	48	crystalline
Polyethylene ($d = 0.922$)	19	55	352	800	2.9	19	42	some crystalline
Polystyrene	2.9	11	88	1200	3.8	30	4100	glassy
Polypropylene	—	23	92	680	—	—	—	crystalline
Butyl rubber	3.12	13.0	51.8	—	4.1	16.2	—	rubbery
Methyl rubber	4.8	21.1	75	—	4.4	15.6	—	rubbery
Polybutadiene	64.5	191	1380	—	3.0	21.4	—	rubbery
Natural rubber	80.8	233	1310	—	2.9	16.2	—	rubbery

Below the glass transition temperature the segments have little mobility and there is also a reduction of 'free volume'. This means that not only are there less voids but in addition a diffusing particle will have a much more tortuous path through the polymer to find its way through. About the glass transition temperature there are often complicating effects as diffusing particles may plasticise the polymers and thus reduce the effective glass transition temperature.

Crystalline structures have a much greater degree of molecular packing and the individual lamellae can be considered as almost impermeable so that diffusion can occur only in amorphous zones or through zones of imperfection. Hence crystalline polymers will tend to resist diffusion more than either rubbers or glassy polymers.

Of particular interest in the usage of polymers is the permeability of a gas, vapour or liquid through a film. Permeation is a three-part process and involves solution of small molecules in polymer, migration or diffusion through the polymer according to the concentration gradient, and emergence of the small particle at the outer surface. Hence permeability is the product of solubility and diffusion and it is possible to write, where the solubility obeys Henry's law,

$$P = DS$$

where P is the permeability, D is the diffusion coefficient and S is the solubility coefficient.

Hence polyethylene will be more permeable to liquids of similar solubility parameter, e.g. hydrocarbons, than to liquids of different solubility parameter but of similar size. The permeabilities of a number of polymers to a number of gases are given the *Table 5.11*.^{12,13}

Stannett and Szwarc¹² have argued that the permeability is a product of a factor F determined by the nature of the polymer, a factor G determined by the nature of gas and an interaction factor H (considered to be of little significance and assumed to be unity).

Thus the permeability of polymer i to a gas k can be expressed as

$$P_{ik} = F_i G_k$$

Hence the ratio of the permeability of a polymer i to two gases k and l can be seen to be the same as the ratio between the two G factors

$$\frac{P_{ik}}{P_{il}} = \frac{G_k}{G_l}$$

similarly between two polymers (i and j)

$$\frac{P_{ik}}{P_{jk}} = \frac{F_i}{F_j}$$

From a knowledge of various values of P it is possible to calculate F values for specific polymers and G values for specific gases if the G value for one of the gases, usually nitrogen, is taken as unity. These values are generally found to be accurate within a factor of 2 for gases but unreliable with water vapour. Some

Table 5.12 *F* and *G* constants for polymers and gases¹²

<i>Polymer</i>	<i>F</i>	<i>Gas</i>	<i>G</i>
Poly(vinylidene chloride) (Saran)	0.0094	N ₂	1.0
PCTFE	0.03		
Poly(ethylene terephthalate)	0.05	O ₂	3.8
Rubber hydrochloride (Pliofilm)	0.08	H ₂ S	21.9
Nylon 6	0.1	CO ₂	24.2
Nitrile rubber (Hycar OR-15)	2.35		
Butyl rubber	3.12		
Methyl rubber	4.8		
Cellulose acetate (+ 15% plasticiser)	5.0		
Polychloroprene	11.8		
Low-density polyethylene	19.0		
Polybutadiene	64.5		
Natural rubber	80.8		
Plasticised ethyl cellulose	84		

values are given in *Table 5.12*.. It will be realised that the *F* values correspond to the first column of *Table 5.11* and the *G* values for oxygen and carbon dioxide are the averages of the P_{O_2}/P_{N_2} and P_{CO_2}/P_{N_2} ratios.

5.8 TOXICITY

No attempt will be made here to relate the toxicity of plastics materials to chemical structure. Nevertheless this is a topic about which a few words must be said in a book of this nature.

A material may be considered toxic if it has an adverse effect on health. Although it is often not difficult to prove that a material is toxic it is almost impossible to prove that a material is not toxic. Tobacco was smoked for many centuries before the dangerous effects of cigarette smoking were appreciated. Whilst some materials may have an immediate effect, others may take many years. Some toxic materials are purged out of the body and providing they do not go above a certain concentration appear to cause little havoc; others accumulate and eventually a lethal dose may be present in the body.

Toxic chemicals can enter the body in various ways, in particular by swallowing, inhalation and skin absorption. Skin absorption may lead to dermatitis and this can be a most annoying complaint. Whereas some chemicals may have an almost universal effect on human beings, others may attack only a few persons. A person who has worked with a given chemical for some years may suddenly become sensitised to it and from then on be unable to withstand the slightest trace of that material in the atmosphere. He may as a result also be sensitised not only to the specific chemical that caused the initial trouble but to a host of related products. Unfortunately a number of chemicals used in the plastics industry have a tendency to be dermatitic, including certain halogenated aromatic materials, formaldehyde and aliphatic amines.

In addition many other chemicals used can attack the body, both externally and internally, in many ways. It is necessary that the effects of any material used should be known and appropriate precautions taken if trouble is to be

avoided. Amongst the materials used in the plastics industry for which special care should be taken are lead salts, phenol, aromatic hydrocarbons, isocyanates and aromatic amines. In many plastics articles these toxic materials are often used only in trace doses. Provided they are surrounded by polymer or other inert material and they do not bleed or bloom and are not leached out under certain conditions of service it is sometimes possible to tolerate them. This can, however, be done with confidence only after exhaustive testing. The results of such testing of a chemical and the incidence of any adverse toxic effects should be readily available to all potential handlers of that chemical. There is, unfortunately, in many countries a lack of an appropriate organisation which can collect and disseminate such information. This is, however, a matter which must be dealt with elsewhere.¹⁴

Most toxicity problems associated with the finished product arise from the nature of the additives and seldom from the polymer. Mention should, however, be made of poly(vinyl carbazole) and the polychloroacrylates which, when monomer is present, can cause unpleasant effects, whilst in the 1970s there arose considerable discussion on possible links between vinyl chloride and a rare form of cancer known as angiosarcoma of the liver.¹⁵

5.9 FIRE AND PLASTICS

Over the years plastics users have demanded progressively improving fire performance. By this is meant that plastics materials should resist burning and in addition that levels of smoke and toxic gases emitted should be negligible. That a measure of success has been achieved is the result of two approaches:

- (1) The development of new polymers of intrinsically better performance.
- (2) The development of flame retardants.

Although many improvements have been made on empirical bases, developments more and more depend on a fuller understanding of the process of combustion. This is a complex process but a number of stages are now generally recognised. They are:

- (1) Primary thermal processes where energy from an external source is applied to the polymer, causing a gradual rise in temperature. The rate of temperature rise will depend on the rate of supply of energy and on the thermal and geometrical characteristics of the material being heated.
- (2) Primary chemical processes. The external heat source may supply free radicals which accelerate combustion. The heating material might also be activated by autocatalytic or autoignition mechanisms.
- (3) Decomposition of the polymer becomes rapid once a certain temperature has been reached and a variety of products such as combustible and non-combustible gases and liquids, charred solids and smoke may also be produced. Some of these products may accelerate further decomposition whilst others may retard it and this may depend not only on the nature of the compound but also on the environmental conditions.
- (4) Ignition will occur when both combustible gases and oxygen are available in sufficient quantity above the ignition temperature. The amount of oxygen required for ignition varies from one polymer to another. For example, in an

atmosphere of 15% oxygen, polyoxymethylenes (polyacetals) will burn whereas 49% oxygen is required for PVC to continue burning.

- (5) Combustion follows ignition and the ease of combustion is a function of the cohesive energy of the bonds present.
- (6) Such combustion will be followed by flame propagation and possibly by non-flaming degradation and physical changes such as shrinkage, melting and charring. A large amount of smoke and toxic gases may be evolved and it is worth noting that the number of deaths due to such products is probably greater than the number due to burning.

Over the years a very large number of tests have been developed to try and assess the burning behaviour of polymers, this in itself being a reflection of the difficulty of assessing the phenomenon. These tests can roughly be divided into two groups:

- (1) Simple laboratory tests on the basic polymers and their compounds.
- (2) Larger scale tests on fabricated structures.

The first group, i.e. simple laboratory tests, is frequently criticised in that, although results may be reproducible, they do not give a good indication of how the material will behave in a real fire situation. On the other hand, the second group is criticised because correlation between various tests proposed by different regulatory bodies is very poor. In spite of these limitations there are, however, a few tests which are very widely used and whose results are widely quoted.

Perhaps the best known of these is the limited oxygen index test (described for example in ASTM D2863—74). In this test the minimum oxygen fraction in an oxygen/nitrogen mixture that will enable a slowly rising sample of the gas mixture to support combustion of a candle-light sample under specified test conditions is measured. Some typical figures are given in *Table 5.13*.

The reasons for the differences between the polymers are various but in particular two factors may be noted:

- (1) The higher the hydrogen to carbon ratio in the polymer the greater is the tendency to burning (other factors being equal).
- (2) Some polymers on burning emit blanketing gases that suppress burning.

Whilst the limiting oxygen index (LOI) test is quite fundamental, it does not characterise the burning behaviour of the polymer. One way of doing this is the ASTM D635—74 test for flammability of self-supporting plastics. In this test a horizontal rod-like sample is held at one end in a controlled flame. The rate of burning, the average burning time before extinction and the average extent of burning before extinction (if any) is measured.

The most widely used flammability performance standards for plastics materials are the Underwriters Laboratories UL94 ratings. These rate the ability of a material to extinguish a flame once ignited. The ratings given depend on such factors as rate of burning, time to extinguish, ability to resist dripping and whether or not the drips are burning.

Tests are carried out on a bar of material 5 inches long and 0.5 inches wide and are made both horizontally and vertically. In the horizontal test the sample is held, horizontally, at one end, and a flame, held at about 45°, is applied to the

Table 5.13 Collected data for limiting oxygen index for a variety of polymers

<i>Polymer</i>	<i>Limiting oxygen index (%)</i>
Polyacetal	15
Poly(methyl methacrylate)	17
Polypropylene	17
Polyethylene	17
Poly(butylene terephthalate)	18
Polystyrene	18
Poly(ethylene terephthalate) (unfilled)	21
<hr/>	
Nylon 6	21–34
Nylon 66	21–30
Nylon 11	25–32
PPO	29–35
ABS	29–35
Polycarbonate of bis-phenol TMC	24
Polycarbonate of bis-phenol A	26
Polysulphone	30
Poly(ethylene terephthalate) (30% G.F.)	31–33
Polyimide (Ciba-Geigy P13N)	32
Polyarylate (Solvay Arylef)	34
Liq. Xtal Polymer (Vectra)	34–50
TFE–HFP Copolymer (Teflon FEP)	34
Polyether sulphone	34–38
Polyether ether ketone	35
Phenol–formaldehyde resin	35
Poly(vinyl chloride)	23–43
Poly(vinylidene fluoride)	44
Polyamide–imides (Torlon)	42–50
Polyether–imides (Uitem)	44–47
Poly(phenylene sulphide)	44–53
Friedel–Crafts resins	55
Poly(vinylidene chloride)	60
Poly(carborane siloxane)	62
Polytetrafluoroethylene	90

Note % oxygen in air = 20.9. Polymers below the line burn with increasing difficulty as the LOI increases.

Where a spread of figures is given, the higher values generally refer to grades with mineral or glass-fibre filler and/or fire retardant. With most other materials, where only one figure is given, higher values may generally be obtained with the use of such additives.

other end. To qualify for an HB rating the burning rate should be <76 mm/min for samples of thickness <3 mm, and <38 mm/min for samples of thickness >3 mm. This is the lowest UL94 flammability rating.

Greater attention is usually paid to the results of a vertical test, in which the sample is clamped at the top end and a bunsen flame of height 19 mm is applied to the lower end at a point 9.5 mm above the top of the bunsen burner (i.e. half-way along the flame). The material is classified as V-2, V-1 or V-0 in increasing order of flammability rating by reference to the conditions given in *Table 5.14*.

A much more severe test is that leading to UL-94-5V classifications. This involves two stages. In the first stage a standard 5 × 0.5 inch bar is mounted vertically and subjected to a 5 inch flame five times for 5 seconds duration with an interval of 5 seconds. To pass the specification no specimen may burn with

Table 5.14

Rating	Explanation
V-0	No test specimens burn longer than 10 seconds after each removal from the flame. No specimens exhibit flaming drip that ignites dry surgical cotton placed 12" below the test specimen. Nor does afterglow persist for longer than 30 seconds.
V-1	This rating is essentially identical to V-0 except that specimens must extinguish within a 30 second interval after flame removal and there should be no afterglow persisting after 60 seconds.
V-2	Identical to V-1 except that the flaming drip from some specimens ignites the dry cotton placed below the specimens.

flaming or glowing combustion for more than 60 seconds after the fifth flame application. In addition, no burning drips are allowed that ignite cotton placed between the samples. The total procedure is repeated with five bars.

In the second stage a plaque of the same thickness as the bars is tested in a horizontal position with the same-sized flame. The total procedure is repeated with three plaques. If this results in a hole being formed the material is given a UL94-5VB rating. If no hole is formed the material is given the highest classification, UL94-5VA.

The UL94 rating is awarded to a specific grade of material and may also vary with the colour. It is also dependent on the thickness of the sample and this should also be stated. Clearly, if two materials are given, for example, a V-0 rating, that which achieves the rating with a thinner sample will be the more fire retardant.

The importance of specifying grade and thickness may be illustrated by taking the example of two grades of poly(butylene terephthalate) compounds marketed by General Electric. The grade Valox 325 is given an HB rating at 1.47 mm thickness whereas Valox 310SEO is given a V-0 rating at 0.71 mm thickness and a 5VA rating at 3.05 mm thickness.

Some UL94 flammability ratings are given by way of example in *Table 5.15*.

A test used to simulate thermal stresses that may be produced by sources of heat or ignition such as overloaded resistors or glowing elements is the *IEC 695-2-1 Glow Wire Test*. In outline the basis of the test is that a sample of material is held against a heated glowing wire tip for 30 seconds. The sample passes the test if any flames or glowing of the sample extinguish within 30 seconds of removal of the glow wire. The test may be carried out at a variety of test temperatures, such as 550, 650, 750, 850 or 960°C. Amongst materials that pass the test at 960°C at 3.2 mm thickness are normal grades of poly(phenylene sulphides) and polyether-imides and some flame-retardant-modified grades of ABS, styrenic PPOs and poly(butylene terephthalates). Certain polycarbonate/polyether-imides and polycarbonate/ABS grades even pass the test at the same temperature but with thinner samples.

To simulate the effect of small flames that may result from faulty conditions within electronic equipment, the *IEC 695-2-2 Needle Flame Test* may be used. In this case a small test flame is applied to the sample for a specified period and observations made concerning ability to ignite, extent of burning along the sample, flame spread onto adjacent material and time of burning.

Table 5.15 Some collected UL94 flammability ratings

<i>Polymer</i>		<i>UL 94 Rating</i>
Polycarbonate	Lexan 101	V-2 at 1.04 mm
	Lexan 120*	V-0 at 1.04 mm, 5VA at 3.05 mm
Nylon 66	Maranyl A100	V-2
Polyphthalamide	Amodel AS-1133	HB at 3.2 mm
	Amodel AF-1145*	V-0 at 0.8 mm
Polysulphone	Udel P-1720	V-0
Polyethersulphone	Victrex 200P	V-0
Polybutylene terephthalate	Pocan B1305	HB at 0.84 mm
	Pocan KL1-7835*	V-0 at 1.55 mm
Polyethylene terephthalate GF	Pocan 4630*	V-0 at 0.38 mm
PPO	Noryl N-110	HB at 1.65 mm
	Noryl N-190*	V-0 at 1.52 mm, 5VA at 3.12 mm
Polyacetal	Delrin 500	HB
Polyphenylene sulphide GF	Fortron grades	V-0 at 0.4 mm
Liquid Xtal Polymer	Vectra (30% GF)	V-0 at 0.4 mm
Polyether-imide	Ultem 1000	V-0 at 0.41 mm, 5VA at 1.60 mm
Polyketones	PEEK X941	V-0 at 0.8 mm
ABS Standard Grades		HB
ABS/polycarbonate alloy	Cycoloy C2800*	V-0 at 1.50 mm, 5VA at 2.50 mm

* Indicates grade with flame retardant added.

Records show that more fatalities occur through victims being suffocated by smoke or poisoned by toxic gases emitted during a fire than by being burnt to death. This is particularly worrying when it is realised that many additives incorporated into a polymer to retard its flammability are often found to increase the amount of smoke emitted as the rate of flame propagation decreases. Most

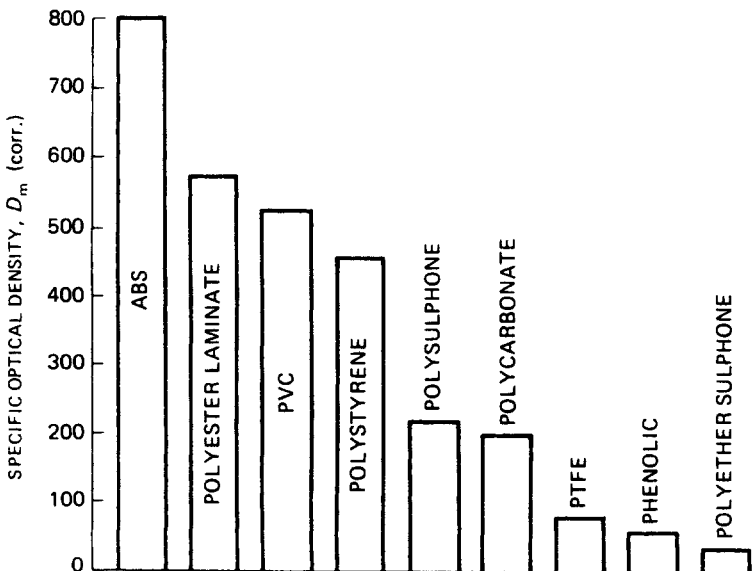


Figure 5.11. NBS smoke chamber data in flaming conditions test on 3.2 mm samples

often the smoke emitted contains large amounts of carbon in the form of soot which readily obscures light. For this reason, no programme of study of the fire performance of a polymer or flame retardant additive should ignore studies on smoke emission and smoke density. In addition the gases emitted during burning should be subjected to chemical analysis and toxicological assessment.

One particularly widely used test is the National Bureau of Standards (NBS) smoke chamber test. This provides a measure of the obscuration of visible light by smoke in units of specific optical density. The NBS smoke test can be run in either of two modes:

- (1) Flaming, and
- (2) Non-flaming (i.e. smouldering condition).

Figure 5.11 gives some comparative data for a selection of polymers subjected to the flaming condition mode.

References

1. HANSEN, C. M., *Ind. Eng. Chem. Prod. Res. Devpt*, **8**, 2 (1969)
2. SMALL, P. A. J., *J. Appl. Chem.*, **3**, 71 (1953)
3. BURRELL, H., *Interchem. Rev.*, **14**, 3 (1955); BERNARDO, J. J., and BURRELL, H., Chapter in *Polymer Science* (Ed. JENKINS, A. D.), North-Holland, Amsterdam (1972)
4. HILDEBRAND, J., and SCOTT, R., *The Solubility of Non-Electrolytes*, Reinhold, New York, 3rd Edn (1949)
5. TOMPA, H., *Polymer Solutions*, Butterworths, London (1956).
6. BILLMEYER, F. W., *Textbook of Polymer Science*, John Wiley, New York (1962)
7. ACHHAMMER, B. G., TRYON, M., and KLINE, G. M., *Mod. Plastics*, **37**(4), 131 (1959)
8. GRASSIE, N., *Trans. Inst. Rubber Ind.*, **39**, 200 (1963)
9. GRASSIE, N., *Chemistry of High Polymer Degradation Processes*, Butterworths, London (1956)
10. BALLANTINE, D. S. *Mod. Plastics*, **32**(3), 131 (1954)
11. JONES, S. T., *Canad. Plastics*, April, 32 (1955)
12. STANNETT, V. T., and SZWARC, M., *J. Polymer Sci.*, **16**, 89 (1955)
13. PAINE, F. A., *J. Roy. Inst. Chem.*, **86**, 263 (1962)
14. LEFAUX, R., *Practical Toxicology of Plastics* (translation edited by HOPF, P. P.), Iliffe, London (1968)
15. KAUFMAN, M., *Plastics and Rubber Weekly*, No. 529, May 17, 22 (1974)

Bibliography

- BILLMEYER, F. W., *Textbook of Polymer Science*, John Wiley, New York (1962)
- CRANK, J., and PARK, J. S., *Diffusion in Polymers*, Academic Press, London and New York (1968)
- GARDON, J. L., Article entitled 'Cohesive Energy Density' in *Encyclopaedia of Polymer Science and Technology*, Vol. 3, p. 833, Interscience, New York (1969)
- GORDON, M., *High Polymers—Structure and Physical Properties*, Iliffe, London, 2nd Edn (1963)
- HILDEBRAND, J., and SCOTT, R., *The Solubility of Non-Electrolytes*, Reinhold, New York, 3rd Edn (1949)
- HINDERSINN, R., Article entitled 'Fire Retardancy' in *Encyclopaedia of Polymer Science and Technology*, Supplement Vol. 2, pp. 270–340, Interscience, New York (1977)
- LEFAUX, R., *Practical Toxicology of Plastics* (translation edited by HOPF, P. P.), Iliffe, London (1968)
- PAULING, L., *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 3rd Edn (1960)
- RITCHIE, P. D. (Ed.), *Plasticisers, Stabilisers, and Fillers*, Iliffe (published for The Plastics Institute), London (1972)
- SAUNDERS, K. J., *Organic Polymer Chemistry*, Chapman and Hall, London (1973)
- TOMPA, H., *Polymer Solutions*, Butterworths, London (1956)
- TROITZSCH, J., *Plastics Flammability Handbook*, Hanser, München (English translation) (1983)

Relation of Structure to Electrical and Optical Properties

6.1 INTRODUCTION

Most plastics materials may be considered as electrical insulators, i.e., they are able to withstand a potential difference between different points of a given piece of material with the passage of only a small electric current and a low dissipation energy. When assessing a potential insulating material, information on the following properties will be required:

- (1) Dielectric constant (specific inductive capacity, relative permittivity) over a wide range of temperature and frequency.
- (2) Power factor over a range of temperature and frequency.
- (3) Dielectric strength (usually measured in V/0.001 in or kV/cm).
- (4) Volume resistivity (usually measured in Ω cm or Ω m).
- (5) Surface resistivity (usually measured in Ω).
- (6) Tracking and arc resistance.

Typical properties for the selection of well-known plastics materials are tabulated in *Table 6.1*.

Some brief notes on the testing of electrical properties are given in the appendix at the end of this chapter.

6.2 DIELECTRIC CONSTANT, POWER FACTOR AND STRUCTURE

The materials in *Table 6.1* may be divided roughly into two groups:

- (1) Polymers with outstandingly high resistivity, low dielectric constant and negligible power factor, all substantially unaffected by temperature, frequency and humidity over the usual range of service conditions.
- (2) Moderate insulators with lower resistivity and higher dielectric constant and power factor affected further by the conditions of the test. These materials are often referred to as polar polymers.

Table 6.1 Typical electrical properties of some selected plastics materials at 20°C

Polymer	Volume resistivity (Ω m)	Dielectric strength (kV/cm) ($\frac{1}{8}$ in sample)	Dielectric constant		Power factor	
			60 Hz	10^6 Hz	60 Hz	10^6 Hz
PTFE	$>10^{20}$	180	2.1	2.1	<0.0003	<0.0003
Polyethylene (LD)	10^{20}	180	2.3	2.3	<0.0003	<0.0003
Polystyrene	10^{20}	240	2.55	2.55	<0.0003	<0.0003
Polypropylene	$>10^{19}$	320	2.15	2.15	0.0008	0.0004
PMMA	10^{16}	140	3.7	3.0	0.06	0.02
PVC	10^{17}	240	3.2	2.9	0.013	0.016
PVC (plasticised) ^a	10^{15}	280	6.9	3.6	0.082	0.089
Nylon 66 ^b	10^{15}	145	4.0	3.4	0.014	0.04
Polycarbonate ^c	10^{18}	160	3.17	2.96	0.0009	0.01
Phenolic ^d	10^{13}	100	5.0–9.0	5.0	0.08	0.04
Urea formaldehyde ^d	10^{14}	120	4.0	4.5	0.04	0.3

a PVC 59%, di-(2-ethylhexyl) phthalate 30%, filler 5%, stabiliser 6%.

b 0.2% water content.

c Makrolon.

d General purpose moulding compositions.

It is not difficult to relate the differences between these two groups to molecular structure. In order to do this the structure and electrical properties of atoms, symmetrical molecules, simple polar molecules and polymeric polar molecules will be considered in turn.

An atom consists essentially of a positively charged nucleus surrounded by a cloud of light negatively charged electrons which are in motion around the nucleus. In the absence of an electric field, the centres of both negative and positive charges are coincident and there is no external effect of these two charges (*Figure 6.1* (a)). In a molecule we have a number of positive nuclei surrounded by overlapping electron clouds. In a truly covalent molecule the centres of negative and positive charges again coincide and there is no external effect.

If an atom or covalent molecule is placed in an electric field there will be a displacement of the light electron cloud in one direction and a considerably smaller displacement of the nucleus in the other direction (*Figure 6.1* (b)). The effect of the electron cloud displacement is known as *electron polarisation*. In these circumstances the centres of negative and positive charge are no longer coincident.

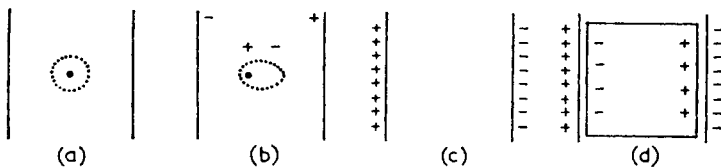


Figure 6.1. (a) Atom not subject to external electric field. Centre of electron cloud and nucleus coincident. (b) Electron cloud displacement through application of external electric field. (c) Charged condenser plates separated by vacuum. (d) Condenser plates separated by dielectric

Let us now consider a condenser system in which a massive quantity of a species of atom or molecule is placed between the two plates, i.e., forming the dielectric. The condenser is a device for storing charge. If two parallel plates are separated by a vacuum and one of the plates is brought to a given potential it will become charged (a *conduction charge*). This conduction charge will induce an equal, but opposite charge on the second plate. For a condenser, the relationship between the charge Q and the potential difference V between the plates is given by

$$Q = CV \quad (6.1)$$

where the constant of proportionality C is known as the *capacitance* and is a characteristic of a given condenser (see *Figure 6.1 (c)*).

If the slab of dielectric composed of a mass of atoms or molecules is inserted between the plates, each of the atoms or molecules will be subject to electron polarisation. In the centre of the dielectric there will be no apparent effect but the edges of the slab adjacent to the metal plates will have a resultant charge, known as a *polarisation charge*. Since the charge near each metal plate is of opposite sign to the conduction charge, it tends to offset the conduction charge in electrostatic effects (*Figure 6.1 (d)*). This includes the potential difference V between the plates which is reduced when polarisation charges are present. In any use of a condenser it is the conduction charge Q that is relevant and this is unaltered by the polarisation. From equation (6.1) it will be seen that since the insertion of a dielectric reduces the potential difference but maintains a constant conduction charge the capacitance of the system is increased.

The influence of a particular dielectric on the capacitance of a condenser is conveniently assessed by the *dielectric constant*, also known as the *relative permittivity* or rarely specific inductive capacity. This is defined as the ratio of the relative condenser capacity, using the given material as a dielectric, to the capacity of the same condenser, without dielectric, in a vacuum (or for all practical intents and purposes, air).

In the case of symmetrical molecules such as carbon tetrachloride, benzene, polyethylene and polyisobutylene the only polarisation effect is electronic and such materials have low dielectric constants. Since electronic polarisation may be assumed to be instantaneous, the influence of frequency and temperature will be very small. Furthermore, since the charge displacement is able to remain in phase with the alternating field there are negligible power losses.

Many intra-atomic bonds are not truly covalent and in a given linkage one atom may have a slight positive charge and the other a slight negative charge. Such a bond is said to be polar. In a number of these molecules, such as carbon tetrachloride, the molecules are symmetrical and there is no external effect. In the case of other molecules, the disposition of the polar linkage is unbalanced, as in the case of water (*Figure 6.2*).

In the water molecule, the oxygen atom has a stronger attraction for the electrons than the hydrogen atoms and becomes negatively charged. Since the

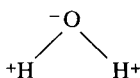


Figure 6.2

angle between the O—H bonds is fixed (approx. 105 degrees) the molecule is electrically unbalanced and the centres of positive and negative charge do not coincide. As a consequence the molecule will tend to turn in an electric field. The effect is known as *dipole polarisation*; it does not occur in balanced molecules where the centres of positive and negative charge are coincident.

In the dielectric of a condenser the dipole polarisation would increase the polarisation charge and such materials would have a higher dielectric constant than materials whose dielectric constant was only a function of electronic polarisation.

There is an important practical distinction between electronic and dipole polarisation: whereas the former involves only movement of electrons the latter entails movement of part or even the whole of the molecule. Molecular movements take a finite time and complete orientation as induced by an alternating current may or may not be possible depending on the frequency of the change of direction of the electric field. Thus at zero frequency the dielectric constant will be at a maximum and this will remain approximately constant until the dipole orientation time is of the same order as the reciprocal of the frequency. Dipole movement will now be limited and the dipole polarisation effect and the dielectric constant will be reduced. As the frequency further increases, the dipole polarisation effect will tend to zero and the dielectric constant will tend to be dependent only on the electronic polarisation (*Figure 6.3*). Where there are two dipole species differing in ease of orientation there will be two points of inflection in the dielectric constant–frequency curve.

The dielectric constant of unsymmetrical molecules containing dipoles (polar molecules) will be dependent on the internal viscosity of the dielectric. If very hard frozen ethyl alcohol is used as the dielectric the dielectric constant is approximately 3; at the melting point, when the molecules are free to orient themselves, the dielectric constant is about 55. Further heating reduces the ratio by increasing the energy of molecular motions which tend to disorient the molecules but at room temperature the dielectric constant is still as high as 35.

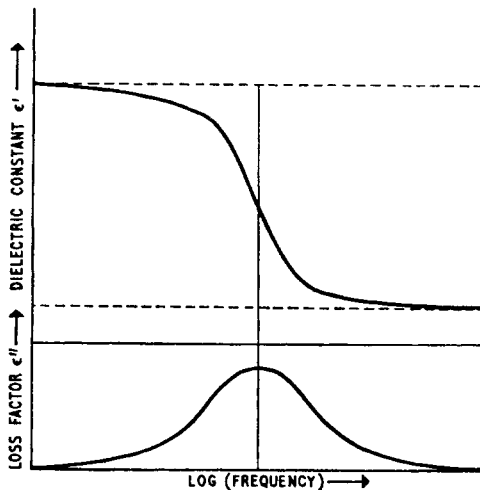


Figure 6.3. The variation of dielectric constant ϵ' and the loss factor ϵ'' with frequency. (After Frith and Tuckett¹, reproduced by permission of Longmans, Green and Co. Ltd.)

In addition to an enhanced dielectric constant dependent on temperature and frequency, polar molecules exhibit quite high dielectric power losses at certain frequencies, the maximum power loss corresponding to the point of inflection in the dielectric constant–frequency curve (*Figure 6.3*). At very low frequencies, as already mentioned, the dipole movements are able to keep in phase with changes in the electric field and power losses are low. As the frequency is increased the point is reached when the dipole orientation cannot be completed in the time available and the dipole becomes out of phase. It is possible to have a mental picture of internal friction due to out-of-step motions of the dipoles leading to the generation of heat. Measures of the fraction of energy absorbed per cycle by the dielectric from the field are the *power factor* and *dissipation factor*. These terms arise by considering the delay between the changes in the field and the change in polarisation which in turn leads to a current in a condenser leading the voltage across it when a dielectric is present. The angle of lead is known as the phase angle and given the symbol θ . The value $90-\theta$ is known as the loss angle and is given the symbol δ . The power factor is defined as $\cos \theta$ (or $\sin \delta$) and the dissipation factor as $\tan \delta$ (or $\cot \theta$). When δ is small the two are equivalent. Also quoted in the literature is the *loss factor* which is numerically the product of the dissipation factor and the dielectric constant.

At low frequencies when power losses are low these values are also low but they increase when such frequencies are reached that the dipoles cannot keep in phase. After passing through a peak at some characteristic frequency they fall in value as the frequency further increases. This is because at such high frequencies there is no time for substantial dipole movement and so the power losses are reduced. Because of the dependence of the dipole movement on the internal viscosity, the power factor like the dielectric constant, is strongly dependent on temperature.

In the case of polar polymers the situation is more complex, since there are a large number of dipoles attached to one chain. These dipoles may either be attached to the main chain (as with poly(vinyl chloride), polyesters and polycarbonates) or the polar groups may not be directly attached to the main chain and the dipoles may, to some extent, rotate independently of it, e.g. as with poly(methyl methacrylate).

In the first case, that is with dipoles integral with the main chain, in the absence of an electric field the dipoles will be randomly disposed but will be fixed by the disposition of the main chain atoms. On application of an electric field complete dipole orientation is not possible because of spatial requirements imposed by the chain structure. Furthermore in the polymeric system the different molecules are coiled in different ways and the time for orientation will be dependent on the particular disposition. Thus whereas simple polar molecules have a sharply defined power loss maxima the power loss–frequency curve of polar polymers is broad, due to the dispersion of orientation times.

When dipoles are directly attached to the chain their movement will obviously depend on the ability of chain segments to move. Thus the dipole polarisation effect will be much less below the glass transition temperature, than above it (*Figure 6.4*). For this reason unplasticised PVC, poly(ethylene terephthalate) and the bis-phenol A polycarbonates are better high-frequency insulators at room temperature, which is below the glass temperature of each of these polymers, than would be expected in polymers of similar polarity but with the polar groups in the side chains.

It was pointed out in Chapter 3 that the glass temperature is dependent on the time scale of the experiment and thus will be allocated slightly different values

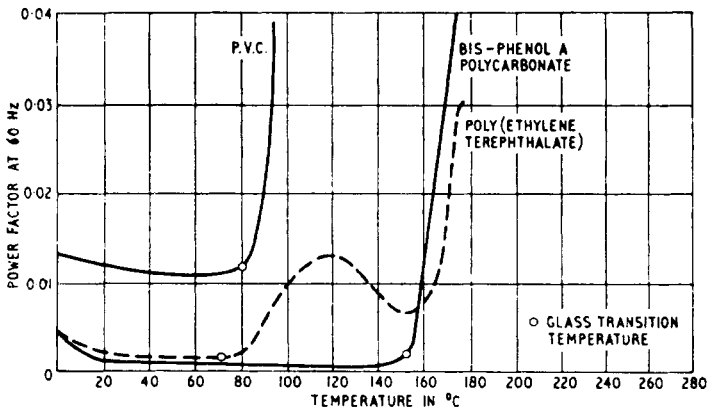


Figure 6.4. Power factor-temperature curves for three polar polymers whose polar groups are integral with or directly attached to the main chain. The rise in power factor above the glass transition point is clearly seen in these three examples

according to the method of measurement. One test carried out at a slower rate than in a second test will allow more time for segmental motion and thus lead to lower measured values of the glass temperature. In the case of electrical tests the lower the frequency of the alternating current the lower will be the temperature at the maxima of the power factor-temperature curve and of the temperature at the point of inflection in the dielectric constant-temperature curve (Figure 6.5).

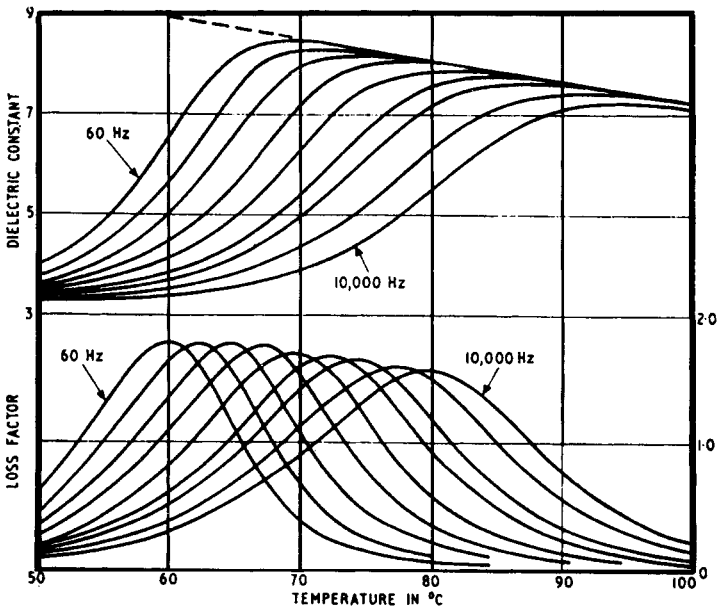


Figure 6.5. Electrical properties of poly(vinyl acetate) (Gelva 60) at 60, 120, 240, 500, 1000, 2000, 3000, 6000 and 10,000 Hz.² (Copyright 1941 by the American Chemical Society and reprinted by permission of the copyright holder)

Since the incorporation of plasticisers into a polymer compound brings about a reduction in glass temperature they will also have an effect on the electrical properties. Plasticised PVC with a glass temperature below that of the testing temperature will have a much higher dielectric constant than unplasticised PVC at the same temperature (*Figure 6.6*).

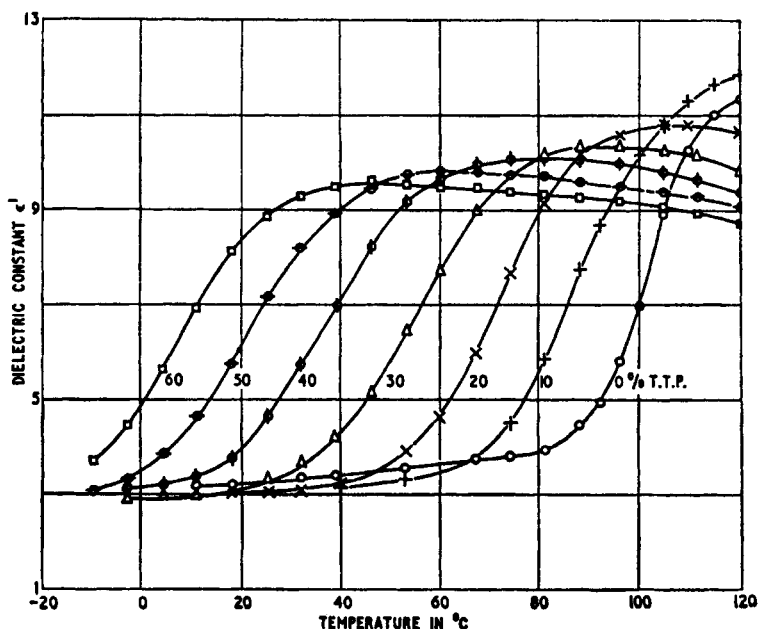


Figure 6.6. Effect of temperature on the 1000 Hz dielectric constant of stabilised poly(vinyl chloride)-tritolyl phosphate systems.³ (Copyright 1941 by the American Chemical Society and reprinted by permission of the copyright holder)

In the case of polymer molecules where the dipoles are not directly attached to the main chain, segmental movement of the chain is not essential for dipole polarisation and dipole movement is possible at temperatures below the glass transition temperature. Such materials are less effective as electrical insulators at temperatures in the glassy range. With many of these polymers, e.g., poly(methyl methacrylate), there are two or more maxima in the power factor-temperature curve for a given frequency. The presence of two such maxima is due to the different orientation times of the dipoles with and without associated segmental motion of the main chain.

The above discussion in so far as it applies to polymers may be summarised as follows:

- (1) For non-polar materials (i.e. materials free from dipoles or in which the dipoles are vectorially balanced) the dielectric constant is due to electronic polarisation only and will generally have a value of less than 3. Since polarisation is instantaneous the dielectric constant is independent of temperature and frequency. Power losses are also negligible irrespective of temperature and frequency.

- (2) With polar molecules the value of the dielectric constant is additionally dependent on dipole polarisation and commonly has values between 3.0 and 7.0. The extent of dipole polarisation will depend on frequency, an increase in frequency eventually leading to a reduction in dielectric constant. Power factor–frequency curves will go through a maximum.
- (3) The dielectric properties of polar materials will depend on whether or not the dipoles are attached to the main chain. When they are, dipole polarisation will depend on segmental mobility and is thus low at temperatures below the glass transition temperatures. Such polymers are therefore better insulators below the glass temperature than above it.

Finally mention may be made about the influence of humidity on the electrical insulating properties of plastics. Once again the polymers may be classified into two groups, those which do not absorb water and those which do. The non-absorbent materials are little affected by humidity whereas the insulation characteristics of the absorbent materials deteriorate seriously. These latter materials are generally certain polar materials which all appear capable of forming some sort of bond, probably a hydrogen bond, with water. Three reasons may be given for the deleterious effects of the water.

- (1) Its higher electrical conductivity lowers the resistivity of the compound.
- (2) Its higher dielectric constant raises the overall value of the polymer–water mixture.
- (3) Its plasticising effect on some polymers which increases segmental mobility and enhances the value of the dielectric constant of the polymer itself.

6.3. SOME QUANTITATIVE RELATIONSHIPS OF DIELECTRICS

There are a number of properties of molecules that are additive to a reasonable approximation, i.e. the value of such a property of a given molecule is an approximate sum of the values of the properties of either the atoms or bonds present. It has been shown that the dielectric constant is related to some additive properties and it is thus possible to make some estimate of dielectric properties from consideration of molecular structure.

The total polarisation of a molecule in an electric field P is

$$P = P_E + P_A + P_O \tag{6.2}$$

where P_E is the electronic polarisation

P_A is the nuclear polarisation (considered to be negligible and hence ignored in further discussion)

P_O the dipole or orientation polarisation

P itself is defined by the Clausius–Mosotti Equation

$$P = \left(\frac{D - 1}{D + 2} \right) \frac{M}{\rho} \tag{6.3}$$

where D is the dielectric constant

M is the molecular weight

ρ is the density

It may be shown that for electron polarisation

$$P_E = \frac{4}{3}\pi N\alpha_E \tag{6.4}$$

where N is the Avagadro number
 α_E is the electron polarisability.

It has also been observed that

$$P_E = \left(\frac{n^2 - 1}{n^2 + 2}\right) \frac{M}{\rho} \tag{6.5}$$

where n is the refractive index.

It is thus seen that for polymers in which polarisations other than electronic ones are negligible (i.e. $P = P_E$) the dielectric constant is equal to the square of the refractive index (*Table 6.2*).

Table 6.2

	D	n	n^2
Polyethelene	2.28	1.51	2.28
Polystyrene	2.55	1.60	2.56
PTFE	2.05	1.40	1.96
Polyisobutylene	2.30	1.51	2.28

Where dipole polarisation occurs it may be shown that

$$P_O = \frac{4}{3}\pi N \left(\frac{\mu^2}{3KT}\right) \tag{6.6}$$

where μ is the permanent dipole moment
 K is the Boltzmann constant
 T the absolute temperature

Hence

$$P = \left(\frac{D - 1}{D + 2}\right) \frac{M}{\rho} = \frac{4}{3}\pi N\alpha_E + \frac{4}{3}\pi N \left(\frac{\mu^2}{3KT}\right) \tag{6.7}$$

This expression is known as the Debye equation. It is therefore obvious that if α_E and μ were to be additive properties then it would be possible to calculate the dielectric constant from a knowledge of molecular structure.

Table 6.3 Refractions of some electron groups (measured by sodium D line)

<i>Electron group</i>	<i>Refraction</i>	<i>Electron group</i>	<i>Refraction</i>
C—H	1.705	C≡C	6.025
C—C	1.209	C—Cl	6.57
C=C	4.15	C—F	1.60

Now P_E is numerically equal to the molar refraction R which is an additive property. It has been shown that R is a property which can be calculated by adding the refractions of various electron groups. Six values for such partial molar refractions are given in *Table 6.3*.

Assuming that in polyethylene the polarisation is solely electronic, that the degree of polymerisation is r and that the repeating unit is as shown in *Figure 6.7*.

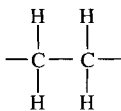


Figure 6.7

Then if M is the weight of the repeating unit

$$\left(\frac{D-1}{D+2} \right) \frac{Mr}{\rho} = r[4R_{\text{C-H}} + 2R_{\text{C-C}}] \quad (6.8)$$

then for polyethylene of density 0.92 the calculated dielectric constant is equal to 2.27 (c.f. observed value of 2.28 ± 0.01).

The calculated value for polypropylene (2.27) is also within the range of observed values (2.15–2.30) but the calculated value for PTFE (1.7) is less than the observed values of about 2.0.

The dipole moment of a molecule is another additive property since it arises from the difference in electronegativity of two atoms connected by a double bond. It should therefore be possible to associate a dipole moment with every linkage. Eucken and Meyer⁴ have suggested the following moments for various linkages (in units of 10^{-18} e.s.cm)

C—H	0.4	C—Cl	1.5
C—O	0.7	C=O	2.3
H—O		1.6	

In each case the left-hand atom of the pair as written is the least electro-negative. Since dipole moments have direction as well as magnitude it is necessary to add the moments of each bond vertically. For this reason the individual dipole moments cancel each other out in carbon tetrachloride but only partially in chloroform. In other molecules, such as that of water, it is necessary to know the bond angle to calculate the dipole moment. Alternatively since the dipole moment of the molecule is measurable the method may be used to compute the bond angle.

Computation of the dipole moment and hence the dielectric constant in polymers becomes complex but consideration of the bond dispositions allows useful qualitative prediction to be made.

6.4 ELECTRONIC APPLICATIONS OF POLYMERS

Whilst plastics materials have been associated with electrical and electronic applications since the early days of the electrical industry, developments over the

past 20 years have been particularly spectacular. Amongst applications that may be mentioned are:

- (1) Encapsulation of semiconductors. The usual material is epoxide resin (see Chapter 26) and the preferred method transfer moulding. It has been estimated that by 1980 annual production of such encapsulated parts exceeded 10 billion units.
- (2) Manufacture of semiconductors using lithographic techniques involving either the selective degradation or cross-linking of polymers with the associated stages of etching, doping and passivation of the substrate using the imaged protective coating or resist. Polymers used include cyclised synthetic polyisoprene rubber and phenolic novolak resins.
- (3) Printed circuit board component such as laminates, conformal coatings, solder masks, masking tapes, component attachment adhesives, vibration dampers and photoresists.

The technical requirements for such applications are highly specific, and the technology is also highly specialised and beyond the scope of this book.

6.5 ELECTRICALLY CONDUCTIVE POLYMERS

For very many years it has been common practice to improve the electrical conductivity of plastics and rubbers by the incorporation of certain additives like special grades of carbon black. Such materials were important, for example, in hospital operating theatres where it was essential that static charges did not build up, leading to explosions involving anaesthetics.

During the past 30 years considerable research work has been undertaken that has led to the appearance of electrically conducting polymers which do not require the use of fillers. Most of the polymers produced in this work contain conjugated double bonds and furthermore only become conductive when they have been treated with oxidising or reducing agents; the process is referred to as 'doping'. Such polymers are therefore of potential interest in such areas as lightweight batteries, particularly for aerospace and medical applications.

The polymers which have stimulated the greatest interest are the polyacetylenes, poly-*p*-phenylene, poly(*p*-phenylene sulphide), polypyrrole and poly-1,6-heptadiyne. The mechanisms by which they function are not fully understood, and the materials available to date are still inferior, in terms of conductivity, to most metal conductors. If, however, the differences in density are taken into account, the polymers become comparable with some of the moderately conductive metals. Unfortunately, most of these polymers also have other disadvantages such as improcessability, poor mechanical strength, instability of the doped materials, sensitivity to oxygen, poor storage stability leading to a loss in conductivity, and poor stability in the presence of electrolytes. Whilst many industrial companies have been active in their development (including Allied, BSASF, IBM and Rohm and Haas,) they have to date remained as developmental products. For a further discussion see Chapter 31.

6.6 OPTICAL PROPERTIES

In addition to the refractive index (already seen to be closely linked with molecular structure) there are a number of other optical properties of importance

with plastics materials.⁵ These include clarity, haze and birefringence, colour, transmittance and reflectance.

In order to achieve a product with a high *clarity* it is important that the refractive index is constant throughout the sample in the line of direction between the object in view and the eye. The presence of interfaces between regions of different refractive index will cause scatter of the light rays. This effect is easily demonstrated when fine fillers or even air bubbles are incorporated into an otherwise transparent polymer. Amorphous polymers free from fillers or other impurities are transparent unless chemical groups are present which absorb visible light radiation. Crystalline polymers may or may not be transparent, dependent on a number of factors. Where the crystalline structures such as spherulites are smaller than the wavelength of light then they do not interfere with the passage of light and the polymer is transparent. This occurs with rapidly quenched films of polyethylene. Where the structures formed are greater in diameter than the wavelength of light then the light waves will be scattered if the crystal structures have a different refractive index to that of the amorphous regions. Since this property is dependent on density it follows that where the crystalline and amorphous densities of polymers differ there will be a difference in refractive index. In the case of thick polyethylene objects fast quenching is not possible and as the spherulites formed have a significantly higher density (about 1.01) than the amorphous region (0.84–0.85) the polymer is opaque. In the case of polypropylene the difference is less marked (crystal density = 0.94, amorphous density = 0.85) (all in g/cm³) and mouldings are more translucent. With poly(4-methylpent-1-ene) amorphous and crystal densities are similar and the polymer is transparent even when large spherulites are present.

As the polarity across a molecule is different from the polarity along its length the refractive index of crystal structures depends on the direction in which it is measured (the crystal is said to be birefringent). Light scatter will then occur at the interface between structures aligned in different directions. By biaxial stretching, the crystal structures will be aligned into planes so that light travelling through films so oriented will pass through in a direction generally at right angles to the direction of the molecule. These light waves will thus not be affected by large changes in refractive index and the films will appear transparent. This phenomenon has been utilised in the manufacture of biaxially oriented polypropylene and poly(ethylene terephthalate) films of high clarity.

For transparent plastics materials *transparency* may be defined as the state permitting perception of objects through or beyond the specimen. It is often assessed as that fraction of the normally incident light transmitted with deviation from the primary beam direction of less than 0.1 degree.

Some polymers, although transparent, may have a cloudy or milky appearance, generally known as *haze*. It is often measured quantitatively as the amount of light deviating by more than 2.5 degrees from the transmitted beam direction. Haze is often the result of surface imperfections, particularly with thin films of low-density polyethylene.

When light falls on a material some is transmitted, some is reflected and some absorbed. The *transmittance* is the ratio of the light passing through to the light incident on the specimens and the *reflectance* the ratio of the light reflected to the light incident. The *gloss* of a film is a function of the reflectance and the surface finish of a material. Where transmittance and reflectance do not add up to unity then some of the light waves are absorbed. This does not usually occur uniformly over the visible spectrum but is selective according to the chemical structures

present. The uneven absorption of incident light results in the material being coloured. Comparatively few groupings present in commercial polymers are affected by visible radiation and so in the absence of impurities polymers are often water-white. Two important instances of the presence of colour-forming groups in polymers occur in the curing of novolak resins and in the dehydrochlorination of PVC. Although coloured polymers have been produced by the deliberate use of monomers containing chromophoric groups it is generally desirable to have a water-white polymer which may then be given any desired colour by the appropriate addition of dyes or pigments.

APPENDIX—ELECTRICAL TESTING

In recent years test methods have been largely standardised by the International Electrotechnical Commission (IEC) in close collaboration with the International Standards Organisation (ISO). The most important tests are:

- (1) Dielectric Strength IEC 243-1. This is a measure of the dielectric breakdown resistance of a material under an applied voltage. The applied voltage just before breakdown is divided by the specimen thickness to give the value in kV/mm. Since, however, the result depends on the thickness this should also be specified.
- (2) Volume Resistivity IEC 93 (ASTM D257). This is the electrical resistance when an electrical potential is applied between the opposite faces of a unit cube of material. It is usually measured in ohm.cm.
- (3) Surface Resistivity IEC 93 (ASTM D257). If an insulating material is subjected to a voltage, some portion of the resulting current will flow along the surface if there is another conductor or ground attached to the same surface. Surface resistivity is a measure of the ability to resist that surface current. It is the resistance when a direct voltage is applied between two surface-mounted electrodes of unit width and unit spacing. The value is expressed in ohms.
- (4) Relative Permittivity IEC 250. The term relative permittivity is currently more commonly used than the term 'dielectric constant' used by the author and most of the references quoted in this chapter. As explained in this chapter, it is a ratio and thus dimensionless.
- (5) Dissipation factor (loss tangent) IEC 250. As explained in the chapter, this is the tangent of the dielectric loss angle and is now more commonly used than the power factor, which is the sine of the loss angle. When the angle is small the two are almost identical (e.g. for a loss angle of 10° the difference is about 1.5%).
- (6) Comparative Tracking Index IEC 112. The tracking index is the relative resistance of electrical insulating materials to tracking when the surface is exposed—under electrical stress—to contaminants containing water. In the basic test the comparative tracking index (CTI) is defined as the maximum voltage at which no failure occurs on exposure to 50 drops of ammonium chloride in water in a standardised test rig.
- (7) Arc Resistance ASTM D495. When an electric current is allowed to travel across the surface of an insulator the surface will become damaged over time and become more conductive. The arc resistance is a measure of the time (in seconds) required to make an insulating surface conductive under a high-voltage, low-current arc.

References

1. FRITH E. M., and TUCKETT, R. F., *Linear Polymers*, Longmans Green, London (1951)
2. MEAD, D. J. and FUOSS, R. M., *J. Am. Chem. Soc.*, **63**, 2832 (1941)
3. DAVIES, J. M., MILLER, R. F., and BUSSE, W. F., *J. Am. Chem. Soc.*, **63**, 361 (1941)
4. EUCKEN, A., and MEYER, L., *Phys. Z.*, **30**, 397 (1929)
5. PRITCHARD, R., *Soc. Plastics Engrs. Trans.*, **4**, 66 (1964)

Bibliography

- BEAR, E., *Engineering Design for Plastics*, Rheinhold, New York (1964)
- BAIRD, M. E., *Electrical Properties of Polymeric Materials*, The Plastics Institute, London (1973)
- BLYTHE, A. R., *Electrical Properties of Polymers*, Cambridge University Press, Cambridge (1979)
- FROMMER, J. E. and CHANCE, R. R., Chapter in *Encyclopedia of Polymer Science and Technology*, 2nd Edn, Vol. 5, p. 462, Wiley, New York (1986)
- JENKINS, A. D. (Ed.), *Polymer Science*, North-Holland, Amsterdam, Chapters 7 (by MILLS, N. J.), 17 (by SEANOR, D. A.), 18 (by LINK, G. L.) and 19 (by PARKER, T. G.) (1972).
- MATHER, K. N., Chapter in *Encyclopedia of Polymer Science and Technology*, 2nd Edn, Vol. 5, p. 507, Wiley, New York (1986)
- MCCRUM, N. G., READ, B. E. and WILLIAMS, G., *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, London (1967)
- RITCHIE, P. D. (Ed.), *Physics of Plastics*, Iliffe, London (1965)
- SMYTH, C. P., *Dielectric Behaviour and Structure*, McGraw-Hill, New York (1955)

Electronic applications

- GOOSEY, M. T. (Ed.), *Plastics for Electronics*, Elsevier Applied Science, London (1985)

Electrically conductive polymers

- ELIAS, H.-G. and VOHWINKEL, F., *New Commercial Polymers—2* (Chapter 14), Gordon and Breach, New York, London (1986)
- SEYMOUR, R. B. (Ed.), *Conductive Polymers*, Plenum Press, New York (1981)

Additives for Plastics

7.1 INTRODUCTION

The bulk properties of a polymer can often be altered considerably by the incorporation of additives. Probably the most well-known examples of this occur in rubber technology where variations in the choice of additives can produce such widely differing products as tyres, battery boxes, latex foam upholstery, elastic bands and erasers. It is also possible to achieve variations as extensive as this amongst plastics materials, in particular with PVC from which rigid rainwater piping, baby pants, conveyor belting, footballs and domestic insulating flex may all be prepared.

In some cases an additive may be encountered in a variety of polymers for a wide range of end uses, for example certain antioxidants. In other instances the additive may be very specific to a certain polymer for a particular end use.

Physically, additives may be divided into four groups, solids, rubbers, liquids and gases, the last of these being employed for making cellular polymers. In terms of function there are rather larger numbers of groups, of which the following are the most important:

- (1) Fillers.
- (2) Plasticisers and softeners.
- (3) Lubricants and flow promoters.
- (4) Anti-aging additives.
- (5) Flame retarders.
- (6) Colorants.
- (7) Blowing agents.
- (8) Cross-linking agents.
- (9) Ultraviolet-degradable additives.

In general, additives should have the following features unless by virtue of their function such requirements are excluded:

- (1) They should be efficient in their function.
- (2) They should be stable under processing conditions.

- (3) They should be stable under service conditions.
- (4) They should not bleed or bloom.
- (5) They should be non-toxic and not impart taste or odour.
- (6) They should be cheap.
- (7) They should not adversely affect the properties of the polymer.

Most of the above requirements are self-explanatory but the phenomena of bleeding and blooming require some discussion. *Bleeding* of an additive into an adjacent material occurs when the additive has a degree of solubility in the polymer into which it is incorporated and also in the adjacent material, which could be liquid or solid. Such bleeding could colour or otherwise contaminate the adjacent material. When conditions causing bleeding are fulfilled the rates of bleeding will be covered by the laws of diffusion. It will therefore depend on the size of the 'holes' in the polymer, and on the size of the diffusing molecules and on the concentration of these molecules in the original polymer. It is not surprising to find that bleeding is much more extensive from polymers which are above their T_g (and melting point T_m if crystalline) than from polymers below this temperature. It is also quite common practice to replace small molecules, with a propensity to bleed, with larger molecules of similar structure in order to reduce the effect.

Blooming is a separate phenomenon but is again associated with solubility. It occurs when an additive has totally dissolved in the polymer at the processing temperature but is only partially soluble at ambient temperature. As a result some of the additive is thrown out of solution on cooling and some of this may collect on the surface of the polymer mass. If the additive is only partially soluble at the processing temperature the residual material may form nuclei around which the additive molecules, which are thrown out of solution, can congregate so that much less of the additive will bloom on to the surface. It is also possible that another additive might form suitable nuclei in each of the two above instances. Blooming will not occur either if the additive is totally insoluble at processing temperature or if it is totally soluble at room temperature. It should be pointed out that solubility should be considered with respect to the polymer compound as a whole, including, for example, plasticisers and lubricants and not just to the polymer itself.

Table 7.1 summarises the blooming expectancies of additives in polymer compounds but it should be stressed that there may be exceptions to these very general rules.

Table 7.1 Blooming in polymer compounds

Example	Concentration of additive	Solubility at ambient temperature	Solubility at processing temperature	Expected effect
1	x	0	0	No blooming
2	x	$<x$	$<x$	No blooming
3	x	$<x$	$>x$	Blooming unless nucleated <i>in situ</i> by another additive
4	x	$>x$	$>x$	No blooming

7.2 FILLERS

The term filler is usually applied to solid additives incorporated into the polymer to modify its physical (usually mechanical) properties. Air and other gases which could be considered as fillers in cellular polymers are dealt with separately. A number of types of filler are generally recognised in polymer technology and these are summarised in *Figure 7.1*.

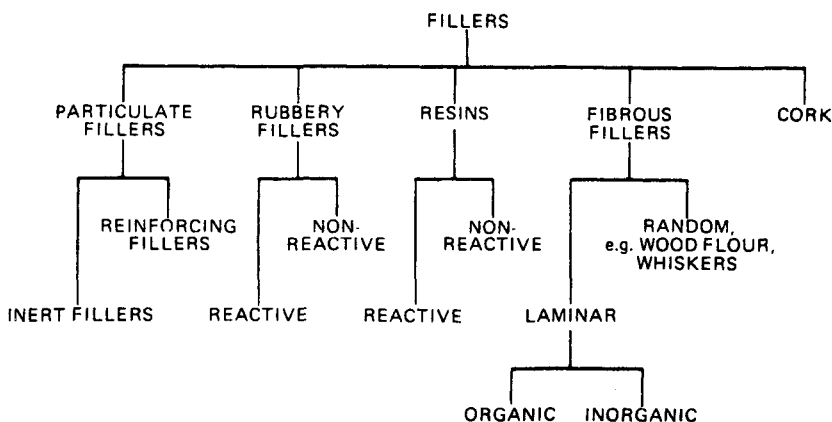


Figure 7.1. Classification of fillers in polymer compounds

Particulate fillers are divided into two types, 'inert' fillers and reinforcing fillers. The term *inert filler* is something of a misnomer as many properties may be affected by incorporation of such a filler. For example, in a plasticised PVC compound the addition of an inert filler will reduce die swell on extrusion, increase modulus and hardness, may provide a white base for colouring, improve electrical insulation properties and reduce tackiness. Inert fillers will also usually substantially reduce the cost of the compound. Amongst the fillers used are calcium carbonates, china clay, talc, and barium sulphate. For normal uses such fillers should be quite insoluble in any liquids with which the polymer compound is liable to come into contact.

It is important to stress that with each chemical type of filler a number of grades are usually available. Such grades may differ in the following ways:

- (1) Average particle size and size distribution.
- (2) Particle shape and porosity.
- (3) Chemical nature of the surface.
- (4) Impurities such as grit and metal ions.

When employed in elastomeric systems it is commonly observed that the finer the *particle size* the higher the values of such properties as tensile strength, modulus and hardness. Coarser particles will tend to give compounds less strong than compounds with the filler absent, but if the particle size is sufficiently fine there is an enhancement in the above-mentioned properties (at least up to an optimum loading of filler) and the phenomenon is known as reinforcement. The *particle shape* also has an influence; for example, the somewhat plate-like china

clay particles tend to be oriented during processing to give products that are anisotropic. Other particles tend to have an uneven surface and are difficult to wet with polymer whilst others are porous and may absorb other additives and render them ineffective.

The *chemical nature* of the surface can have a vital effect. Mineral fillers often have polar groups, for example hydroxyl groups, on the surface which render them attractive to water but not to organic polymer. To improve the wetting of polymers to fillers and hence obtain better products mineral fillers are often treated. For example, calcium carbonate may be treated with stearic acid, the acid group attaching itself to the filler particles whilst the aliphatic chain is compatible with the polymer. Some clays are amine-treated whilst others are coated with a glycol or similar product. Besides improved wetting such treatment can have a second function. Surface hydroxyl groups tend to H-bond to other additives such as antioxidants and some cross-linking components, making them ineffective. Preferential absorption by a less expensive additive such as a glycol can give much improved results. The most recent developments are *coupling agents* such as certain silanes which in effect form a polymer shell around the surface of the particle and improve the wetting to the main polymer. These are discussed further in the next section.

Impurities in mineral fillers can have serious effects. Coarse particles (grit) will lead to points of weakness in soft polymers which will therefore fail under stresses below that which might be expected. Traces of copper, manganese and iron can affect the oxidative stability whilst lead may react with sulphur-containing additives or sulphurous fumes in the atmosphere to give a discoloured product.

Reinforcing particulate fillers are effective primarily with elastomers although they can cause an increase in tensile strength with plasticised PVC. Pure gum styrene-butadiene rubber (SBR) vulcanisates have tensile strengths of about 3 MPa. By mixing in 50 phr of a reinforcing carbon black the tensile strength can be increased to over 20 MPa. In a crystalline rubber such as natural rubber such large increases in tensile strength are not observed but as with SBR an increase in modulus, tear resistance and abrasion resistance can be seen. It is often found that a property such as tensile strength usually goes through a maximum value with change in carbon black loading. At first the increase in polymer-black interfacial area is the dominating effect but if the black concentration becomes too high the diminishing volume of rubber in the composite is insufficient to hold the filler particles together. In general reinforcement appears to depend on three factors:

- (1) An extensity factor—the total amount of surface area of filler per unit volume in contact with the elastomer.
- (2) An intensity factor—the specific activity of the filler-polymer interface causing chemical and/or physical bonding.
- (3) Geometrical factors such as structure (aggregation) and porosity of the particles.

For equivalent particle size the carbon blacks are the most powerful reinforcing fillers. However, fine particle size silicas can be very useful in non-black compounds whilst other fillers such as aluminium hydroxide, zinc oxide and calcium silicate have some reinforcing effect.

Rubbery materials are often incorporated into rigid amorphous thermoplastics to improve their toughness but it is a moot point whether or not they should be

referred to as *rubbery fillers*. Attempts were made in Chapter 3 to explain the mechanism by which such materials functioned. Well-known examples are SBR and polybutadiene in polystyrene, butadiene–acrylonitrile rubbers in PVC and ethylene–propylene rubbers in polypropylene. These materials will be discussed further in the appropriate chapters.

Whilst the plastics technologist may incorporate rubber into his resins or plastics materials the rubber technologist often incorporates *synthetic resins* or *plastics* into his rubbers. Butadiene–styrene resins containing at least 50% styrene may be blended with rubber to produce compounds for shoe soles and for making car wash brushes. Phenolic resins which have a low viscosity at processing temperatures may enhance the flow and hence processability of rubber compounds but during the vulcanisation of the rubber will simultaneously cross-link, leading to a comparatively rigid product.

Fibrous fillers have been long used in plastics materials. Wood flour, cotton flock, macerated fabric, macerated paper and short lengths of synthetic organic fibres such as nylon can improve the impact strength and often the rigidity and toughness of moulding compositions. Inorganic fibres such as asbestos and glass fibre are also used in moulding compositions, both thermoplastic and thermosetting, where heat resistance and strength respectively are required. More recently, chopped carbon fibre and whiskers (single crystals of high length–diameter ratio of very high strength) have been used for highly specialised purposes.

Fibrous fillers are often embedded in a laminar form. The fibres used have higher moduli than the resins in which they are embedded so that when the *composite* of resin plus fibre is strained in the plane of the fibrous layer the bulk of the stress is taken up by the fibre. This results in an enhancement of both strength and modulus when compared with the unfilled resin.

As a general rule woven fabrics give higher figures for strength and moduli than papers and mats, an exception occurring with asbestos mats. Of the woven fabrics in common use, those from glass fibres suitably treated to ensure good wetting give the highest strength. Exceptionally high tensile strengths can sometimes be obtained using carbon fibres but the resulting laminates have a low interlaminar strength. Attempts to improve on this by stitching between layers with carbon fibre have been described. Fibrous fillers are dealt with in further detail in the chapters on phenolics, aminoplastics and polyesters.

7.2.1 Coupling Agents

A filler cannot be used to best advantage in a polymer unless there is good adhesion between them. In particular the filler particle–polymer interface will not be stress-bearing and therefore provides a point of mechanical weakness.

One way of improving the adhesion between polymer and filler is to improve the level of wetting of the filler by the polymer. One approach, which has been used for many years, is to coat the filler with an additive that may be considered to have two active parts. One part is compatible with the filler, the other with the polymer. Probably the best known example is the coating of calcium carbonate with stearic acid. Such coated or ‘activated’ whittings have been used particularly with hydrocarbon rubbers. It is generally believed that the polar end attaches itself to the filler particle whilst the aliphatic hydrocarbon end is compatible with the rubbery matrix. In a similar manner clays have been treated with amines.

A much more positive attempt to increase the adhesion between polymer and filler was to link them by covalent bonds using *coupling agents*. The earliest of these were the methacrylato-chrome chloride coupling agents introduced in the mid-1940s. These materials were used primarily in conjunction with glass fibres and marketed as Volan or, later, Volan A treatments for use in polyester-glass reinforced plastics. They were believed to react as shown in *Figure 7.2*. Chemical bonding to the surface of the glass fibre occurs through Cr—O—Si links. Bonding to the unsaturated polyester resins occurs via a polymerisation reaction involving double bonds in the polyester, in styrene monomer present as diluent and in the methacrylato groups present in the coupling agent. Reaction is also sometimes possible with saturated polymers via the hydroxyl, CrCl, CrOH and carboxyl groups that are present.

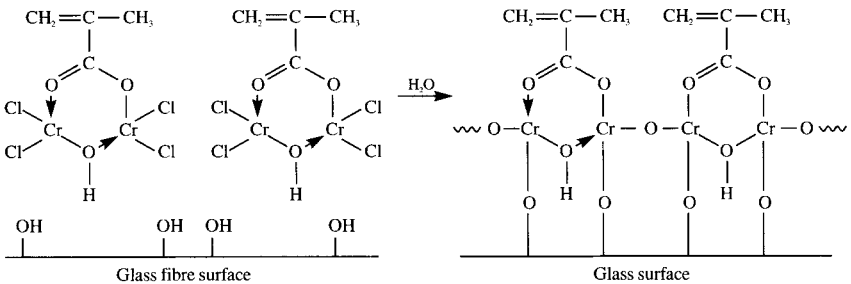


Figure 7.2

The appearance of the methacrylato-chrome chloride treatments was soon followed by glass fibre treatments involving silanes. One of the first such materials was vinyltrichlorosilane. As can be seen in *Figure 7.3* these are joined to the glass via Si—O—Si (siloxane) linkages. As with the chrome complexes the coupling agent may then be linked to an unsaturated polyester resin via the unsaturated vinyl group.

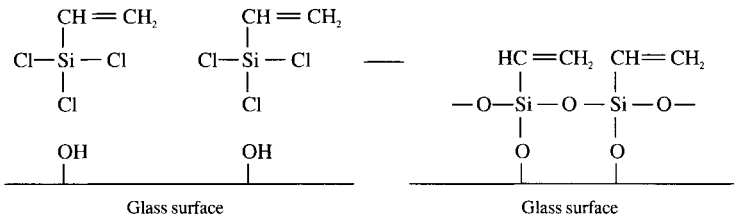
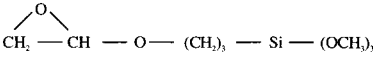
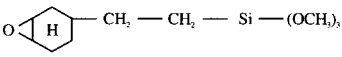
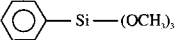


Figure 7.3

For the first few years after their introduction the main use for coupling agents, and one of continuing great importance, was for coupling glass fibre to polyester laminating resins. In due course coupling agents were developed to increase the adhesion of other polymers to glass fibres and, later, to other fillers, particularly particulate fillers and even to other types of additives. For example silane coupling agents with epoxy or amino functional groups were used to couple glass

fibre to epoxide resins and, in some cases phenolics. Coupling agents with mercaptan groups were used in conjunction with diene rubbers. A number of silanes, including some of the above, were also introduced for use with thermoplastics. In many cases the materials were non-reactive but the presence of saturated alkyl, haloalkyl, aryl or haloaryl groups, for example, improved the level of wetting, and hence the adhesion, between polymer and glass fibre. It is a debatable point as to whether such materials should be referred to as coupling agents in these circumstances since covalent bonding to the polymer does not occur. Nevertheless examples of this type are included in *Table 7.2*, which lists some examples of coupling agents.

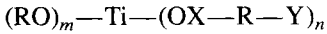
Table 7.2 Examples of silane coupling agents

<i>Name</i>	<i>Composition</i>	<i>Used with</i>
1. Trichlorovinylsilane	$\text{CH}_2 = \text{CH} - \text{SiCl}_3$	Polyester
2. Triethoxyvinylsilane	$\text{CH}_2 = \text{CH} - \text{Si} - (\text{OC}_2\text{H}_5)_3$	Polyester
3. γ -Glycidoxypropyl-trimethoxysilane		Polyester Epoxide M/F P/F
4. γ -Aminopropyltrimethoxysilane	$\text{H}_2\text{N} - (\text{CH}_2)_3 - \text{Si} - (\text{OC}_2\text{H}_5)_3$	Epoxide M/F P/F
5. [β -(3,4-Epoxy-cyclohexyl)-ethyl]trimethoxysilane		Polyester Epoxide Polycarbonate
6. γ -Mercaptopropyl-trimethoxysilane	$\text{HS} - (\text{CH}_2)_3 - \text{Si} - (\text{OCH}_3)_3$	Diene rubbers
7. Trichloromethoxysilane	$\text{CH}_3 - \text{Si} - \text{Cl}_2$	
8. Trimethoxyphenylsilane		

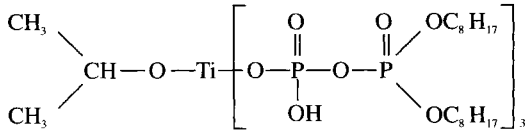
It is perhaps worthwhile observing at this point that it is quite feasible to couple a chemical onto the surface of a material such as glass to *reduce* wetting and hence the level of adhesion by a polymer by incorporating some group incompatible with or even repellent to the polymer.

In the 1960s and 1970s development with coupling agents was extended to use with particulate fillers, in particular silicas, silicates and clays for use in rubber compounds. One useful feature was that the coupling agent could be added during the rubber compounding stage when rubber, filler and other additives were being mixed together. Later, attention turned to fillers in PVC, hydrated alumina fire retarders in unsaturated polyester resins and to fillers such as

calcium carbonate in polypropylene. More recently there has been interest in *titanium coupling agents*. The most important of these have the general form



typified by isopropyl tri(dioctyl pyrophosphate) titanate:



Use of as little as 0.1% of materials of this type on the total formulation can, it is claimed, significantly reduce the viscosity of filled PVC plastisols (see Chapter 12). It is also claimed that when used in polypropylene or high molecular weight polyethylene a '70% loading of titanium-treated calcium carbonate filler gives a product with an impact strength some 7.5 times greater than obtained with untreated polymer'. In addition to improving impact strength the flow properties of the melts of filled polymers are also claimed to be improved. Thus it is reported that a 90% loading of a titanium-treated ferric oxide in polypropylene had similar flow properties to an unfilled polymer.

Another interesting innovation is that developed by the Malaysian Rubber Producers Research Association. In this case the coupling agent is first joined to a natural rubber molecule involving an 'ene' molecular reaction. The complex group added contains a silane portion which subsequently couples to filler particles when these are mixed into the rubber.

7.3 PLASTICISERS AND SOFTENERS

It has been common practice to blend plasticisers with certain polymers since the early days of the plastics industry when Alexander Parkes introduced Parkesine. When they were first used their function was primarily to act as spacers between the polymer molecules. Less energy was therefore required for molecular bond rotation and polymers became capable of flow at temperatures below their decomposition temperature. It was subsequently found that plasticisers could serve two additional purposes, to lower the melt viscosity and to change physical properties of the product such as to increase softness and flexibility and decrease the cold flex temperature (a measure of the temperature below which the polymer compound loses its flexibility).

Today plasticisers are used in a variety of polymers such as polyvinyl acetate, acrylic polymers, cellulose acetate and, most important of all, poly(vinyl chloride).

It was pointed out in Chapter 5 that plasticisers were essentially non-volatile solvents. Consequently they were required to have solubility parameters close to that of the polymer and a molecular weight of at least 300. If the polymer or the plasticisers had a tendency to crystallise then there would need to be some sort of specific interaction between the polymer and the plasticiser. *Tables 5.4 and 5.6* gave some figures for the solubility parameters of polymers and plasticisers.

Of particular interest is the fact that two plasticisers of similar molecular weight and solubility parameter can, when blended with polymers, lead to compounds of greatly differing properties. Many explanations have been offered of which the most widely quoted are the polar theory and the hydrogen bonding theory.

The polar theory suggests that plasticisers do not simply act as spacers but form links, albeit possibly momentary, with the polymer molecules. Dipole interaction is said to occur between a polar group on the polymer molecule, for example a chlorine atom forming part of a carbon–chlorine dipole, and a polar group on the plasticiser, for example an ester group. Where there are links from the plasticiser to two or more molecules a form of polar cross-linking occurs. Some molecules not only contain polar groups but may also contain polarisable groups such as benzene rings which reinforce the polar linkage. A range of plasticisers therefore exist which have varying degrees of polarity and polarisability. It is suggested that it is this difference that accounts for the different effects of the highly polar and highly polarisable tritolyl phosphate and the less polar dioctyl sebacate when used as plasticisers in PVC. The stronger linking of the phosphate tends to affect the spacing effect of a plasticiser so that the resultant compounds have a greater modulus and hardness and higher cold flex temperature than would be expected through a spacing effect alone. With a sebacate the spacing effect is much less offset by any polar linking.

Doubts have been cast as to whether differences in polarity could account for such extensive differences in properties and the hydrogen bonding theory is preferred by many. This suggests that links between plasticiser and polymer are through hydrogen bonds. In the case of PVC the hydrogen on the same carbon as the chlorine atom is activated so that the polymer molecule acts as a proton donor. Certain chemical groups in plasticiser molecules are proton acceptors. In general, phosphates are strong acceptors as also are esters and ethers. Aromatic esters are more powerful acceptors than aliphatic ethers. The intermediate position of general purpose phthalates compared to phosphates and sebacates can be seen in this context.

In the rubber industry hydrocarbon oils are often used to reduce the softness and facilitate the processing of hydrocarbon rubbers. These appear to have a small interaction with the polymer but spacing effects predominate. Such materials are generally referred to as *softeners*. The rubber industry, like the plastics industry, commonly uses the term plasticisers to describe the phthalates, phosphates and sebacates which are more commonly used with the more polar rubbers.

It has already been mentioned in Chapter 5 that plasticisers are often replaced in part by *extenders*, materials which in themselves are not plasticisers but which can be tolerated up to a given concentration in a polymer–plasticiser system. Refinery oils and chlorinated waxes are widely used in PVC for this purpose with the prime aim of reducing cost although the chlorinated waxes may also be of use as flame retardants (q.v.).

7.4 LUBRICANTS AND FLOW PROMOTERS

The term lubricant or lubricating agent is often encountered to describe certain additives incorporated into plastics materials. There are, however, various types

of lubricants with varying functions and it is important to distinguish between them. The three main types are:

- (1) Materials which reduce the friction of mouldings and other finished products when these are rubbed against adjacent materials which may or may not be of the same composition. The most well-known examples here are graphite and molybdenum disulphide used in quantities of the order of 1–2% in nylons and other thermoplastics used in gear and bearing applications.
- (2) Materials which during processing exude from the polymer composition to the interface between the molten polymer and the metal surfaces of the processing equipment with which they are in contact. The resultant thin film layer then helps to prevent the plastics composition from sticking to the machinery and thus in the normal way facilitates processing. Such materials, known commonly as *external* lubricants, have a low compatibility with the polymer and in addition often possess polar groups to enhance their affinity to metals. The choice of lubricant will depend not only on the type of polymer but also on processing temperatures involved. With PVC typical external lubricants are stearic acid and its calcium, lead, cadmium and barium salts, myristic acid, hydrocarbons such as paraffin wax and low molecular weight polythene and certain esters such as ethyl palmitate.

Because by their very nature these materials exude from the polymer mass during processing, problems can occur in their use, particularly if employed to excess (1% is a common maximum figure for PVC external lubricants although in some cases it may be less). For example, the exudation may contain traces of other additives such as colorants which contaminate, colour or stain the processing equipment and hence contaminate subsequent batches of material being processed. This is most common under conditions of high shear and/or pressure such as occurs in high-speed calendering and in the head of an extruder. The presence of such lubricants may also affect clarity and haze of sheet and the ability to print on to or heat seal such sheet. A further possible problem occurs when gelling PVC but this phenomenon will be considered in Chapter 12.

The choice of lubricant for a particular composition and process can be quite critical but beyond stating that such materials will normally be fluid at processing temperature and should have a solubility parameter at least $3 \text{ MPa}^{1/2}$ different from the polymer, little further fundamental guidance can be given and selection is normally made by an empirical trial and error basis.

- (3) The third group of lubricants comprise low molecular weight materials which promote the flow of the polymer in the melt but which unlike plasticisers have little effect on the solid state properties—the term *internal lubricant* has been applied here. Some external lubricants appear also to function as internal lubricants but for this function incompatibility is not a requirement and may be a disadvantage. Amongst internal lubricants used for PVC are amine waxes, montan wax ester derivatives, glyceryl esters such as glyceryl monostearate and long chain esters such as cetyl palmitate. As with external lubricants the choice and amount of lubricant can be highly critical and tests on laboratory scale equipment may well not reflect behaviour on full scale plant.

It has been seen that internal lubricants are essentially low molecular weight flow promoters which, unlike plasticisers, have little effect on the

finished polymer. This realisation has led to the search for other materials, quite different from traditional lubricant-like chemicals, which might function in a similar way with perhaps additional desirable features being conferred on the polymer. This has led to a number of *polymeric flow promoters* being introduced, particularly for PVC. These materials generally have similar solubility parameters to the base polymer but are much lower in viscosity at processing temperature although not necessarily much softer at room temperature. In some cases, however, the additives are somewhat rubbery whilst in other instances, and as with the use of phenolic resin in natural and synthetic rubbers, cross-linking of the flow promoter during moulding can result in an increase in hardness. Polymeric flow promoters have been developed to the greatest extent for unplasticised and often transparent PVC compounds and include certain ethylene–vinyl acetate copolymers, styrene–acrylonitrile copolymers, styrene–methyl methacrylate copolymers and chlorinated polyethylenes. It is interesting that other polymers in these and related classes which are somewhat less compatible with PVC are often used as *impact modifiers*, i.e. to enhance impact strength, for PVC compositions.

7.5 ANTI-AGING ADDITIVES

The properties of most plastics materials change with the passage of time and usually in an adverse manner. These property changes are a result of structural modifications of which there are four main types:

- (1) Chain scission—resulting in a loss in strength and toughness.
- (2) Cross-linking which may lead to hardening, brittleness and changes in solubility.
- (3) Development of chromophoric groups leading to colour formation.
- (4) Development of polar groups such as carbonyl groups in polyolefins causing a deterioration in electrical insulation properties and also changes in chemical activity.

Such structural changes are a consequence of chemical reactions of which the most common are oxidation, ozone attack, dehydrochlorination and ultraviolet attack. (Reactions due to high-energy radiation or to high temperature are not considered here as causing natural aging.) Over the years many materials have been introduced as antioxidants, antiozonants, dehydrochlorination stabilisers and ultraviolet absorbers—originally on an empirical basis but today more and more as the result of fundamental studies. Each of these additive types will be considered in turn.

7.5.1 Antioxidants

The oxidation of hydrocarbons, including hydrocarbon polymers, takes the form of a free-radical chain reaction. As a result of mechanical shearing, exposure of ultraviolet radiation, attack by metal ions such as those of copper and manganese as well as other possible mechanisms, a hydrocarbon molecule breaks down into two radicals



Such hydrocarbon radicals ($R\cdot$) rapidly combine with oxygen to form a peroxide radical



Such a radical will then react with a hydrocarbon by the following propagation reaction



Whilst the $R\cdot$ radical again reacts as in equation (7.2) the hydroperoxide may decompose by the following mechanisms



or react as follows

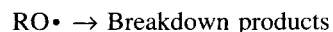


Reactions (7.2), (7.3) and (7.4) form a series of chain reactions, with reaction (7.3) the rate-determining stage. The chain reaction terminates by the reactions



It will be seen that reactions (7.5b) and (7.5c) if they occur more than once per hydrocarbon molecule (radical) will lead to chain extension and, if on average more than twice, to cross-linking.

It is also possible that reactions may occur which cause decomposition of the peroxide radicals by reactions of schematic form



Whether decomposition or cross-linking occurs is therefore a function of both the polymer type and the environmental conditions. If an antioxidant is to function it must interrupt the above reaction sequence. It is usual to recognise two types of antioxidant:

- (1) Preventive antioxidants which prevent the formation of radicals by reactions (7.1) and (7.3).
- (2) Chain-breaking antioxidants which interrupt the propagation cycle by reacting with the radicals $R\cdot$ and $RO_2\cdot$, introducing new termination reactions.

In addition, other additives may exist which react with $R\cdot$ and $RO_2\cdot$, introducing new propagation reactions which lead to a slower chain reaction. Such materials would be referred to as *oxidation retarders*.

In the past the greatest attention has been paid to the chain-breaking antioxidants and oxidation retarders of general structure AH, which may function in the following ways.



Reaction (7.7) is largely pro-oxidant; reactions (7.8a) and (7.8b) are propagation reactions and reactions (7.9a) and (7.9b) termination reactions. For chain breaking, reactions (7.8a), (7.9a) and (7.9b) should be preferred. In cases where reaction (7.8a) is preferred to reaction (7.3) and when (7.8b) is rate determining it is possible for the material to be an effective oxidation retarder.

It will be noticed that with chain-breaking antioxidants the additive will be consumed whilst if we assume that the AO_2H molecule will regenerate $\text{A}\cdot$ radicals the oxidation retarder is not effectively consumed. The difference between the two is illustrated schematically in *Figure 7.4*.

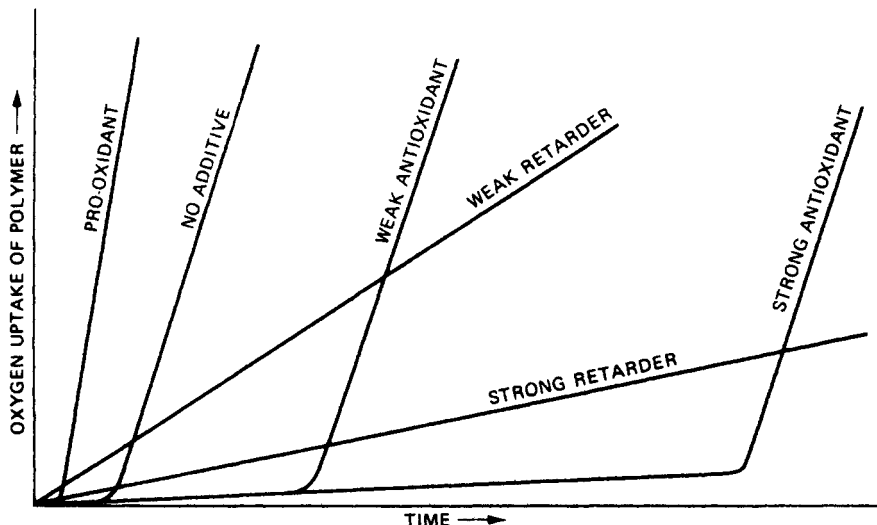


Figure 7.4. Schematic relationship showing effect of pro-oxidants, antioxidants and oxidation retarders on the oxygen uptake of a polymer

The shape of the 'curves' is of some interest. An induction period is noted during which no oxygen uptake, i.e. oxidation, is observed. At the end of this induction period, when in effect antioxidant moieties have been consumed, oxygen uptake is rapid unless some retardation mechanism is at work.

Table 7.3 Main types of chain-breaking antioxidants

<i>Class</i>	<i>Example</i>	<i>Staining</i>	<i>Comments</i>
<i>Amines</i>			
Ketone–amines	Acetone–diphenylamine and acetone–aniline (I)	Yes	Main use in rubber compounds for good heat aging.
Aldehyde–amines	Aldol–naphthylamines	Yes	Not often used. Possibilities of carcinogenic hazard with some types.
Phenyl-naphthylamines	<i>N</i> -Phenyl- β -naphthylamine (II)	Yes	Once widely used in rubber industry because of good all-round effect in diene rubbers. Now almost obsolete.
Substituted diphenylamines	4,4'-Dioctyldiphenylamine (III)	Yes	Moderate antioxidants. Some use in polychloroprene rubbers.
Paraphenylene-diamine derivatives	<i>N,N'</i> -Diphenyl- <i>p</i> -phenylenediamine (IV) <i>N,N'</i> -Di- β -naphthyl- <i>p</i> -phenylenediamine (V)	Yes Yes	Powerful antioxidants. Have been used in a variety of plastics materials. Tendency to bloom, bleed and stain mitigates against more extensive use. Compound (V) now withdrawn by some suppliers.
<i>Phenols</i>			
Substituted phenols	4-Methyl-2, 6-di- <i>t</i> -butylphenol (VI)	No	Often used in non-toxic formulations. Very low level of staining. Widely used to protect polymers during synthesis and fabrication. Volatility restricts high-temperature and long-term use.
Phenylalkanes	Bis-[2-hydroxy-5-methyl-3-(1-methylcyclohexyl)phenyl]methane (VII)	Very slight	Most powerful phenolic antioxidants. Widely used in polyolefins and some usage in PVC.
	1,1,3-Tris-(4-hydroxy-2-methyl-5- <i>t</i> -butylphenyl)butane (VIII)	Very slight	
Phenyl sulphides	4,4'-Thiobis-(6- <i>t</i> -butyl- <i>m</i> -cresol) (IX)	Very slight	Not so powerful as phenylalkanes as a class but synergistic with carbon black.
Phosphites	Tris-(<i>p</i> -nonylphenyl) phosphite (X)	No	Widely used in conjunction with conventional stabilisers (q.v.) in PVC. Some types appear to be useful heat and light stabilisers in polyolefins. Function primarily as peroxide decomposers rather than chain-breaking antioxidants.

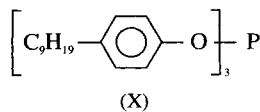
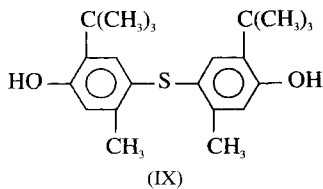
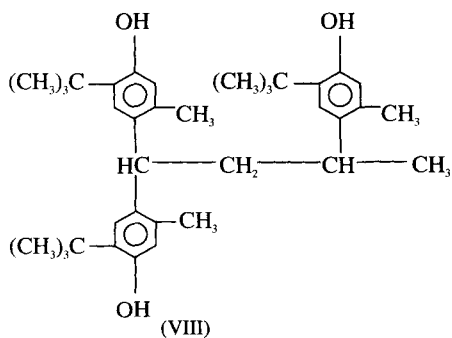
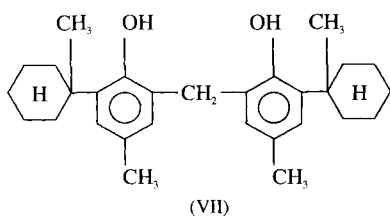
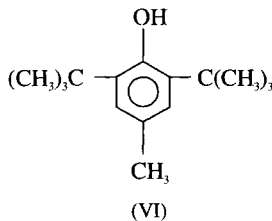
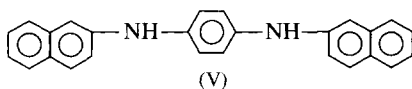
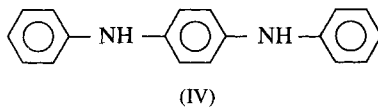
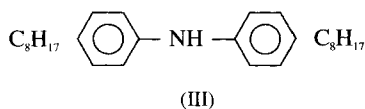
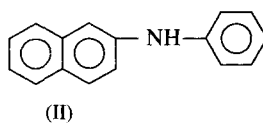
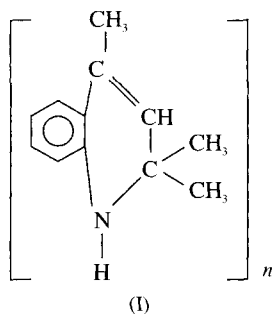


Figure 7.5. Chemical formulae of typical antioxidants referred to in Table 7.3

Table 7.4 Reactions responsible for initiation of autoxidation. (After Scott¹)

Reactant	Radical products				
	Heat	Light	Metal ions		Ozone
			M ⁺	M ⁺⁺	
1. Saturated hydrocarbon RH	$R\cdot + H\cdot$	$R\cdot + H\cdot$	-	$R\cdot$	$RO\cdot + \cdot OOH$
2. Unsaturated hydrocarbon $RCH=CHCH_2R'$	$RCH=CH\dot{C}HR' + H\cdot$	$R\dot{C}H-\dot{C}HCH_2R'$ or $RCH=CH\dot{C}HR' + H\cdot$	-	$R\dot{C}H\dot{C}HCH_2R'$	$RCH=CH\overset{R'}{\underset{ }{C}}HO\cdot + \cdot OOH$
3. Chlorinated hydrocarbon RCl	$R\cdot + Cl\cdot$	$R\cdot + Cl\cdot$	-	-	-
4. Carbonyl compound RCOR'	$RCO + R'\cdot$	$R \begin{array}{l} \diagup \\ \diagdown \end{array} \dot{C}-\dot{O}$ or $R\dot{C}O + R'\cdot$	-	-	-
5. Hydroperoxide ROOH	$RO\cdot + \cdot OH$ $ROO\cdot + \cdot OH + H_2O$	$RO\cdot + \cdot OH$	$RO\cdot$	$RO_2\cdot$	-

In the absence of added radical generators the relatively unstable hydroperoxides, which are themselves generated by the oxidation process, are the major source of chain initiating radicals.

Two main classes of *chain-breaking antioxidant* have been developed over the years, amines and phenols. The latter are usually preferred in polymers because of their lower preponderance to staining, discoloration, blooming and bleeding. Amines are still used, however, particularly in rubber tyres where such disadvantages are outweighed by the favourable cost and high effectiveness of some of these materials. The main types of chain-breaking antioxidants are indicated in *Table 7.3* and *Figure 7.5*. Such materials are used in quantities of the order of 0.02–1%. In excess they may show pro-oxidant tendencies, that is they will facilitate oxidation.

Free-radical initiation of the chain reaction of oxidation can arise from the action of heat, light, metal ions and, sometimes, ozone on a variety of chemical moieties such as those indicated in *Table 7.4*.

Any agent which functions to prevent the formation of radicals by these processes may be considered as a *preventive antioxidant*. In practice three classes are generally recognised:

- (1) Peroxide decomposers.
- (2) Metal deactivators.
- (3) Ultraviolet light absorbers.

Materials that promote the decomposition of organic hydroperoxide to form stable products rather than chain-initiating free radicals are known as peroxide decomposers. Amongst the materials that function in this way may be included a number of mercaptans, sulphonic acids, zinc dialkylthiophosphate and zinc dimethyldithiocarbamate. There is also evidence that some of the phenol and aryl amine chain-breaking antioxidants may function in addition by this mechanism. In saturated hydrocarbon polymers diaryl thiodipropionate has achieved a pre-eminent position as a peroxide decomposer.

Phosphites are also believed to function, at least in part, in this way. Proposed mechanisms for the thio and phosphite compositions are shown in *Figure 7.6*.

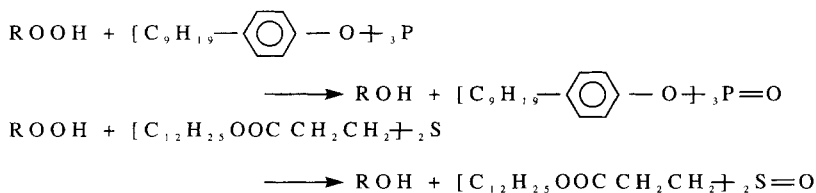
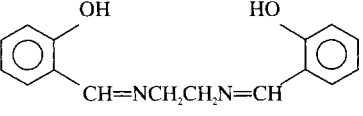
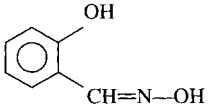
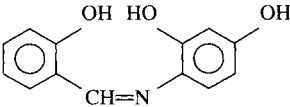
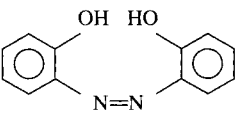
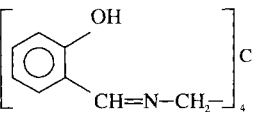


Figure 7.6

Manganese, copper, iron, cobalt and nickel ions can all initiate oxidation. Untinned copper wire can have a catastrophic effect on natural rubber compounds with which it comes into contact. Inert fillers for use in rubbers are usually tested for traces of such metal ions, particularly copper and manganese. The problem is perhaps less serious in saturated hydrocarbon polymers but still exists.

Where there is a danger of contamination of a hydrocarbon polymer with such ions it is common practice to use a *chelating agent* which forms a complex with the metal. It is, however, important to stress that a chelating agent which effectively slows down oxidation initiated by one metal ion may have a pro-oxidant effect with another metal ion. *Table 7.5* summarises some work by

Table 7.5 Catalytic and deactivating effects of ligands on metal-catalysed autoxidation of petroleum. (After Pedersen²)

Metal oleate ($1.6 \times 10^{-8} M$) Chelating agent (0.002%)	Deactivating efficiency, E_D				
	Mn	Fe	Co	Ni	Cu
	-103	-43	-833	-	100
	-	0	-96	100	100
	-84	100	96	-55	100
	-73	100	-	-124	100
	100	100	100	100	100

Pedersen² on the effect of various chelating agents upon the autoxidation of petroleum (a useful 'model' system) catalysed by various transition metals. The deactivating efficiency E_D is the percentage restoration of the original induction period observed with a control sample of petroleum without metal or deactivator. Only N,N',N'',N''' -tetrasalicylidene tetra(aminomethyl)methane was effective against all of the metals, all others having a negative effect with at least one ion.

Amongst other materials sometimes used as deactivators are, 1,8-bis(salicylideneamino)-3,6-dithiaoctane and certain *p*-phenylenediamine derivatives. It is interesting to note that the last named materials also function as chain-breaking antioxidants and in part as peroxide decomposers.

Ultraviolet light absorbers will be discussed in more detail under another section. Suffice it to say that their incorporation into a polymer can provide a useful antioxidant function.

Antioxidants are today often used in combination. One reason for this is that certain combinations can exhibit in a polymer an effect sometimes found with other additives, that known as *synergism*. In these circumstances two antioxidants may exhibit a co-operative effect and be more powerful than either antioxidant used alone, even when the total antioxidant concentration is the same. Certain terms are sometimes encountered here and these are defined in *Table 7.6*.

Table 7.6 Definition of terms associated with combinations of additives

Description of effect	Additive concentration (arbitrary units)		Effect
	[X]	[Y]	
	1	—	x
		1	y
	2		$2x$
		2	$2y$
Additive effect	1	1	$x + y$
Antagonism	1	1	$<(x + y)$
Synergism	1	1	$>(x + y)$
Practical synergism	1	1	$>(x + y)$ and also $> 2x$ and $> 2y$

In commercially practical terms it may be that although synergism occurs, one additive may be sufficiently less expensive for more to be used to achieve the required stability and still give the lowest overall cost.

In antioxidants, synergism appears to arise either from one antioxidant effectively regenerating another so that the latter does not become consumed or by the two antioxidants functioning by differing mechanisms. The latter is more important and it is easy to see how effective a combination of peroxide decomposer and chain-breaking antioxidant can be.

The peroxide decomposer will drastically reduce the number of radicals, which can then be more effectively 'mopped up' by the chain-breaking materials. A widely used combination is 4-methyl-2,6-di-*t*-butylphenol and dilauryl thioldipropionate. It is possible to envisage most powerful combinations where a chain-breaking antioxidant, a regenerating agent, a peroxide decomposer, a metal deactivator and an ultraviolet absorber are all employed together.

Two final points should be made while considering antioxidant synergism. Firstly, some antioxidants which function by more than one mechanism are in all probability autosynergistic. Secondly, certain additives which appear to act

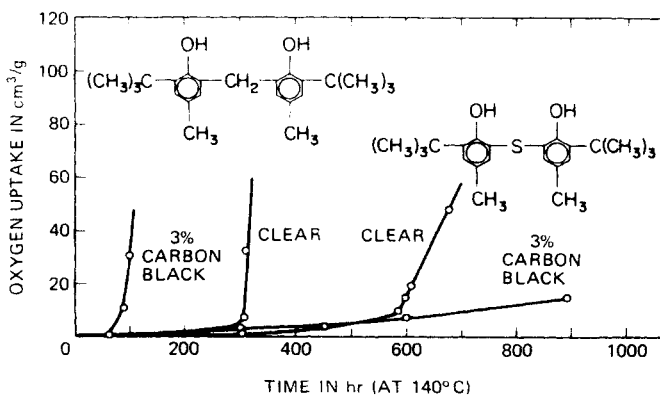


Figure 7.7. The synergism of sulphur antioxidants with carbon black as contrasted to the adverse effect shown with conventional antioxidants (in polyethylene)

synergistically with one antioxidant may be antagonistic to a second. The most well-known and important example of this is carbon black, which has an adverse effect with many phenols and amines but which is synergistic with some phenolic sulphides. This is illustrated clearly in *Figure 7.7*.

Antioxidants may be assessed in a variety of ways. For screening and for fundamental studies the induction period and rate of oxidation of petroleum fractions with and without antioxidants present provide useful model systems. Since the effect of oxidation differs from polymer to polymer it is important to evaluate the efficacy of the antioxidant with respect to some property seriously affected by oxidation. Thus for polyethylene it is common to study changes in flow properties and in power factor; in polypropylene, flow properties and tendency to embrittlement; in natural rubber vulcanisates, changes in tensile strength and tear strength.

7.5.2 Antiozonants

When diene rubbers are exposed to ozone under stressed conditions cracks develop which are perpendicular to the direction of stress. Whilst ozone must react with unstressed rubber no cracking occurs in such circumstances nor when such rubber is subsequently stressed after removal of the ozone environment. For many years such rubbers were protected by waxes which bloomed on to the surface of the rubber to form an impermeable film. This was satisfactory for static applications but where the rubber was operating under dynamic conditions the wax layer became broken and hence less effective.

Since the mid-1950s several materials have been found effective in combating ozone-initiated degradation, in particular certain *p*-phenylenediamine derivatives. The actual choice of such antiozonants depends on the type of polymer and on whether or not the polymer is to be subject to dynamic stressing in service. Since antiozonants are not known to have any use in plastics materials, even those which may have certain rubber particles for toughening, they will not be dealt with further here. Anyone interested further should consult references 3–5.

7.5.3 Stabilisers Against Dehydrochlorination

Whilst such stabilisers have found use in many chlorine-containing polymers their main application has been with poly(vinyl chloride). These additives will be considered in Chapter 12.

7.5.4 Ultraviolet Absorbers and Related materials

On exposure to ultraviolet light, particularly in an oxygen-containing atmosphere, physical and chemical processes may occur leading to such effects as discolouration, surface cracking, hardening and changes in electrical properties. Because polymers vary in their chemical nature the effects differ from one polymer to another. For most purposes the effects are undesirable but occasionally may be utilised in a positive manner—for example, to effect cross-linking or deliberately to initiate degradation.

The greatest damage is caused by shorter wavelengths, i.e. less than 400 nm, but as the earth's atmosphere absorbs most light rays shorter than about 300 nm the main damage is done, in terrestrial applications, by rays of wavelength in the range 300–400 nm (*Figure 7.8*).

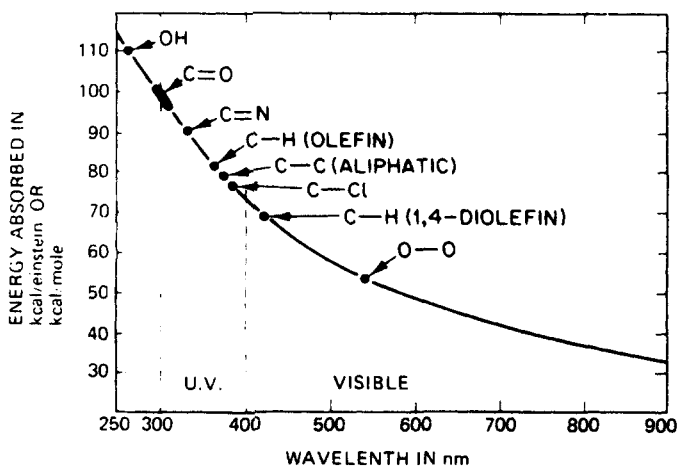
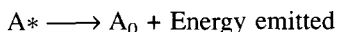


Figure 7.8. Relationship of energy absorbed by molecule to wavelength of incident light. Dissociation energies of various bonds are indicated to show wavelength below which breakdown may occur. (After Scott¹)

When a molecule (A) absorbs a quantum of light it is activated to an electronically excited state A^* , after which a number of process may occur. These may be summarised as follows:

(1) *Photophysical processes*

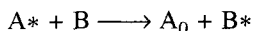
- (a) Emission of energy (e.g. phosphorescence or fluorescence)



- (b) Generation of heat (radiationless conversion)

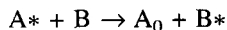


- (c) Energy transfer



(2) *Photochemical processes*

- (d) Consequent on energy transfer



└─ Products

- (e) Reaction of excited molecule equivalent to effect occurring with thermally excited molecules

Reactions (d) and (e) occur much less frequently than reactions (a)–(c) but do so at a sufficient rate to cause changes in most polymers. There are three methods available for combating such effects; light screens, ultraviolet absorbers and quenching agents.

Light screens

Light screens function by absorbing damaging radiation before it reaches the polymer surface or by limiting penetration of the radiation into the polymer mass. Coatings including pigment-loaded paints have been long used to protect a natural polymer composite, wood. It is also possible to coat a polymer with a layer of polymer containing a high concentration of an ultraviolet absorber or alternatively with a polymer which itself is capable of absorbing radiation without undergoing a deleterious chemical change. In addition to coatings light screens may be dispersed as powders into the polymers. Such materials should not scatter radiation and for this reason carbon black, which is also something of a thermal antioxidant, is uniquely effective. Such carbon black must, however, be of fine particle size (15–25 nm), used in concentrations of at least 2% and very well dispersed.

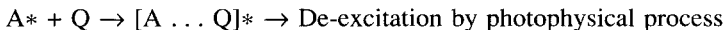
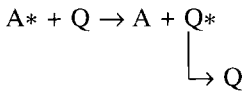
Ultraviolet absorbers

Ultraviolet absorbers are a form of light screen which absorb primarily in the ultraviolet range. It is a requirement for most ultraviolet absorbers that absorption in the visible range should be negligible; if this were not so the resultant instant colour formation could be worse than that experienced after prolonged exposure of the polymer.

The ultraviolet absorber could dispose of absorbed energy by radiation, by conversion into heat or by chemical changes leading to stable products. The most important commercial absorbers, such as the *o*-hydroxybenzophenones, *o*-hydroxyphenylbenzotriazoles and salicylates, appear to function by conversion of electronic energy into heat. The properties of the main types of ultraviolet absorbers are summarised in *Table 7.7*.

Quenching agents

Such agents are not in themselves powerful absorbers of ultraviolet light. They are, however, capable of reacting with activated polymer molecules by the following mechanisms:



In the above scheme A represents the excited polymer, Q the quenching agent and [A.....Q]* an excited complex.

The use of quenching agents in polymers is a recent development. Of particular interest are the nickel(II) chelates in polypropylene film and fibre and the even newer hindered amines which appear to combine the roles of antioxidant and quenching agent.

7.6 FLAME RETARDERS

For some applications of plastics, such as in packaging where disposability has to be considered, it may be desirable for plastics materials to burn without difficulty. There are, however, a number of uses such as in building, furniture and fitting

Table 7.7. Some commercial ultraviolet absorbers

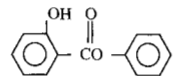
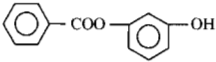
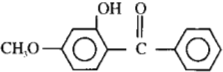
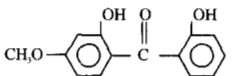
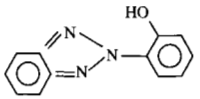
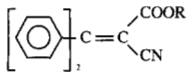
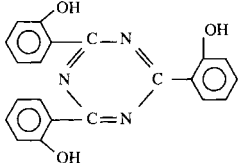
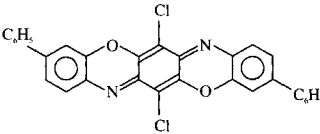
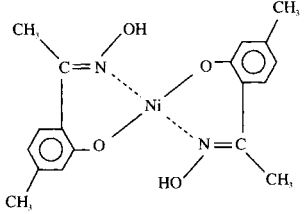
<i>Ultraviolet absorber</i>	<i>Formula</i>	<i>Type</i>	<i>Comments</i>
Phenyl salicylate		Salicylate	Rather weak.
Resorcinol monobenzoate		Benzoate	Converted in sunlight to a dihydroxybenzophenone. Used in celluloses.
2-Hydroxy-4-methoxybenzophenone		Substituted monohydroxybenzophenone	Negligible absorption in visible range.
2,2'-Dihydroxy-4-methoxybenzophenone		Substituted dihydroxybenzophenone	Stronger than the monohydroxy compound but some absorption in the visible range.
2-(2-Hydroxyphenyl)benzotriazole		Benzotriazole	Powerful.
		Substituted acrylonitrile	Some use in PVC and polyolefins.

Table 7.7 (continued)

<i>Ultraviolet absorber</i>	<i>Formula</i>	<i>Type</i>	<i>Comments</i>
1,3,5-Tris-(2-hydroxyphenyl)-triazine		Triazine	Powerful but some absorption in visible range
6,13-Dichloro-3,10-diphenyltriphenodioxazine		Oxazine	Excitation dissipated by radiation (fluorescence). Very effective in cellulose acetate-butylate but reddish brown in colour
-		Nickel(II) chelate	Appears to function as a quenching agent in polypropylene

applications where products from plastics materials should have an adequate degree of fire resistance. Whilst such an adequate resistance is often shown by products from unplasticised PVC, phenolic resins and aminoplastics, other materials, notably the aliphatic polyolefins, polystyrene and polyurethanes, are deficient. This has led to the progressively increasing use of flame retardants.

Whilst the development of flame retarders has in the past been largely based on a systematic trial-and-error basis, future developments will depend more and more on a fuller understanding of the processes of polymer combustion. This is a complex process but a number of stages are now generally recognised and were discussed in Chapter 5.

From what was said in that chapter it will be seen that flame retardants might be capable of acting at several stages in the process and that a combination of retardants might be employed, different components acting at different stages. In industrial practice flame retardants may be divided into two classes, reactive components and additives. The 'reactives' are used primarily with thermosetting plastics and are special intermediates which are inserted into the polymer structure during cross-linking. Used largely with polyesters, epoxides and polyurethanes, such materials are usually either highly halogenated or are phosphorus compounds. Whilst such reactives do not lead to problems of leaching, migration and volatility which can occur with additives they do suffer from certain disadvantages. Firstly, it is often difficult to incorporate enough bromine, chlorine or phosphorus into the structure to give sufficient flame retardance; secondly, such systems are often lacking in flexibility; and thirdly, such highly specialised chemicals produced in small quantities tend to be expensive. For this reason the bulk of flame retardants are of the additive type and these will be dealt with below. Reactives specific to a given class of polymer will be considered in the appropriate chapter.

Flame retardants appear to function by one or more of four mechanisms:

- (1) They chemically interfere with the flame propagation mechanism.
- (2) They may produce large volumes of incombustible gases which dilute the air supply.
- (3) They may react, decompose or change state endothermically, thus absorbing heat.
- (4) They may form an impervious fire-resistant coating preventing access of oxygen to the polymer.

In volume terms the most important class of fire retardants are the phosphates. Tritolyl phosphate and trixylyl phosphate are widely used plasticisers which more or less maintain the fire-retarding characteristics of PVC (unlike the phthalates, which reduce the flame resistance of PVC products). Better results are, however, sometimes obtained using halophosphates such as tri(chloroethyl) phosphate, particularly when used in conjunction with antimony oxide, triphenyl stibine or antimony oxychloride.

Halogen-containing compounds are also of importance. Chlorinated paraffins have found use in PVC and in polyesters and like the halophosphates are most effective in conjunction with antimony oxide. Bromine compounds tend to be more powerful than chlorine compounds and a range of aromatic bromine-containing compounds, including tribromotoluene and pentabromophenyl allyl ether, is available. Such halogen-based systems appear to function through the diluting effect of HCl, HBr or bromine.

The role of antimony oxide is not entirely understood. On its own it is a rather weak fire retardant although it appears to function by all of the mechanisms listed above. It is, however, synergistic with phosphorus and halogen compounds and consequently widely used. Other oxides are sometimes used as alternatives or partial replacements for antimony oxide. These include titanium dioxide, zinc oxide and molybdenic oxide. Zinc borate has also been used.

Where the polymer does not have to be subjected to high processing temperatures aluminium trihydrate may be used. One very large area of use for this material is in polyester laminating resins. An inorganic material which has been particularly successful as a flame retardant in the nylons is, perhaps surprisingly, red phosphorus. This material conferred a V-0 rating for the Underwriters Laboratories UL 94 specification (see Chapter 5) even with glass-filled grades (which are not self-extinguishing like unfilled nylons). Although the mouldings were dark in colour there was little loss in toughness or electrical insulation characteristics.

Also of interest are salts of melamine (see Chapter 24). In the nylons these can be used with bright colours (unlike red phosphorus) and do not adversely affect electrical properties. They do, however, decompose at about 320°C. Similar materials are very important in giving flame-retardant properties to polyurethane foams.

Many methods have been evolved in recent years for assessing flame retardants and the combustion characteristics of plastics and these have been the subject of comprehensive reviews.⁶⁻⁹

The use of fire retardants in polymers has become more complicated with the realisation that more deaths are probably caused by smoke and toxic combustion products than by fire itself. The suppression of a fire by the use of fire retardants may well result in smouldering and the production of smoke, rather than complete combustion with little smoke evolution. Furthermore, whilst complete combustion of organic materials leads to the formation of simple molecules such as CO₂, H₂O, N₂, SO₂ and hydrogen halides, incomplete combustion leads to the production of more complex and noxious materials as well as the simple structured but highly poisonous hydrogen cyanide and carbon monoxide.

There has also been considerable concern at the presence of toxic and corrosive halogen-containing fire degradation products in confined spaces such as submarines, mines, subways and aircraft. This is beginning to restrict the use of some chlorine-containing polymers in spite of the fact that they often have good flame retardant properties. For this and other reasons several of the halogen-containing flame retardants are no longer used with some polymers.

One possible solution to the problem is to make greater use of intumescent materials which when heated swell up and screen the combustible material from fire and oxygen. Another approach is to try to develop polymers like the phenolic resins that on burning yield a hard ablative char which also functions by shielding the underlying combustible material.

7.7 COLORANTS

There are basically four methods used for colouring polymers. These are surface coating (e.g. painting), surface dyeing, introduction of colour-forming groups into the polymer molecules and mass colouration. Surface coating involves extra processing and can substantially increase the cost of the product and is avoided where possible except in the case of fibres. Surface dyeing can be of limited use

with some polar polymers such as the nylons where only a small quantity of material is required to be coloured. Whilst academically interesting, the deliberate introduction of chromophoric groups is an inflexible and expensive method. Therefore, for most applications of rubbers and plastics the mass colouration approach is favoured.

Colorants are sometimes divided into two classes, insoluble colorants (pigments) and soluble colorants (dyestuffs). It should, however, be noted that many colorants have a low but finite solubility so that such a rigorous classification can be misleading. As explained previously, such a low solubility may in certain circumstances lead to blooming. One way of reducing blooming tendencies is to use colorants of high molecular weight. For a material to be a successful colorant it should meet all the requirements listed on p. 120.

For example, to be efficient they should have a strong covering power although in some circumstances a colorant of lower covering power than another might be favoured if it was so much cheaper that more of the colorant could be incorporated and still lead to a cheaper compound. Stability to processing covers not only the obvious aspect of heat resistance but also resistance to shear. Particles of some colorants break down under intensive shearing and as a result may change colour. When colorants are added before polymerisation they should not interfere with the polymerisation reaction nor should they be affected by the presence of some of the polymerisation additives. Blooming and bleeding can both be problems. Some colorants may also adversely affect polymer properties such as oxidation resistance and electrical insulation behaviour. Anisotropic pigments may become oriented during processing to give anomalous effects.

7.8 BLOWING AGENTS¹⁰

Many polymers are used in a cellular form in which the polymer matrix is filled with gas-filled cells which may or may not be intercommunicating. Over the years many methods have been devised for producing cellular polymers of which the most important are the following:

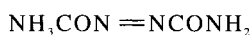
- (1) Incorporation of a chemical compound which decomposes at some stage of the processing operation to yield volatile reaction products. These are known as chemical blowing agents.
- (2) Incorporation of low boiling liquids which volatilise during processing. Such volatile blowing agents are important with polystyrene and polyurethanes and will be dealt with in the appropriate chapters.
- (3) Diffusion of gases into the polymer under pressure with subsequent expansion of the composition at elevated temperatures after decompression. Such a process can be employed with a wide variety of polymers.
- (4) Incorporation of powdered solid carbon dioxide which volatilises at elevated temperatures. This process has been used in conjunction with PVC pastes.
- (5) Chemical reactions of polymer intermediate during polymerisation and/or cross-linking. This is important with polyurethanes.
- (6) Mechanical whipping of polymers in a liquid form and subsequent 'setting' in the whipped state. The manufacture of latex rubber foam is the best-known example of this approach.
- (7) Incorporation of hollow or expandable spheres of resin or of glass (microballoons).
- (8) Leaching out of soluble additives.

Table 7.8 Chemical blowing agents in commercial use

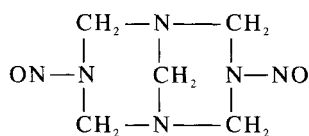
<i>Blowing agent</i>		<i>Class</i>	<i>Volatiles produced</i>	<i>Decomposition range (°C)</i>	<i>Gas yield (cm³/g)</i>	<i>Comments</i>
Azocarbonamide	(I)	Carbonamide	N ₂ , CO, CO ₂	190–230	220	Most widely used blowing agent in PVC and polyolefins. High decomposition temperature reduced by a variety of metal salts and oxides such as lead carbonate, lead phosphite and zinc oxide. High gas yield. Reaction products show little odour or discoloration*.
Dinitrosopentamethylene-tetramine	(II)	Nitrosoamine	N ₂ , NO, H ₂ O, CH ₃ , NH ₂	160–200	210	Widely used in natural and synthetic rubbers. Some use in polyolefins.
Benzenesulphonohydrazide	(III)	Hydrazide	N ₂ , H ₂ O	146	170–250	Blowing power affected by phthalate and phosphate plasticisers.
4, 4'-Oxybis(benzenesulphono-hydrazide)	(IV)	Hydrazide	N ₂ , H ₂ O	150	120–180	Faster decomposition rate than azodicarbonamide but low blowing power limits use.
<i>N,N'</i> -Dimethyl- <i>N,N'</i> -dinitrosoterephthalamide	(V)	Terephthalamide	N ₂ , H ₂ O, CO ₂	90–105	180	Low exotherm on decomposition but low decomposition temperature restricts use largely to open-cell foams.
Azoisobutyronitrile	(VI)	Azo	N ₂	95–98	136	Effective but decomposition products are toxic.
Sodium bicarbonate	(VII)	Inorganic	CO ₂	100–130	125–130	Low cost. Suitable for cellular rubber but insufficiently powerful for most plastics. Erratic in decomposition.
Terephthalazide	(VIII)	Acid azide	N ₂	85–112	207–311	Generates a di-isocyanate on decomposition which may cross-link some polymer species. Subsidiary reactions may increase blowing power.
Trihydrazinotriazine	(IX)	Hydrazine	N ₂ , NH ₃	275	225	Used with high softening point polymers, e.g. polycarbonates, nylons and glass-reinforced thermoplastics.

* Problems of corrosion and staining can occur under conditions of high melt pressure. Modified grades are now available that largely overcome these difficulties.

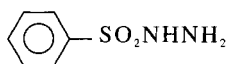
In volume terms annual production of cellular plastics products is of the same order as for non-cellular products and it is not surprising that the mechanisms of cell nucleation, growth and stabilisation have been extensively studied. As a result of this the texture and properties of cellular plastics can be widely controlled through such variables as average cell size, cell size distributions (including the possibility of some very large cells being present in a structure largely composed of small cells), degree of intercommunication between cells and the use of non-cellular skins. Such variables are in turn controlled by processing conditions and by the use of *cell nucleating agents* and *cell stabilisers* in addition to the *blowing agent*.



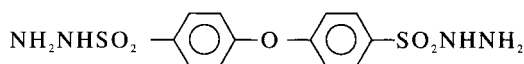
(I)



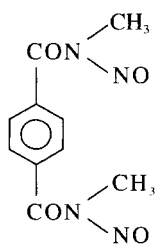
(II)



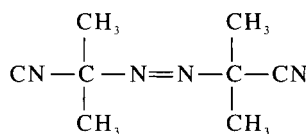
(III)



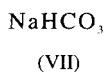
(IV)



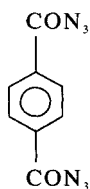
(V)



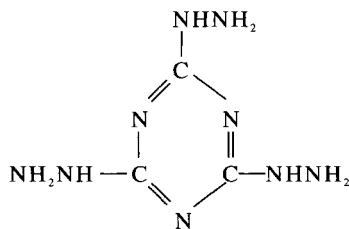
(VI)



(VII)



(VIII)



(IX)

Figure 7.9. Formulae of blowing agents listed in Table 7.8

A number of general comments may be made about *chemical blowing agents*. In addition to the requirements common to all additives there are some special requirements. These include:

- (1) The need for gases to be evolved within a narrow but clearly defined temperature range and in a controlled and reproducible manner.
- (2) The decomposition temperature should be suitable for the polymer. For example, a decomposition temperature for a blowing agent system for PVC should not be above the maximum possible processing temperature that can be used if significant degradation is not to occur.
- (3) Gases evolved should not corrode processing equipment. Whilst many hundreds of materials have been investigated as blowing agents the number in actual use is very small. Some details of such materials are summarised in *Table 7.8* and *Figure 7.9*.

7.9 CROSS-LINKING AGENTS

In order to produce thermoset plastics or vulcanised rubbers the process of cross-linking has to occur. Before cross-linking, the polymer may be substantially or completely linear but contain active sites for cross-linking. Such a situation occurs with natural rubber and other diene polymers where the double bond and adjacent alpha-methylene groups provide cross-linking sites. Alternatively the polymer may be a small branched polymer which cross-links by intermolecular combination at the chain ends. The term cross-linking agents is a very general one and covers molecules which bridge two polymer molecules during cross-linking (*Figure 7.10(a)*), molecules which initiate a cross-linking reaction (*Figure 7.10(b)*), those which are purely catalytic in their action (*Figure 7.10(c)*) and those which attack the main polymer chain to generate active sites (*Figure 7.10(d)*).

The first type includes vulcanising agents, such as sulphur, selenium and sulphur monochloride, for diene rubbers; formaldehyde for phenolics; diisocyanates for reaction with hydrogen atoms in polyesters and polyethers; and polyamines in fluoroelastomers and epoxide resins. Perhaps the most well-known cross-linking initiators are peroxides, which initiate a double-bond

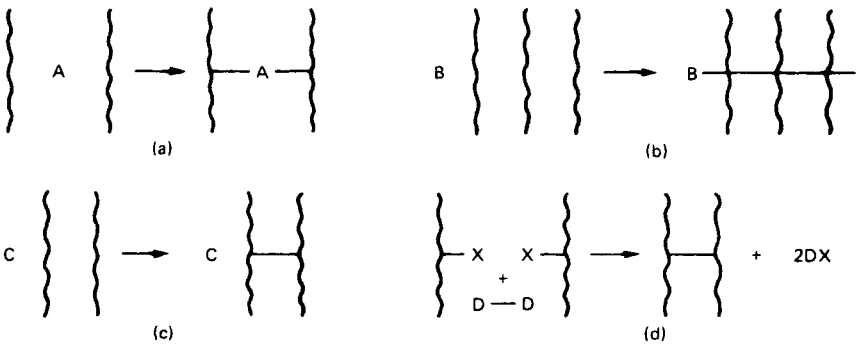


Figure 7.10. (a) Bridging agents. (b) Cross-linking initiators. (c) Catalytic cross-linking agents. (d) Active site generators

polymerisation type of cross-linking in unsaturated polyesters. Catalytic agents include acids for phenolic resins and amino-plastics and certain amines in epoxides. Peroxides are very useful active site generators, abstracting protons from the polymer chains. With some polymers this leads to scission but in other cases cross-linking occurs. Applications of cross-linking agents to specific polymers are dealt with in the appropriate chapters.

7.10 PHOTODEGRADANTS

During the past two decades the quantity of plastics materials used in packaging application has increased annually at a phenomenal rate. At the present time something like 1000 square miles of polyethylene film are produced in the United Kingdom alone each year. Even if a large percentage of the population can be persuaded to take care against creating litter and even if litter-collection systems are reasonably efficient, a quantity of unsightly rubbish is bound to accumulate.

Whereas cellulose films are biodegradable, that is they are readily attacked by bacteria, films and packaging from synthetic polymers are normally attacked at a very low rate. This has led to work carried out to find methods of rendering such polymers accessible to biodegradation. The usual approach is to incorporate into the polymer (either into the polymer chain or as a simple additive) a component which is an ultraviolet light absorber. However, instead of dissipating the absorbed energy as heat it is used to generate highly reactive chemical intermediates which destroy the polymer. Iron dithiocarbamate is one such photo-activator used by G. Scott in his researches at the University of Aston in Birmingham, England. Once the photo-activator has reduced the molecular weight down to about 9000 the polymer becomes biodegradable. Some commercial success has been achieved using starch as a biodegradable filler in low-density polyethylene.¹¹ With the introduction of auto-oxidisable oil additives¹² that make the polymer sensitive to traces of transition metals in soils and garbage, film may be produced which is significantly more biodegradable than that from LDPE itself.

It is important that any photodegradation should be controlled. The use of photo-activators activated by light only of wavelengths shorter than that transmitted by ordinary window glass will help to ensure that samples kept indoors will not deteriorate on storage. Dyestuffs which change colour shortly before the onset of photodegradation can also be used to warn of impending breakdown.

The rate of degradation will depend not only on the type and amount of photodegradant present and the degree of outdoor exposure but also on the thickness of the plastics article, the amount of pigment, other additives present and, of course, the type of polymer used. Special care has to be taken when reprocessing components containing photodegradants and special stabilisers may have to be added to provide stability during processing.

At the time of preparing the third edition of this book the author wrote:

At the time of writing photodegradants are in an early stage of development and have not yet been fully evaluated. It is a moot point whether or not manufacturers will put such materials into polymer compounds and thus increase the price about 5% without legal necessity. However, if such legislation, considered socially desirable by many, took place one might expect polyethylene

film, fertiliser sacks and detergent containers to contain such photodegrading additives.

In 1994, it is apparent that time has largely borne out these predictions. Where there has been no legislation the use of photodegradants appears to be diminishing. However, in at least one major industrial country legislation has taken place which will prevent use of non-degradable packaging films.

7.11 2-OXAZOLINES

These materials, first introduced in the 1990s, do not fit into the conventional pattern of additives and are used for three quite distinct purposes:

- (1) To produce viable blends of incompatible polymers.
- (2) To protect condensation polymers, in particular PET and PBT, against hydrolysis by capping terminal groups.
- (3) To increase the average molecular weight of somewhat degraded recycled polymer.¹³

2-Oxazolines are prepared by the reaction of a fatty acid with ethanolamine (Figure 7.11).

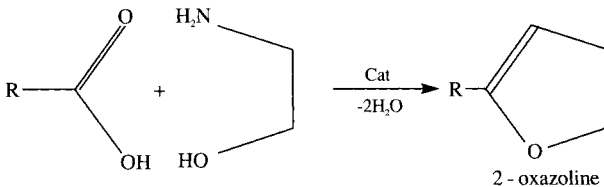


Figure 7.11

Examples of such materials are isopropenyl 2-oxazoline (IPO), which was one of the earlier materials to be developed, and ricinloxazolinmaleinate, with the outline structure given in Figure 7.12.

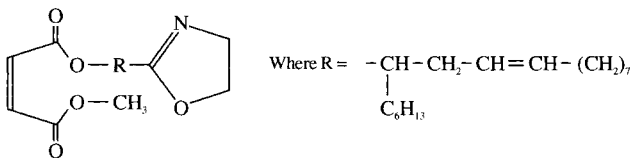


Figure 7.12

Polymers containing oxazoline groups are obtained either by grafting the 2-oxazoline onto a suitable existing polymer such as polyethylene or polyphenylene oxide or alternatively by copolymerising a monomer such as styrene or methyl methacrylate with a small quantity (<1%) of a 2-oxazoline. The grafting reaction may be carried out very rapidly (3–5 min) in an extruder at temperatures of about 200°C in the presence of a peroxide such as di-*t*-butyl peroxide (Figure 7.13).

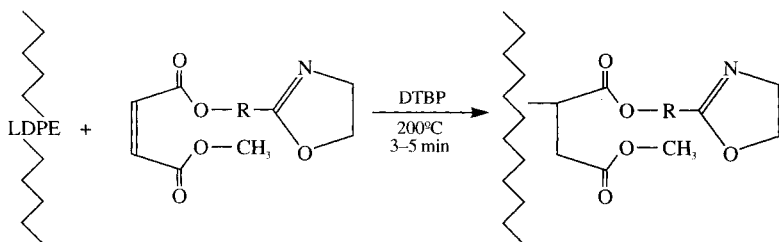


Figure 7.13

In turn the oxazoline-containing polymer may then react very rapidly (e.g. at 240°C) with such groups as carboxyls, amines, phenols, anhydrides or epoxides, which may be present in other polymers. This reaction will link the two polymers by a rearrangement reaction similar to that involved in a rearrangement polymerisation without the evolution of water or any gaseous condensation products (Figure 7.14).

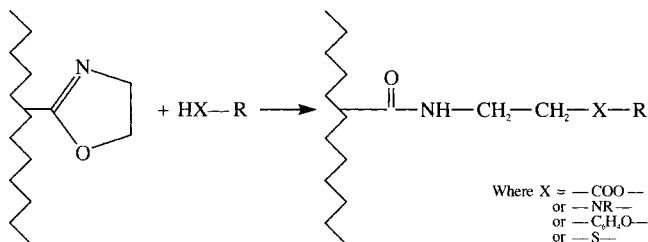


Figure 7.14

Such linking enables two distinct polymers which are normally incompatible to mix intimately. As a result, the properties of blends of such materials may be markedly improved, as shown in Table 7.9.

Table 7.9 Effect of use of isopropenyl 2-oxazoline on the properties of ABS/PET blends (Based on data in *Modern Plastics International*, February 1994)

	ABS/PET	ABS/PET/IPO
Impact strength (J/m)	80.1	170.8
Tensile strength (MPa)	41.4	55.6
Elongation at break (%)	1.8	2.5

2-Oxazolines may be used to react with terminal groups on condensation polymers to improve stability, particularly against hydrolysis. This appears to be of particular interest with poly(ethylene terephthalate).

Also of interest is the use of bis-2-oxazolines, which have molecular weights in excess of 1000 and oxazoline groups at each end of the molecule. These can then react with various terminal groups of condensation polymers to bring about

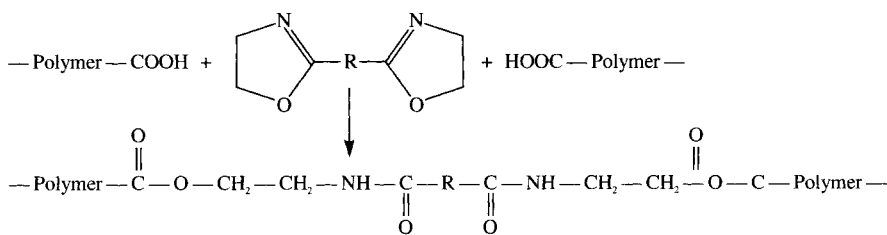


Figure 7.15

chain extension by rearrangement polymerisation, as schematically indicated in Figure 7.15.

This will help to enhance the molecular weight of recycled materials which may have been subject to some molecular degradation.

References

1. SCOTT, G., *Chem. & Ind.*, 271 (1963)
2. PEDERSEN, C. J., *Ind. Eng. Chem.*, **41**, 924 (1949)
3. AMBELANG, J. C., KLINE, R. H., LORENZ, O. M., PARKS, C. R., WADELIN, C., and SHELTON, J. R., *Rubb. Chem. Technol.*, **36**, 1497 (1963)
4. LEYLAND, B. N., and WATTS, J. T., Chapter in *Development with Natural Rubber* (Ed. BRYDSON, J. A.), Maclaren, London (1967)
5. MURRAY, R. W., Chapter entitled 'Prevention of Degradation by Ozone' in *Polymer Stabilization* (Ed. HAWKINS, W. L.), Wiley, New York (1972)
6. THIERY, P., *Fireproofing* (English translation by GOUNDRY, J. H.), Elsevier, Amsterdam (1970)
7. *Fire Performance of Plastics*, RAPRA Review (1972)
8. EINHORN, I. N., Chapter entitled 'Fire Retardance of Polymeric Materials' in *Reviews in Polymer Technology* Vol. 1 (Ed. SKEIST, I.), Dekker, New York (1972)
9. HINDERSINN, R., Article entitled 'Fire Retardancy' in *Encyclopaedia of Polymer Science and Technology*, Supplement Vol. 2, pp. 270–340, Interscience, New York (1977)
10. COLLINGTON, K. T., *Plastics & Polymers*, **41**, 24 (1973)
11. GRIFFIN, G. J. L., *ACS Advances in Chemistry Series*, **134**, 159 (1974)
12. WHITNEY, P. J. and WILLIAMS, W., *Appl. Polymer Symposium*, **35**, 475 (1979)
13. BIRNBRICH, P., FISCHER, H., KLANANN, J.-D. and WEGEMUND, B. *Kunststoffe*, **83**(11), 885–8 (1993)

Bibliography

- BRUINS, P. F. (Ed.), *Plasticiser Technology*, Reinhold, New York (1965)
- CHEVASSUS, F., and DE BROUDELLES, R., *The Stabilisation of Polyvinyl Chloride* (English translation by EICHHORN, C. J. R., and SERMIENTO, E. C.), Arnold, London (1963)
- EINHORN, I. N., Chapter entitled 'Fire Retardance of Polymeric Materials' in *Reviews in Polymer Technology* Vol. 1. (Ed. SKEIST, I.), Dekker, New York (1972)
- FRISCH, K. C., and SAUNDERS, J. H. (Eds.), *Plastic Foams Part I*, Dekker, New York (1972)
- GEUSKENS, G. (Ed.), *Degradation and Stabilisation of Polymers*, Applied Science, London (1975)
- HAWKINS, E. L. (Ed.), *Polymer Stabilisation*, Wiley-Interscience, New York (1972)
- KUZMINSKII, A. S. (Ed.), *The Ageing and Stabilisation of Polymers* (English translation by LEYLAND, B. N.), Elsevier, Amsterdam (1971)
- MASCIA, L., *The Role of Additives in Plastics*, Arnold, London (1974)
- MELLAN, I., *The Behaviour of Plasticisers*, Pergamon, Oxford (1961)
- MELLAN, I., *Industrial Plasticisers*, Pergamon, Oxford (1963)
- RITCHIE, P. D. (Ed.), *Plasticisers, Stabilisers, and Fillers*, Iliffe, London (1972)
- SCOTT, G., *Atmospheric Oxidation and Antioxidants*, Elsevier, Amsterdam (1965)
- SEARS, J. K. and DARBY, J. R., *The Technology of Plasticisers*, John Wiley, New York (1982)
- THIERY, P., *Fireproofing* (English translation by GOUNDRY, J. H.), Elsevier, Amsterdam (1970)
- WAKE, W. C. (Ed.), *Fillers for Plastics*, Iliffe, London (1971)
- WEBBER, T. G. (Ed.), *The Coloring of Plastics*, John Wiley, New York (1979)

8

Principles of the Processing of Plastics

8.1 INTRODUCTION

A large part of polymer processing technology can be summed up in the statement: get the shape then set the shape. The purpose of this chapter will be to try to expand on this, showing how processing behaviour can be related to fundamental polymer properties. We shall not at this instance concern ourselves with compounding techniques but be primarily concerned with the production of objects of definite shape and form.

Such objects may be shaped by the following general techniques:

- (1) Deformation of a polymer melt—either thermoplastic or thermosetting. Processes operating in this way include extrusion, injection moulding and calendaring, and form, in tonnage terms, the most important processing class.
- (2) Deformation of a polymer in the rubber state—of importance in vacuum forming, pressure forming and warm forging techniques.
- (3) Deformation of a solution usually either by spreading or by extrusion as used in making cast film and certain synthetic fibres and filaments.
- (4) Deformation of a suspension. This is of great importance with rubber latex and other latices and with PVC paste.
- (5) Deformation of low molecular weight polymer or polymer precursor such as in the casting of acrylic sheet and preparation of glass-reinforced laminates.
- (6) Machining operations.

The first five of these techniques involve deformation and this has to be followed by some setting operation which stabilises the new shape. In the case of polymer melt deformation this can be affected by cooling of thermoplastics and cross-linking of thermosetting plastics and similar comments can apply to deformation in the rubbery state. Solution-cast film and fibre requires solvent evaporation (with also perhaps some chemical coagulation process). Latex suspensions can simply be dried as with emulsion paints or subjected to some

coacervation process which separates the polymer particles from the liquid (usually aqueous) phase. PVC pastes, which are basically suspensions of polymer particles in plasticiser, will gel on heating by the absorption of plasticiser into the particles. The casting of low molecular weight polymers and polymer precursors is completed by polymerisation and/or cross-linking reactions.

8.2 MELT PROCESSING OF THERMOPLASTICS

The principles of thermoplastic melt processing can perhaps best be illustrated by reference to *Figure 8.1* illustrating extrusion, injection moulding, bottle blowing and calendaring operations. In order to realise the full potential of the process it is necessary to consider the following factors:

- (1) Hygroscopic behaviour of the polymer compound.
- (2) Granule characteristics.
- (3) Thermal properties that influence the melting of the polymer.
- (4) Thermal stability.
- (5) Flow properties.
- (6) Thermal properties that affect the cooling of the polymer.
- (7) Crystallisation.
- (8) Orientation.

8.2.1 Hygroscopic Behaviour

It is essential that polymer compounds shall be free of water and other low boiling solvents. A small volume of water can generate steam which will tend to be trapped within the compound during the processing stage. This will expand on decompression of the melt in latter stages of the process, leading to voids in the finished product. Such voids are sometimes flattened out through shear during the polymer flow, leading to reflecting surfaces known as 'mica marks'. Sometimes the water may just be present on the surface of the compound and is easily removed. In other cases the water may be absorbed into the body of the polymer and long drying periods are necessary. Generally speaking, the higher the processing temperature the lower is the tolerable level of water in the compound, since higher temperatures will generate larger volumes of steam with a fixed mass of water. For example, when polycarbonates are processed at about 300°C the water content should be less than 0.02% whilst with cellulose acetate processed at about 170°C up to 0.3% can sometimes be tolerated.

Compounds based on polymers that are not themselves hygroscopic can sometimes cause problems because of hygroscopic additives.

8.2.2 Granule Characteristics

At one time it was quite common practice to extrude and mould granules of varying shape and size that had been obtained by breaking up sheet between rotating and stationary cutting blades. It was subsequently found¹ that the use of granules of more regular shape and even size can lead to much higher throughput rates in extruders and much more even heating and hence better control in flow properties in all of the processes. Granules are at present obtained either by

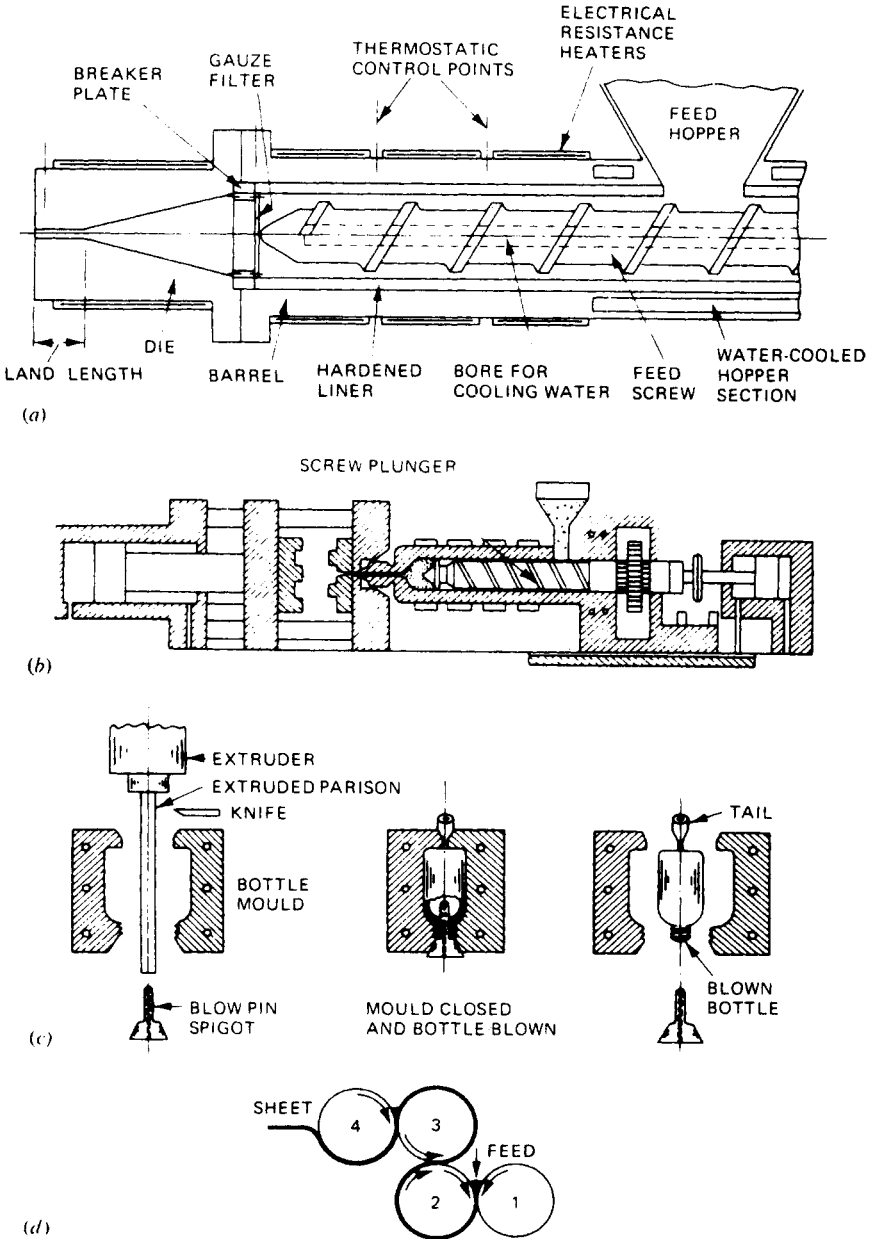


Figure 8.1. (a) Extrusion—material is pumped, in the above case with a screw pump, through a die to give a product of constant cross-section. (b) Injection moulding—material is pumped by a screw pump to the front end of the injection cylinder with the screw moving to the rear in order to provide space for the material; the screw then moves forward as a ram injecting molten material into a relatively cool mould into which the material sets. (c) Extrusion blow moulding—the extruder tube is inflated in the mould while still above softening point. (d) Calendaring—softened material is flattened out into sheet between rolls

dicing using special granulators or by extruding strands which are then either cut up cold to give 'spaghetti-cut' or 'lace-cut' granules or cut hot on the die to give granules of a somewhat ellipsoidal shape.

8.2.3 Thermal Properties Influencing Polymer Melting

Polymer compounds vary considerably in the amount of heat required to bring them up to processing temperatures. These differences arise not so much as a result of differing processing temperatures but because of different specific heats. Crystalline polymers additionally have a latent heat of fusion of the crystalline structure which has to be taken into account.

In principle the heat required to bring the material up to its processing temperature may be calculated in the case of amorphous polymers by multiplying the mass of the material (W) by the specific heat (s) and the difference between the required melt temperature and ambient temperature (ΔT). In the case of crystalline polymers it is also necessary to add the product of mass times latent heat of melting of crystalline structures (L). Thus if the density of the material is D then the enthalpy or heat required (E) to raise volume V to its processing temperature will be given by:

$$E = (Ws\Delta T + WL)/D$$

In earlier editions of this book the enthalpy requirements were estimated in this way, although it was stressed that 'these calculations, however, assume that the specific heat is independent of temperature and this is far from being the case'. It is now possible to obtain enthalpy data directly from differential scanning calorimetry (DSC) measurements without making any assumptions about the specific heat. Indeed it is now more common to obtain average specific heat data over any chosen range from the enthalpy curves rather than the other way round. In this edition, the data in *Table 8.1* have been calculated using the data of Whelan and Goff² which, it is understood, were largely based on DSC data.

The cooling requirements will be discussed further in Section 8.2.6. What is particularly noteworthy is the considerable difference in heating requirements between polymers. For example, the data in *Table 8.1* assume similar melt temperatures for polystyrene and low-density polyethylene, yet the heat requirement per cm³ is only 295 J for polystyrene but 543 J for LDPE. It is also noteworthy that in spite of their high processing temperatures the heat requirements per unit volume for FEP (see Chapter 13) and polyethersulphone are, on the data supplied, the lowest for the polymers listed.

The heat for melting can be generated *externally*, in which case heat transfer distances should be kept to a minimum and the temperature distribution will depend on the thermal conductivity, or *internally* either by a high-frequency heating process or by mechanical working. High-frequency heating is seldom applicable to melt processing but frictional heat due to mechanical working can provide a significant contribution. The amount of frictional heat generated increases with the rate of working and with the polymer viscosity. Since the melt viscosity decreases with increasing temperature the rate of frictional heat input decreases with increase of temperature once the polymer is in the molten state. In some polymer processing operations the frictional heat generated exceeds the total requirement so that provision has to be made for cooling facilities around the main heating chamber, be it an extruder barrel or an injection moulding machine cylinder.

Table 8.1 Heat required (enthalpy required) to raise polymers to their processing temperatures from an ambient temperature of 20°C and the heat required to be removed in cooling a polymer from the melt to mould temperature

Polymer	Melt temperature (°C)	Mould temperature (°C)	SG	Specific heat (J kg ⁻¹ K ⁻¹)	Heat required to melt		Heat removed on cooling	
					J/g	J/cm ³	J/g	J/cm ³
FEP	350	220	2.2	1600	528	240	240	109
Polyethersulphone	360	150	1.37	1150	391	285	242	177
Polyether ether ketone	370	165	1.3	1340	469	361	275	212
Polyethylene terephthalate (crystalline)	275	135	1.38	2180	556	403	305	221
Polystyrene	200	20	1.05	1720	310	295	310	295
Polyacetal	205	90	1.41	3000	555	394	345	245
Polycarbonate	300	90	1.2	1750	490	408	368	307
ABS	240	60	1.04	2050	451	434	369	355
Polymethyl methacrylate	260	60	1.18	1900	456	386	380	322
Polyphenylene sulphide	320	135	1.4	2080	624	446	385	275
PPO (Noryl-type)	280	80	1.06	2120	551	520	434	409
Polysulphone	360	100	1.24	1675	570	459	436	351
Polyethylene terephthalate (amorphous)	265	20	1.34	1970	483	360	483	360
Nylon 11/12	260	60	1.03	2440	586	568	488	474
LDPE	200	20	0.92	2780	500	543	500	543
Nylon 6	250	80	1.13	3060	703	623	520	460
Nylon 66	280	80	1.14	3075	800	701	615	539
Polypropylene	260	20	0.91	2790	670	736	670	736
HDPE	260	20	0.96	3375	810	843	810	843

The melt and mould temperatures and the value of the heat removed per gram on cooling are taken from the paper by Whelan and Goff. The values for the amount of heat required to raise the temperature to the melting point and the heat requirements per unit volume (both for heating and cooling) have been calculated from these data by the author.

8.2.4 Thermal Stability

As has been mentioned in earlier chapters polymers vary enormously in their thermal stability. Before attempting to process any specific polymer compound its thermal stability characteristics should be considered. The most important questions to be answered are:

- (1) How stable is it at elevated temperatures when oxygen is absent, i.e. for how long may it be heated at typical processing temperatures?
- (2) How stable is it at elevated temperatures when oxygen is present?
- (3) If the product is unstable how are the polymer properties affected?
- (4) What degradation products, if any, are given off?
- (5) Is degradation catalysed by any metals which could be present in the processing machinery?
- (6) Is degradation catalysed by any other materials with which the polymer might come into contact?

Some materials are able to withstand quite lengthy 'thermal histories', a term loosely used to describe both the intensity (temperature) and the duration of heating. Polyethylene and polystyrene may often be reprocessed a number of times with little more than a slight discoloration and in the case of polyethylene some deterioration in electrical insulation properties.

Other polymers can be more troublesome. Poly(vinyl chloride) requires the incorporation of stabilisers and even so may discolour and give off hydrochloric acid, the latter having a corrosive effect on many metals. At the same time some metals have a catalytic effect on this polymer so that care has to be taken in the construction of barrels, screws and other metal parts liable to come into contact with the polymer.

Some polymers such as the polyacetals (polyformaldehyde) and poly(methyl methacrylate) depolymerise to monomer on heating. At processing temperatures such monomers are in the gaseous phase and even where there is only a small amount of depolymerisation a large number of bubbles can be formed in the products.

Gaseous monomers may also be trapped within the processing equipment and accidents have occurred as a consequence of the resulting pressure build-up. In the case of the polyacetals and poly(vinyl chloride) it is reported that at elevated temperatures these materials form a more or less explosive combination so that it is important to separate these materials rigorously at the processing stage.

8.2.5 Flow Properties

The flow properties of polymer melts are, to say the least, complex. This is only to be expected when one is trying to deform variously entangled long chain molecules of a distribution of molecular weights. During flow, stresses imposed on the molecules will cause them partly to uncoil and possibly also to roll over and over as they travel down the melt stream. When imposed stresses are released there will be a tendency to re-coil. Furthermore, when convergent flow occurs, as in many processing operations, significant tensile deformation occurs in addition to the shear deformations normally considered in simple analyses. Flow may also be affected by additives.

8.2.5.1 Terminology

In spite of these problems, polymer melts have been sufficiently studied for a number of useful generalisations to be made. However, before discussing these it is necessary to define some terms. This is best accomplished by reference to *Figure 8.2*, which schematically illustrates two parallel plates of very large area A separated by a distance r with the space in between filled with a liquid. The lower plate is fixed and a shear force F applied to the top plate so that there is a *shear stress* ($\tau = F/A$) which causes the plate to move at a uniform velocity u in a direction parallel to the plane of the plate.

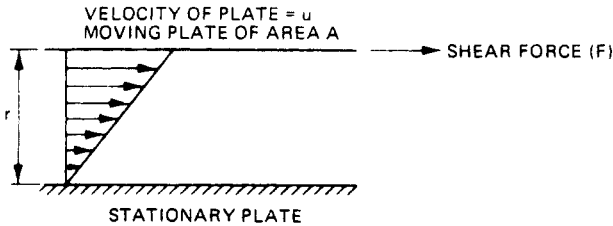


Figure 8.2. Velocity distribution of a fluid between two parallel plates, one stationary, the other moving

It is assumed that the liquid wets the plates and that the molecular layer of liquid adjacent to the top plate moves at the same velocity as the plate whilst the layer adjacent to the stationary plate is also stationary. Intermediate layers of liquid move at intermediate velocities as indicated by the arrows in the diagram. The term *shear rate* is defined as the rate of change of velocity with cross-section (viz. du/dr) and is commonly given the symbol ($\dot{\gamma}$). It is not altogether surprising that with many simple liquids if the shear stresses are doubled then the shear rates are doubled so that a linear relationship of the form

$$\tau = \mu(du/dr) \quad (8.1)$$

may be postulated, the constant of proportionality μ being known as the coefficient of viscosity. Liquids whose viscosity does not change with the time of shearing and obey the above relationship are said to be *Newtonian liquids*.

At the same time it is not surprising that polymer melts are non-Newtonian and do not obey such simple rules. Fortunately, if we make certain assumptions, it is possible to analyse flow in certain viscometer geometries to provide measurements of both shear stress (τ) and shear rate ($\dot{\gamma}$) so that curves relating the two (flow curves) may be drawn.

For example, in a capillary the flow is of the form indicated by *Figure 8.3*. If we assume that the fluid velocity of the capillary wall is zero, that the viscosity

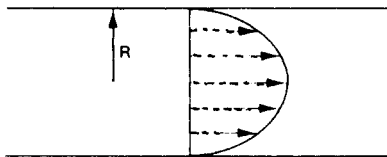


Figure 8.3. Velocity flow profile in a tube for a fluid with zero yield stress and assuming no slip at wall

does not change with time, that flow is isothermal, that the fluid is incompressible and that the flow pattern is constant all the way down the tube, then for any time-independent fluid the shear stress at the wall (τ_w) and the shear rate at the wall $\dot{\gamma}_w$ may be given by the following equations:

$$\tau_w = \frac{\Delta P R}{2L} \quad (8.2)$$

and

$$-\dot{\gamma}_w = \frac{1}{\pi R^3} \left(3Q + \Delta P \frac{dQ}{d\Delta P} \right) \quad (8.3)$$

$$= \frac{3}{4} \left(\frac{4Q}{\pi R^3} \right) + \frac{\tau_w}{4} \frac{d(4Q/\pi R^3)}{d\tau_w} \quad (8.4)$$

$$= \frac{3}{4} \left(\frac{4Q}{\pi R^3} \right) + \frac{1}{4} \left(\frac{4Q}{\pi R^3} \right) \frac{d \log (4Q/\pi R^3)}{d \log \tau_w} \quad (8.5)$$

$$= \left(\frac{3n' + 1}{4n'} \right) \frac{4Q}{\pi R^3} \quad (8.6)$$

where ΔP is the pressure drop between the ends of the capillary of length L and radius R and Q is the volumetric output. The term n' , the flow behaviour index, is defined by

$$n' = \frac{d \log (R\Delta P/2L)}{d \log (4Q/\pi R^3)} \quad (8.7)$$

and is usually a function of shear rate. Equations (8.3) to (8.6) are forms of the Rabinowitsch equation.

In practice n' changes only slowly with changes in $\dot{\gamma}$ and it is possible to postulate that over a range of shear rates it is constant. If equation (8.7) is therefore integrated we obtain

$$\tau_w = K' \left(\frac{4Q}{\pi R^3} \right)^{n'} \quad (8.8)$$

where K' is a constant. This equation is similar in form to a power law relationship between shear stress and shear rate which is often considered to give quite good fits to polymer melt data. This latter equation is

$$\tau = K(\dot{\gamma})^n \quad (8.9)$$

where K and n are constants. Furthermore it may be shown that the shear rate at the capillary wall $\dot{\gamma}_w$ is uniquely related to $4Q/\pi R^3$.

In fact with a Newtonian liquid $\dot{\gamma} = 4Q/\pi R^3$. This latter expression, viz. $4Q/\pi R^3$, is obviously much easier to calculate than the true wall shear rate and, since they are uniquely related and the simple expression is just as useful, in design practice it is very common when plotting flow curves to plot τ_w against

$4Q/\pi R^3$. The latter expression is known as the apparent wall shear rate and usually given the symbol $\dot{\gamma}_{w,a}$.

The term apparent viscosity (μ_a or η) is often encountered but has been defined by both of the following equations.

$$\mu_a = \tau_w / \dot{\gamma}_w \quad (8.10)$$

$$\mu_a = \tau_w / \dot{\gamma}_{w,a} \quad (8.11)$$

which of course give slightly different solutions. In practice real materials have flow curves which may be considered as variants of the types shown in *Figure 8.4* and *Figure 8.5*.

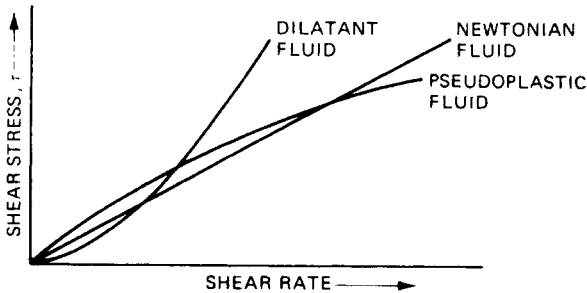


Figure 8.4. Shear stress–shear rate relationships for dilatant and pseudoplastic fluids compared with a Newtonian material

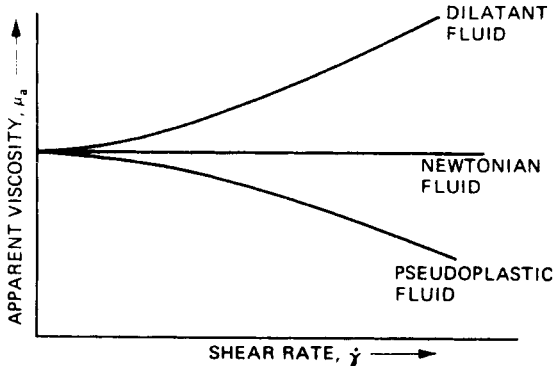


Figure 8.5. Apparent viscosity–shear rate curves for dilatant fluid, a Newtonian fluid and pseudoplastic fluid which have the same apparent viscosity at zero shear rate

In the specific case of polymer melts these almost invariably are of the pseudoplastic type. In such cases the flow behaviour index n' is less than 1; the greater the divergence from Newtonian behaviour the lower its value.

(As a complication some sources define a flow index as the reciprocal of that defined above so that some care has to be taken in interpretation. In such cases the values are greater than unity for polymer melts and the greater the value the greater the divergence from Newtonian behaviour.)

8.2.5.2 Effects of environmental and molecular factors on viscous flow properties

The viscous shear properties at any given shear rate are primarily determined by two factors, the free volume within the molten polymer mass and the amount of entanglement between the molecules. An increase in the former decreases the viscosity whilst an increase in the latter, i.e. the entanglement, increases viscosity. The effects of temperature, pressure, average molecular weight, branching and so on can largely be explained in the these terms.

Let us first consider temperature. An Arrhenius equation of the form

$$\eta = Ae^{E/RT} \quad (8.12)$$

where A is a constant and E the activation energy, has often been used to relate viscosity and temperature. Whilst such an equation can be made to fit experimental data quite well it does nothing to explain the difference between polymers.

If we, however, consider that viscosity is inversely related to the fractional free volume, which increases from a small value at the glass transition temperature T_g linearly with temperature above this figure, then it is possible³ to derive an equation.

$$\log_{10} \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{-(T - T_g)}{2.303 f_g [(f_g/a_2) + (T - T_g)]} \quad (8.13)$$

where f_g is the fractional free volume at the T_g and a_2 the temperature coefficient of free volume given by the difference in the expansion coefficients above and below T_g (see also Chapter 9).

There is some evidence to show that f_g and a_2 are constant for many polymers so that the above equation may simplify to

$$\log_{10} \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (8.14)$$

A little computation shows two features:

- (1) Melt viscosity is a function of $T - T_g$, and a major cause of the difference between the viscosity of poly(methyl methacrylate) at its processing temperature (where $T - T_g = 100^\circ\text{C}$ approx.) and the viscosity of polyethylene at its processing temperature (where $T - T_g = 200^\circ\text{C}$ approx.) is explicable by the above relationship.
- (2) Viscosity is more temperature sensitive with material processed closer to their T_g , for example poly(methyl methacrylate), compared with nylon 6.

Whilst temperature rises at constant pressure cause a decrease in viscosity, pressure rises at constant temperature cause an increase in viscosity since this causes a decrease in free volume. It is in fact found⁴ that within the normal processing temperature range for a polymer it is possible to consider an increase in pressure as equivalent, in its effect on viscosity, to a decrease in temperature.

For example, for most polymers an increase in pressure of 1000 atm is equivalent to a drop of temperature in the range 30–50°C. It is also found that those polymers most sensitive to temperature changes in their normal processing ranges are the most sensitive to pressure.

It is a corollary to this that it is commonly found that

$$\left(\frac{\partial \eta}{\partial T}\right)_v \approx 0 \quad (8.15)$$

In other words if the volume and hence free volume are made constant by increasing pressure as temperature is increased then the viscosity also remains constant.

Having thus seen that environmental factors determine viscosity largely by their effect on free volume let us now consider the influence of molecular factors which affect viscosity largely by entanglement effects.

The general effects of increasing molecular weight M have been well documented in the past. In general it is found that for molecular weights below a critical value M_c , of the order of about 5000–15 000, the viscosity is directly proportional to the weight average molecular weight M_w . Above this point viscosity depends on a higher power (*Figure 8.6*).⁵ It has been found that for many polymers a relation of the form

$$\eta_0 = K \bar{M}_w^{3.4-3.5}$$

where η_0 is the zero shear rate viscosity, holds quite well and Bueche⁶ has argued that this figure of 3.4–3.5 should be expected on theoretical grounds. Two exceptions to this general rule appear to be low-density polyethylene⁵, a polymer with long chain branching, and PVC⁷, which never seems to fit any patterns of behaviour.

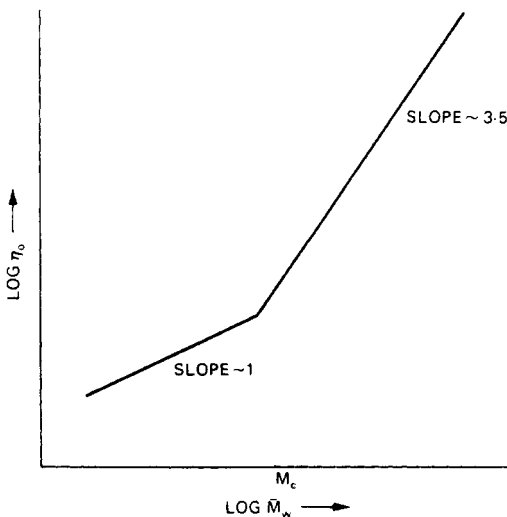


Figure 8.6. Relationship between molecular weight and zero shear rate viscosity for melts of linear polymers

It is tempting to see if it is possible to combine the equation relating viscosity and molecular weight with that relating viscosity with temperature. This gives a surprisingly simple answer of the form

$$\log \eta_0 = 3.4 \log \bar{M}_w - \frac{17.44(T - T_g)}{51.6 + T - T_g} + C \quad (8.16)$$

where C is a constant relative to K in the formula above and η_0 is the viscosity at zero shear rate.

It has already been mentioned that polymer melts are non-Newtonian and are in fact under normal circumstances pseudoplastic. This appears to arise from the elastic nature of the melt which will be touched on only briefly here. In essence, under shear, polymers tend to be oriented. At low shear rates Brownian motion of the segments occurs so polymers can coil up at a faster rate than they are oriented and to some extent disentangled. At high shear rates such re-entangling rates are slower than the orientation rates and the polymer is hence apparently less viscous.

At extremely high shear rates, however, the degree of orientation reaches a maximum so that a further decrease in effective viscosity cannot occur—the polymer in this range again becomes Newtonian.

Generally speaking the larger the polymer molecule the longer the re-coiling (re-entangling, relaxation) time so that high molecular weight materials tend to be more non-Newtonian at lower shear rates than lower molecular weight polymers.

Let us now consider two polymers A and B differing only in molecular weight distribution. Polymer A has a very narrow molecular weight spread, let us say typified by curve 3 in the diagram (*Figure 8.7*). Polymer B also contains some low molecular weight material (curve 1) and high molecular weight material (curve 2). Averaging these curves gives curve W which is more non-Newtonian than curve 3.

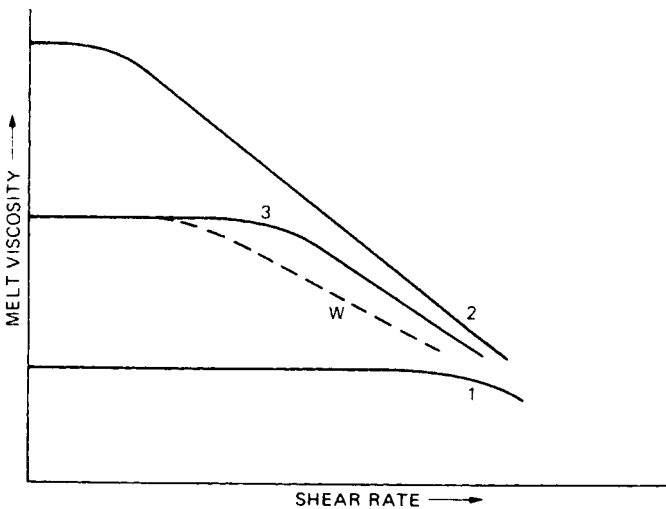


Figure 8.7. The blend W of high and low molecular weight polymers (curves 1 and 2) becomes non-Newtonian at a lower shear rate than a polymer of narrow molecular weight distribution

The third molecular factor which has a big effect on viscous flow properties is the presence or otherwise of long chain branches. If we compare two molecules of equal molecular weight, one linear and the other branched, we would expect the linear polymer to entangle more with its neighbours and hence give a higher viscosity—this we find to be the case. Branching can also be important to other melt flow properties but care must be taken not to confuse experimental results. By their very nature molecules containing long chain branches tend to have a wide molecular weight distribution and one has to be careful in checking whether an effect is due to the wide distribution or due to the branching.

8.2.5.3 Flow in an injection mould

The flow process in an injection mould is complicated by the fact that the mould cavity walls are below the ‘freezing point’ of the polymer melt. In these circumstances the technologist is generally more concerned with the ability to fill the cavity rather than with the magnitude of the melt viscosity. In one analysis made of the injection moulding situation,¹⁴ Barrie showed that it was possible to calculate a mouldability index (μ) for a melt which was a function of the flow parameters K' and n' , the thermal diffusivity and the relevant processing temperatures (melt temperature and mould temperature) but which was independent of the geometry of the cavity and the flow pattern within the cavity.

Some typical data for this mouldability index are given in Figure 8.8. One limitation of these data is that they do not explicitly show whether or not a mould will fill in an injection moulding operation. This will clearly depend on the thickness of the moulding, the flow distances required and operational parameters such as melt and mould temperatures. One very crude estimate that is widely used is the *flow path ratio*, the ratio of flow distance to section thickness. The assumption is that if this is greater than the ratio (distance from gate to furthest point from gate)/section thickness, then the mould will fill. Whilst

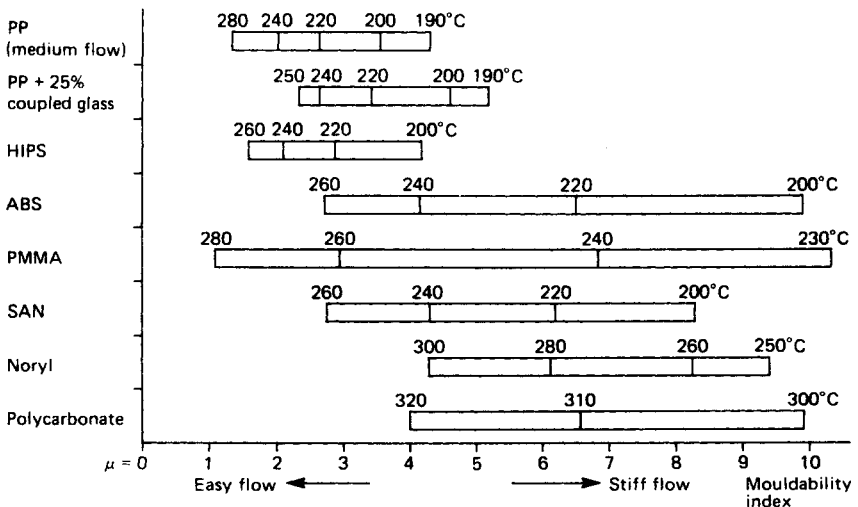


Figure 8.8. Mouldability index of some common moulding materials (after Barrie)

Table 8.2 Some collected values for the flow path ratio of injection moulding materials

<i>Polymer</i>	<i>Flow path ratio</i>
ABS	80–150
Acrylic [poly(methyl methacrylate)]	100–150
Nylon 6	140–340
Nylon 66	180–350
Polyacetals	100–250
Poly(butylene terephthalate)	160–200
Polycarbonates	30–70
Polyether ether ketone	up to 200
Polyethylene (HDPE)	150–200
Polyethylene (LDPE)	200–300
Poly(ethylene terephthalate)	up to 350
Poly(phenylene sulphide)	150
Polypropylene	150–350
Polystyrene	150
Polystyrene (toughened)	130
Polysulphones	30–150
Poly(vinyl chloride) (plasticised)	up to 180
Poly(vinyl chloride) (unplasticised)	60
Styrene-acrylonitrile	140

the ratio may be expected itself to be a function of section thickness, section thicknesses do not vary greatly in normal injection moulding operations. Providing it is also appreciated that the flow path ratio will also be higher at the upper range of possible process temperatures, the ratio can be used to give designers and moulders some idea of mouldability in a particular mould. Some collected values for flow path ratios are given in *Table 8.2*. There is a good (negative) correlation between the mouldability index and the flow path ratio, a low value for the index corresponding to a high value for the flow path ratio (a somewhat unusual example of a good correlation between a theoretically derived property and a rule-of-thumb figure based on practice and experience). For four of the six materials that are common to *Table 8.2* and *Figure 8.8* (polypropylene, ABS, poly(methyl methacrylate) and SAN) a product of the average mouldability index times average flow path ratio gives remarkably similar figures of 750, 748, 750 and 756; unfortunately this uniformity is not maintained by toughened polystyrene (of low mouldability index) and polycarbonate (with a high index).

8.2.5.4 Elastic effects in polymer melts

When polymer melts are deformed, polymer molecules not only slide past each other, but they also tend to uncoil—or at least they are deformed from their random coiled-up configuration. On release of the deforming stresses these molecules tend to revert to random coiled-up forms. Since molecular entanglements cause the molecules to act in a co-operative manner some recovery of shape corresponding to the re-coiling occurs. In phenomenological terms we say that the melt shows elasticity.

Such elastic effects are of great importance in polymer processing. They are dominant in determining die swell and calender swell; via the phenomenon often

known as melt fracture they limit extrusion output rates; they lead to frozen-in stresses in mouldings and extrudates and are an important factor in controlling the sag of parisons produced during bottle blowing. The phenomena have been dealt with at length by the author elsewhere⁸ and only the briefest comments will be made here.

If we consider the total deformation (D_{total}) occurring during flow to be almost entirely composed of a viscous flow (D_{visc}) and a high elastic deformation due to chain uncoiling D_{HE} then we may write

$$D_{\text{total}} = D_{\text{HE}} + D_{\text{visc}}$$

Viscous deformations, at a fixed deforming stress, increase rapidly with temperature whereas elastic deformations change much more slowly. For this reason the high elastic deformation component tends to be more important at lower processing temperatures than at high processing temperatures.

Viscous deformations, at a fixed deforming stress, are also very dependent on molecular weight but in this case an increasing molecular weight, by increasing viscosity, reduces the rate of viscous deformation and increases the proportion of deformation due to chain uncoiling. Hence with high molecular weight materials elastic effects tend to be more important than with low molecular weight materials.

Thus it is found that extrusion die swell, when compared at equivalent shear rates, tends to go down with an increase in temperature and go up with molecular weight. As shear rates are increased, polymer uncoiling is increased and die swell increases (Figure 8.9). A point is reached, however, where the die swell no longer increases and in fact it can be argued that it goes down. At this point it is

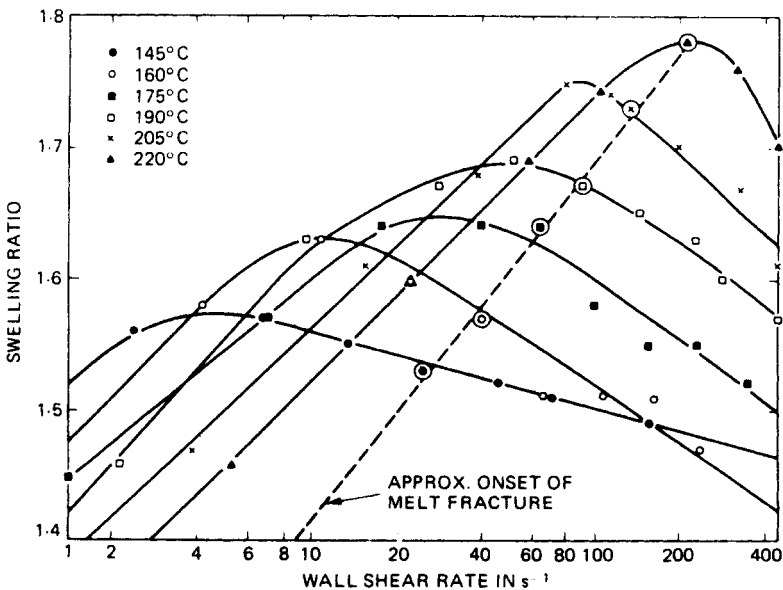


Figure 8.9. Swelling rates against shear rate for a low-density polyethylene at six temperatures. (After Beynon and Glyde⁹)

found that smooth extrudates are no longer formed and the extrudates show perturbations which vary from helical extrudates through spirals and bamboo-like forms to highly irregular and distorted shapes. The point at which this occurs is often known as the critical point and the corresponding shear stress and shear rate as the critical shear stress (τ_c) and critical shear rate ($\dot{\gamma}_c$) respectively.

Whilst the origin of such turbulence (melt fracture) remains a subject of debate it does appear to be associated with the periodic relief of built-up elastic stresses by slippage effects at or near polymer-metal interfaces.

Bearing in mind the general points made previously it is not unexpected that the critical shear rate:

- (1) Increases with increase in temperature (Figure 8.10).
- (2) Decreases with molecular weight (it is commonly observed that the product $\tau_c \bar{M}_w$ is a constant) (Figure 8.11).

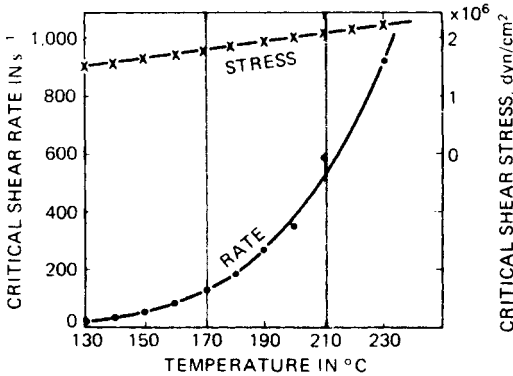


Figure 8.10. Effect of melt temperature on onset of elastic turbulence in polyethylene. (After Howells and Benbow¹⁰)

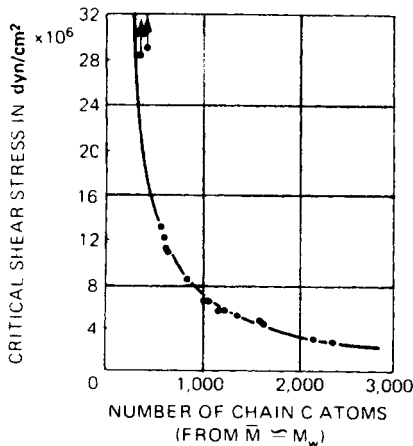


Figure 8.11. Effect of molecular weight on critical shear stress at onset of elastic turbulence in poly(methyl methacrylate). (After Howells and Benbow¹⁰)

8.2.6 Thermal Properties Affecting Cooling

It is the cooling operation that sets the shape of thermoplastics. The rate of cooling affects the process in two ways:

- (1) It is a factor influencing production rates.
- (2) It is a factor influencing the properties of the product.

An example of the effect on production rates is provided by injection moulding. The longer it takes after injection for solidification of the polymer to occur, the longer will be the overall cycle. (Provided the moulding is not distorted on ejection it will only be necessary to form a rigid 'skin' to the moulding.)

The solidification time for an amorphous polymer will be determined by:

- (1) The difference between the temperature of the melt on injection into the mould (T_i) and the mould temperature (T_c).
- (2) The glass transition temperature T_g .
- (3) The average specific heat over the range $T_i - T_g$.

Optimum production rates may be obtained by moulding at the minimum processing temperature and mould temperature consistent with mouldings of satisfactory quality and by using a polymer of sufficiently high molecular weight to give T_g close to that expected of a polymer of infinite molecular weight.

It should be noted that polystyrene with a number average molecular weight of 50 000 has a T_g only about 2°C less than would be expected of a polystyrene of infinitely high molecular weight. Hence increasing the molecular weight beyond this point in order to raise the T_g would not be very effective and at the same time it would lead to large increases in melt viscosity.

In the case of crystalline polymers the solidification time will be determined by:

- (1) The value of $T_i - T_c$, as previously.
- (2) The crystalline melting point T_m .
- (3) The latent heat of fusion of the crystalline structures.
- (4) The average specific heat over the range $T_i - T_m$.

Some data on the amount of heat required to reduce the temperature of a polymer from a typical melt temperature to the temperature of the mould (in terms of both per unit mass and per unit volume) are given in *Table 8.1*. Whilst a moulding will usually be withdrawn at some temperature above the mould temperature, the data do provide some comparison of the different heat requirements of different polymers. *It will be noticed that there is a more than 7-fold difference between the top and bottom polymers in the table.*

Cooling rates can affect product properties in a number of ways. If the polymer melt is sheared into shape the molecules will be oriented. On release of shearing stresses the molecules will tend to re-coil or relax, a process which becomes slower as the temperature is reduced towards the T_g . If the mass solidifies before relaxation is complete (and this is commonly the case) frozen-in orientation will occur and the polymeric mass will be anisotropic with respect to mechanical properties. Sometimes such built-in orientation is deliberately introduced, such as

with films, fibres and integrally hinged mouldings, but often the condition is undesirable, leading to planes of weakness and low impact strength.

Cooling rates can affect the rate of crystalline growth and polymer masses containing large crystalline structure will have quite different properties to those with small structures. In thick mouldings where the low thermal conductivity of the polymer leads to a very low cooling rate in the centre of the moulding the morphology of centre and edge will be quite different. Machined nylon surfaces often have quite different characteristics from moulded surfaces.

Too fast a cooling rate with thick sections leads at an early stage to the formation of a solid shell with a soft centre. On further cooling the polymer tends either to shrink away from the centre towards the solid shell, resulting in the production of voids, or alternatively the shell tends to collapse with distortion of the product.

8.2.7 Crystallisation

Crystallisation provides an efficient way of packing molecules. Such packing raises the density and hence leads to much higher shrinkage on cooling from the melt than is observed with amorphous polymers. (Moulding shrinkage of crystalline polyolefins is in the range 0.015–0.060 cm/cm, whilst amorphous polymers usually have values of about 0.005 cm/cm.) The efficient packing also increases interchain attraction so that mechanical properties may be enhanced.

The extent and manner of packing will clearly influence both shrinkage and mechanical properties. At the same time such packing will also be greatly affected by the manner in which crystallisation occurs, i.e. by whether or not nucleation is homogeneous or whether there are nucleating agents. Rates of cooling will also have an influence. It is thus absolutely essential that if a manufacturer wants to control his product he must strictly control his process. Since successful processing greatly depends on this, further consideration will be given to this aspect in the next section.

8.2.8 Orientation and Shrinkage

As previously stated, molecular orientation occurs during melt processing of polymers. On removal of the deforming stresses the molecules start to coil up again but the process may not go to equilibrium before the polymer cools to below its T_g . This leads to residual orientation (frozen-in strain) and corresponding frozen-in stresses.

The resulting mouldings and extrudates are consequently anisotropic and mouldings can be four to five times as strong in one direction as in another direction. This can lead to planes of weakness and easy fracture when subject to shock (impact) stresses. Generally such orientation is undesirable but there are at least two instances of its being of value:

- (1) The built-in hinge, particularly successful with polypropylene in which molecules are frozen-in oriented at right angles to the axis of the hinge.
- (2) Fibrillated tape, again particularly successful with polypropylene, in which oriented film is stretched so much that fibrillation occurs.

In general it may be said that the amount of frozen-in orientation will depend on:

- (1) The amount of initial orientation—a function of shear rate.
- (2) The average polymer melt relaxation times between the processing temperature T_p and the solidifying temperature T_s (the T_g in amorphous polymers and somewhere between T_g and T_m with polycrystalline polymers).
- (3) The time available for disorientation as the melt cools from T_p to T_s . This will depend on the value of $T_p - T_e$ where T_e is the temperature of the environment (the mould temperature in injection moulding) since this will with the specific heat determine the rate of cooling. The time will also depend on $T_p - T_s$ since this will determine the extent of cooling.

A second persistent processing problem is that of shrinkage. During extrusion and moulding, polymer melts are normally subject to intense hydrostatic pressures which tend to cause compression. For example, in injection moulding the melt is under compression at the moment following mould filling. If the mould was suddenly opened at this stage the moulding would expand (slightly) and also distort gruesomely. However, during cooling molecular movement becomes less and the pressures exerted on the mould cavity walls decrease. In most cases not only do they fall to zero but in addition the moulding shrinks. In the case of amorphous polymers the shrinkage is very small and is about 0.005 cm/cm.

With crystalline polymers the more orderly molecular packing leads to much greater shrinkage. Variations in moulding conditions can lead to large variations in shrinkage and need to be closely controlled. The main factors which cause an increase in shrinkage are:

- (1) An increase in mould temperature (which allows more time for crystallisation to occur at a reasonable rate).
- (2) A decrease of injection time (an increase of injection time—up to a limit—would allow more material to be packed into the mould).
- (3) A decrease of injection pressure (an increase of pressure will cause greater packing of material).

Shrinkage is often different along the lines of flow and perpendicular to them. It is commonly found that an increase in the melt temperature reduces the 'along-flow' shrinkage but increases the shrinkage 'across the flow'. Volumetric shrinkage is, however, virtually unaffected by melt temperature.

After-shrinkage is an additional problem with crystalline polymers and depends on the position of the ambient temperature relative to T_g and T_m . This was discussed in Chapter 3.

8.3 MELT PROCESSING OF THERMOSETTING PLASTICS

The setting of these materials after shaping occurs via a chemical process, that of cross-linking. The most common process is moulding but some extrusion, sintering and other miscellaneous processes are also used. A typical compression moulding process is illustrated in *Figure 8.12*.

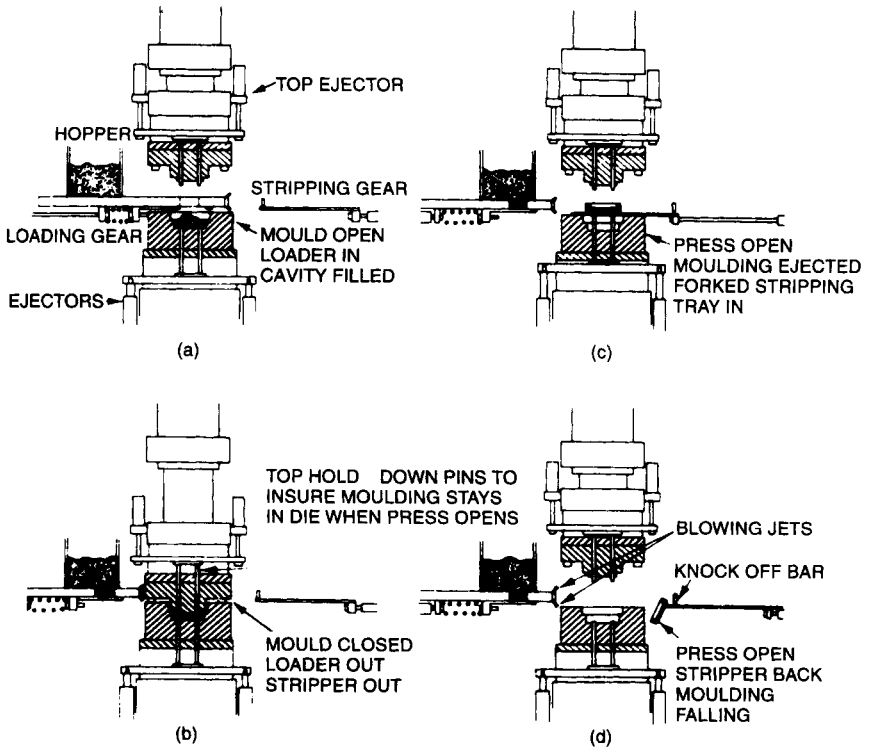


Figure 8.12. Typical process for the compression moulding of thermosetting plastics. (a) Load. (b) Mould. (c) Eject, stripper in. (d) (After Groves¹¹)

As soon as the heated mould is loaded with the thermosetting composition based on a low molecular weight cross-linkable polymer, the polymer starts to cross-link (cure). It is important that the composition completes the flow process before cross-linking reaches such a state that flow is no longer possible. Owing to the low thermal conductivity, the temperature of the moulding composition and hence both viscosity and cure rate will vary with both time and position. The viscosity may also vary with difference in shear rate, which will itself vary from point to point in the mould cavity. Frictional heat from shear, which will affect both viscosity and cure rate, will also vary from point to point—generally being greatest close to the mould cavity wall. Pelleting and preheating of the moulding composition before moulding will also be a variable. An analysis of flow in the thermosetting moulding which accurately described the polymer behaviour would be too complicated to be justified and it is generally preferable to rely on generalisations and rules of thumb.

There are perhaps two generalisations that are both worth noting. The first is that under conditions of constant temperature the viscosity of moulding compositions does not change with time very much during the moulding process until just before the point of hardening. The reason for this lies in the fact that the low molecular weight polymers in the moulding compositions have a *functionality* of at least three. For simplicity consider these molecules to have

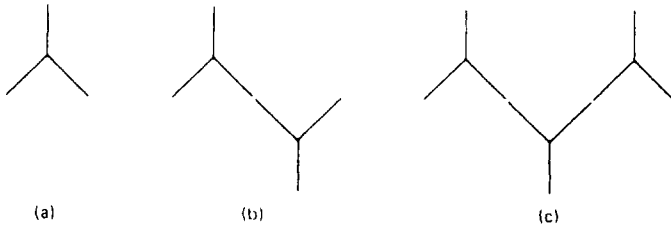


Figure 8.13. Schematic diagram of a trifunctional monomer (a) and its dimer (b) and trimer (c). The monomer has three reactive points and the dimer and trimer four and five respectively. In general, an n -mer has $n + 2$ reactive points

three reactive groups for cross-linking. Under appropriate conditions two of these molecules will join to form a dimer with four reactive groups (Figure 8.13) and this can in turn react with another dimer to form a tetramer with six reactive groups. In general an n -mer will have $n + 2$ reactive groups so that a 100-mer will have 102-reactive groups. Thus the chances of a 100-mer reacting are about 34 times the chances of a trimer reacting. In other words as a molecule grows so its chances of growing faster increase so that very big molecules may suddenly be formed while the number average molecular weight is quite low. Consequently, viscosity changes with time at constant temperature are as indicated in Figure 8.14.

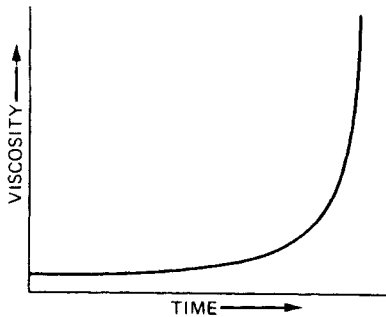


Figure 8.14. Typical curve for viscosity against time of condensation of essentially trifunctional monomer systems under isothermal conditions

The second generalisation relates to the effect of temperature on flow. An increase in temperature increases the *rate of flow*. It also increases the *rate of cross-linking*. It is commonly observed that at low temperatures the effect of temperature on viscosity predominates and the *total flow* occurring before cross-linking increases with temperature.

Temperatures may, however, be reached where a further increase in temperature by so increasing the cure rate cuts down the total flow and curves of the form shown in Figure 8.15 may be produced.

In thermosetting processing operations, cross-linking is never taken to completion in the sense that cross-links are produced across all possible points of cross-linking. There is in fact some evidence that the actual cross-linking may be

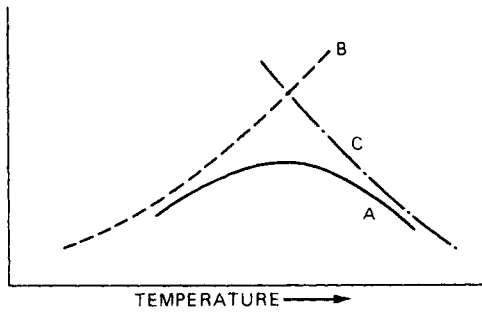


Figure 8.15. The total flow (A) during moulding of a thermosetting material depends on the ease of flow (B) and the time taken for the material to get to such a stage that it is incapable of flow (C). Because of this, total flow goes through a maximum with temperature

only a small fraction of the potential cross-links in the case of phenolic resins. Physical properties differ in their response to degree of cure. Some go down with degree of cure (and hence time of cure), some go up whilst others may rise to a peak and then fall back, the peak point varying with degree of cure (see, for example, *Figure 24.9*). Hence the selection of a degree of cure should be determined by a consideration of what properties are important in any given application.

8.4 PROCESSING IN THE RUBBERY STATE

The most well-known examples of such processing are in the vacuum forming of high-impact polystyrene disposable cups, ABS boats, vinyl chloride–vinyl acetate chocolate-box trays and the pressure shaping of acrylic baths, light fittings and signs. The stamping (coining) of PTFE and poly(methyl methacrylate) blanks are techniques which have been known for a long time. In the late 1960s such stamping of blanks heated to the rubbery state was ‘rediscovered’ and often called ‘cold forming’ although ‘warm forging’ would be a more suitable term.

There are a number of polymers which in fact cannot be melt processed because of their high molecular weights. These include PTFE, very high molecular weight polyethylene and most grades of cast poly(methyl methacrylate). In such cases shaping in the rubbery phase is usually the best alternative.

The processes are best understood by reference to *Figure 3.1*. Successful forming requires working in the rubbery range, that is above the T_g (or T_m in the case of crystalline polymers) and below the temperature at which the polymer either flows or decomposes. If the temperature range of rubberiness is narrow it is important to have very close control of the operation and usually heating is carried out at the point of moulding (as in typical vacuum forming operations). If the range is wider then it is often possible to heat blanks in an oven and transfer these to the shaping tools (as in typical operations for shaping poly(methyl methacrylate) sheet).

In addition to differences in shaping range, polymers also vary in their modulus or resistance to deformation in the rubbery state. If a polymer is to be

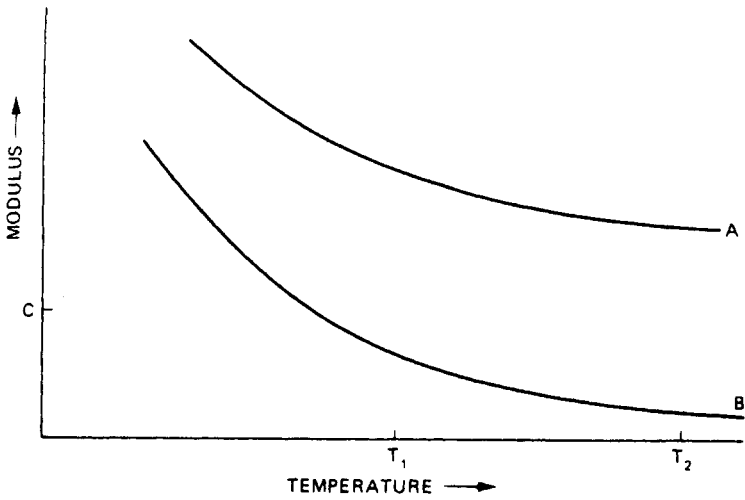


Figure 8.16. Schematic diagram of modulus versus temperature for two materials A and B to be shaped in the rubbery phase in the temperature range T_1-T_2 . In this range the modulus of A is above a critical figure C above which atmospheric pressure is insufficient to shape sheet of a given thickness. Such material could therefore not be vacuum formed. The type B material would, however, present no problem on this score

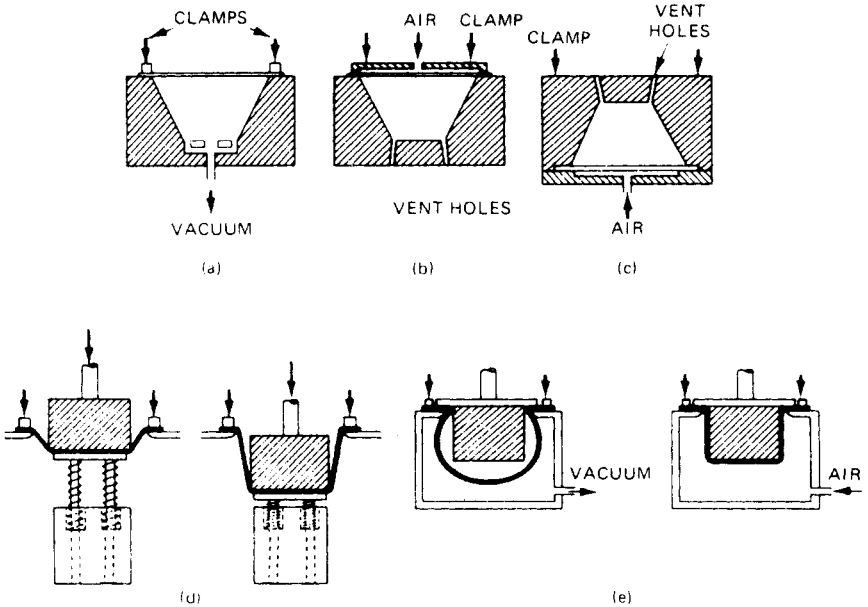


Figure 8.17. Shaping of sheet. (a) Application of vacuum. (b) and (c) Air pressure. (d) Mechanical pressure. (e) Combination of methods (vacuum snap-back). (After Estevez and Powell¹²)

shaped by a vacuum forming technique then the sheet should have a sufficiently low modulus in the shaping range to be deformed by atmospheric pressure (*Figure 8.16*). Whilst this is achieved without great difficulty in the case of high-impact polystyrene, ABS and vinyl chloride–vinyl acetate copolymers, more serious problems can occur with poly(methyl methacrylate) and unplasticised PVC, particularly with thicker gauges of sheet and with complex shaping (*Figure 8.17*). With these two latter materials, vacuum forming is therefore of limited applicability and methods based on either mechanical plungers or positive air pressure (and various combinations of these two, perhaps also with some vacuum) are normally used.

As with thermoplastics melt processes, the setting is achieved by cooling. It will be appreciated that such cooling is carried out while the polymer is under stress so that there is considerable frozen-in orientation. This can be maintained throughout the life of the article. It is possible with the higher molecular weight materials to heat shapes made from blanks many years previously and see them return to the original shape of the blank.

8.5 SOLUTION, SUSPENSION AND CASTING PROCESSES

Although much less important in tonnage terms than processing in the molten and rubbery states, solution, suspension and polymerisation casting processes have a useful role in polymer technology. The main problem in such processes is to achieve a control of the setting of the shape once formed.

Solution processes are used mainly for coating, film casting and fibre spinning, i.e. in processes where the distance the solvent has to diffuse out of the solution once coated, cast or spun is short. Regulation of this diffusion process is important if products of even quality are to be obtained.

In suspension processes the fate of the continuous liquid phase and the associated control of the stabilisation and destabilisation of the system are the most important considerations. Many polymers occur in latex form, i.e. as polymer particles of diameter of the order of $1\ \mu\text{m}$ suspended in a liquid, usually aqueous, medium. Such latices are widely used to produce latex foams, elastic thread, dipped latex rubber goods, emulsion paints and paper additives. In the manufacture and use of such products it is important that premature destabilisation of the latex does not occur but that such destabilisation occurs in a controlled and appropriate manner at the relevant stage in processing. Such control of stability is based on the general precepts of colloid science. As with products from solvent processes diffusion distances for the liquid phase must be kept short; furthermore, care has to be taken that the drying rates are not such that a skin of very low permeability is formed whilst there remains undesirable liquid in the mass of the polymer. For most applications it is desirable that destabilisation leads to a coherent film (or spongy mass in the case of foams) of polymers. To achieve this the T_g of the latex compound should not be above ambient temperature so that at such temperatures intermolecular diffusion of the polymer molecules can occur.

Suspensions other than those of traditional latex type also exist. For example, particles of PVC suspended in plasticisers are widely used. After shaping, PVC pastes, as they are known, are heated to above the T_g of the PVC. At such temperatures the plasticiser diffuses into the PVC particles and this is followed

by interdiffusion of polymer molecules from separate particles to form a coherent homogeneous mass. Success in the use of PVC pastes depends, amongst other things, on the ability to keep plasticiser diffusion to a minimum at storage temperatures but for it to be rapid at the 'setting' temperatures.

A third type of suspension is that in which polymer particles are suspended in monomer which is then polymerised. This is, however, rather more a variant of the casting process in which monomer or low molecular weight polymer is cast into a mould and then polymerised *in situ*.

Polymerisation casting involves mixing monomer or low molecular weight polymer with a polymerisation initiator, pouring the mix into the mould and allowing polymerisation to occur *in situ*. A variation is to impregnate fibres with initiated monomer or other low molecular weight material and polymerise to produce composite structures. The main problem is due to the heat of polymerisation. Unless heat transfer distances are kept short or unless the reaction is carried out very slowly it can easily get out of hand.

An important development of polymerisation casting is that of *reaction injection moulding*. Developed primarily for polyurethanes (and discussed further in Chapter 27), the process has also found some use with polyamides and with epoxide resins.

8.6 SUMMARY

A wide variety of methods is available for both shaping polymers and setting the shapes once formed. In order to obtain the best products in the most economic way processors need an understanding of the underlying polymer science.

It is, however, much easier to write such statements than to achieve perfection in practice. Some idea of the practical difficulties are vividly illustrated in *Figure 8.18* due to Clegg¹³ which shows the complex interrelationships of process variables in an extrusion process.

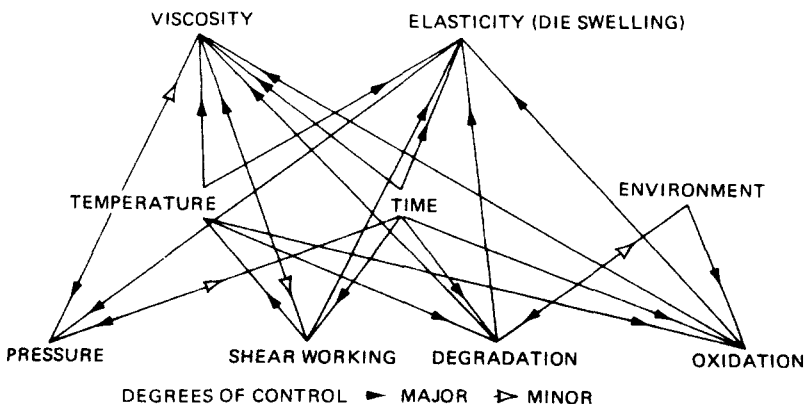


Figure 8.18. Interrelationships of process variables in an extrusion process. (After Clegg¹³)

References

1. KENNAWAY, A., *Brit. Plastics*, **28**, 18 (1955)
2. WHELAN, A. and GOFF, J. P., Paper presented to the PRI Mouldmaking '86 Conference at Solihull, England, January 1986
3. WILLIAMS, M. L., LANDEL, R. F., and FERRY, J. D., *J. Am. Chem. Soc.*, **77**, 3701 (1955)
4. COGSWELL, F. N., *Plastics & Polymers*, **41**, 39 (1973)
5. DOWNS, G. *Vinyl and Allied Polymers* Vol. 1 (Ed. RITCHIE, P. D.), p. 128, Iliffe, London (1968)
6. BUECHE, F., *J. Chem. Phys.*, **20**, 1959 (1952); **25**, 599 (1956); see also a summary in BUECHE, F., *Physical Properties of Polymers*, Interscience, New York (1962)
7. PEZZIN, G., *Pure Appl. Chem.*, **26** (2), 241 (1971)
8. BRYDSON, J. A., *Flow Properties of Polymer Melts* (2nd edn), Geo. Godwin, London (1981)
9. BEYNON, D. L. T., and GLYDE, B. S., *Brit. Plastics Inst.*, **33**, 414 (1960)
10. HOWELLS, E. R., and BENBOW, J. J., *Trans. Plastics Inst.*, **30**, 242 (1962)
11. GROVES, W. R., *Plastics Moulding Plant* Vol. 1, Iliffe, London (1963)
12. ESTEVEZ, J. M. J., and POWELL, D. C., *Manipulation of Thermoplastic Sheet, Rod and Tube*, Iliffe, London (1969)
13. CLEGG, P. L., Chapter in *Thermoplastics: Effects of Processing* (Ed. OGORKIEWICZ, R. M.), Iliffe, London (1960)
14. BARRIE, I. T., Chapter in *Polymer Rheology* (Ed. LENK, R. S.), Elsevier Applied Science Publishers, London (1978)

Bibliography

- BERNHARDT, E. C. (Ed.), *Processing of Thermoplastic Materials*, Reinhold, New York (1959)
- BLACKLEY, D. C., *High Polymer Latices*, Maclaren, London (1966)
- BRYDSON, J. A., *Flow Properties of Polymer Melts*, (2nd Edn), Geo. Godwin, London (1981)
- BRYDSON, J. A., *Handbook for Plastics Processors*, Butterworth-Heinemann, Oxford (1990)
- CRAWFORD, R. J., *Plastics Engineering*, 2nd Edn, Pergamon, Oxford (1990)
- GOGSWELL, F. N., *Polymer Melt Rheology*, Geo. Godwin, London (1981)
- FENNER, R. T., *Principles of Polymer Processing*, Macmillan, London (1979)
- MCKELVEY, J. M., *Polymer Processing*, Wiley, New York (1962)
- OGORKIEWICZ, R. M. (Ed.), *Thermoplastics: Effects of Processing*, Iliffe, London (1969)
- SARVETNICK, H. A. (Ed.), *Plastics and Organosols*, Van Nostrand-Reinhold, New York (1972)
- TADMOR, Z., and GOGOS, C. G., *Principles of Polymer Processing*, Wiley, New York (1979)

9

Principles of Product Design

9.1 INTRODUCTION

Successful product design requires knowledge, intelligence and flair. The knowledge requirement may in turn be subdivided into:

- (1) A knowledge of the requirements of the product.
- (2) A knowledge of the behaviour of plastics materials.
- (3) A knowledge of plastics processes.
- (4) A knowledge of all relevant economic and psychological factors.

Intelligence is required to relate this knowledge, and flair to bring the design to a successful reality. It is not a function of this book to consider points 1, 3 and 4 above but it is a function to consider those material properties that are relevant. Probably enough has been said already about chemical, electrical and optical properties but some additional thoughts on mechanical and thermal properties relevant to design are worth considering.

For successful use a polymer must have appropriate:

- (1) Rigidity.
- (2) Toughness.
- (3) Resistance to long-term deformation (creep).
- (4) Recovery from deformation on release of stress.
- (5) Resistance to thermal degradation adversely affecting properties.

over the range of operating conditions likely to be encountered. This chapter will consider how the diverse properties of plastics in respect of the above properties can be explained by reasonably elementary yet fundamental considerations.

9.2 RIGIDITY OF PLASTICS MATERIALS

The rigidity of a *polymer* is determined by the ease with which polymer molecules are deformed under load. In a polymer at -273°C all load is taken by

bond bending and stretching and for a polymer with no secondary transitions this state of affairs more or less exists up to the region of the glass transition temperature T_g . Several polymers do, however, show additional transitions below the T_g at which point movement of small moieties in the polymer become possible. This allows more response of the polymer to stress and there is a decrease in modulus. Such decreases are usually small but the change at the T_g in an amorphous polymer is considerable as the modulus drops from values of the order of 500 000 lbf/in² (3500 MPa) to values of about 100 lbf/in² (0.7 MPa). Further heating of a polymer such as a commercial polystyrene would rapidly cause a drop of the modulus towards zero but in a high molecular weight polymer such as a cast poly(methyl methacrylate) the entanglements would enable the material to maintain a significant rubbery modulus up to its decomposition temperature. Similar effects are achieved when the polymer is cross-linked and, as might be expected, the more the cross-linking, the higher the modulus.

Molecular movement above the T_g is restricted by crystallinity and, as with chemical cross-linking, the more the crystallinity, the more rigid the polymer. Some polymers tend to melt over a wide temperature range, in which case the modulus may fall over a range of temperatures leading up to the melting point T_m . The above effects are summarised in Figure 9.1.

Plastics materials, in general are blends of polymers with additives and the latter may well affect the modulus. One simple law of use here relates the modulus of the blend or composite E_c to the modulus of the polymer E_p and of the additive E_a by the equation

$$E_c = V_F E_p + (1 - V_F) E_a \quad (9.1)$$

where V_F is the volume fraction of polymer in the blend. Such a relationship only holds when there is no real interaction between polymer and additive such as

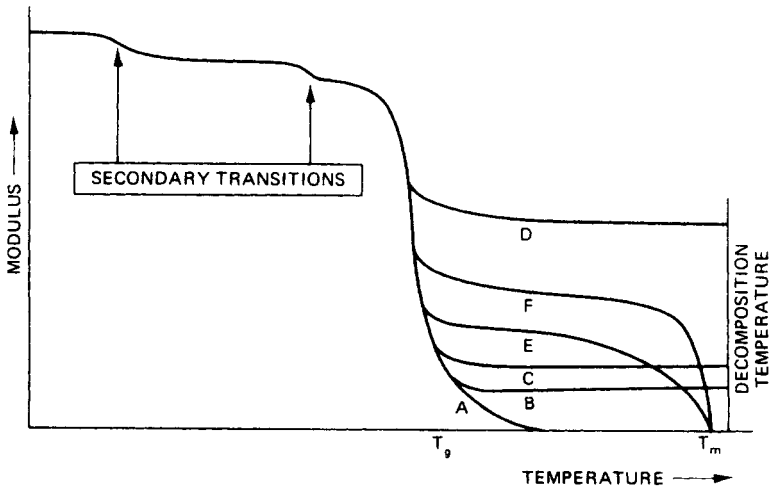


Figure 9.1. Schematic illustration of dependence of the modulus of a polymer on a variety of factors. A is an amorphous polymer of moderate molecular weight whereas B is of such a high molecular weight that entanglements inhibit flow. Similar effects are shown in C and D, where the polymer is respectively lightly and highly cross-linked. In E and F the polymer is capable of crystallisation, F being more highly crystalline than E

occurs between diene rubbers and carbon black where a form of cross-linking may be considered to occur.

In practice one is basically concerned with the rigidity of the product and this involves not only the modulus of the material but also the shape and size of the product. From the points of view of weight saving, economics in material and ease of processing, it is an important aim to keep section thicknesses down in size. Since flat or singly curved surfaces have a minimum rigidity the designer may wish to incorporate domed or other doubly curved surfaces or ribbing into the product in order to increase stiffness. Corrugation can also enhance stiffness but in this case the enhancement varies with position, being greatest when measured at right angles to the corrugation.

9.2.1 The Assessment of Maximum Service Temperature

The design engineer often requires to know the maximum temperature for which a polymer can be used in a given application. This depends largely on two independent factors:

- (1) The thermal stability of the polymer, particularly in air.
- (2) The softening behaviour of the polymer.

Let us consider two polymers A and B. Let A 'soften' at 120°C but have long-term thermal stability to 200°C. On the other hand polymer B softens at 200°C but degrades 'at a measurable rate' above 90°C. Consideration of these figures, even allowing for the loose terminology, indicates that material A could not be used much above 90°C for either long or short periods. In the case of polymer B short-term service might be possible up to about 160–170°C but it could not be used for prolonged periods much above 70–80°C.

9.2.1.1 Assessment of thermal stability

Over the years many attempts have been made to provide some measure of the maximum service temperature which a material will be able to withstand without thermal degradation rendering it unfit for service. Quite clearly any figure will depend on the time the material is likely to be exposed to elevated temperatures. One assessment that is being increasingly quoted is the UL 746B Relative Temperature Index Test of the Underwriters Laboratories (previously known as the Continuous Use Temperature Rating or Index).

In order to obtain a temperature index rating a large number of samples are subjected to oven aging at a variety of temperatures for periods up to a year. During the course of this time samples are periodically withdrawn and tested. A plot is then made of the percentage retention in the value of the property measured (compared to its original control value) against time. A note is then made of the time, at each temperature tested, which gives a 50% reduction in value of the property. Somewhat arbitrarily this is taken as the failure time at that temperature. Using the data from experiments carried out after aging at various temperatures, the logarithm of the failure time is plotted against $1/K$ (where K is the temperature in kelvin). The resultant linear Arrhenius plot is then extrapolated to the arbitrary time of 10 000 hours. The temperature at which the failure time (as defined above) is 10 000 hours is known as the *relative temperature index* (RTI).

This long-term thermal performance of a material is tested alongside a second, control, material which already has an established RTI and which exhibits a good performance. Such a control is necessary because thermal degradation characteristics are sensitive to variables in the testing programme. Since the control material will also be affected by the same unique combination of these factors during the tests, there is a valid basis for comparison of test and control materials.

It is to be expected that the RTI obtained would depend on the property assessed and in UL 746B three properties are assessed:

- (1) 'Mechanical with impact'—by measuring tensile impact strength.
- (2) 'Mechanical without impact'—by measuring tensile strength.
- (3) 'Electrical'—by measuring dielectric strength.

A value for the RTI is provided for each of these tests although in common experience it is found that similar numerical values are obtained.

In addition, the RTI may be affected by the thickness of the sample, so this should be given in any RTI specification.

Such a value for relative temperature index will be specific to a particular grade of a polymer, sometimes even to a specific colour. The difference between grades of a particular species of polymer can be substantial, depending both on the variation in the inherent stability of a material between differing manufacturing methods and also on the type and amount of additives used. It is possible to obtain from the Laboratories a Generic Temperature Index to cover a species of material but this will usually be considerably lower than for many of the individual grades within that species.

Some collected values for RTI taken from the literature are given in Table 9.1. (These are given for guidance only and should not be taken to imply official UL ratings.)

Table 9.1 Some collected values for Relative Temperature Index (RTI) (Unless otherwise stated, data are for 'mechanical without impact' and for unreinforced grades)

<i>Polymer</i>	RTI (°C)
ABS	60–80
Nylons	75
Polyacetal	90
Styrenic PPO	105
Polycarbonate	125
	(Lexan 3414R)
	130 (40% glass filled)
Polyarylate	130
	(Ardel D100)
Poly(butylene terephthalate)	140
	(Pocan B1305)
	140 (30% g/f)
	(Pocan B3235)
Poly(ethylene terephthalate)	150 (30% g/f)
	(Petlon 4630)
Polysulphone	160
Polyetherimide	170
	(Ultem 1000)
Polyphthalamide	180
	(Amodel A1133HS)
Polyethersulphone	180
	(Victrex 200P)
Poly(phenylene sulphide)	200 (40% g/f)
	(Supec G401)
Aromatic polyester	220
	(Ekkcel I-2000)
Liquid crystal polyester	220
Polyether ether ketone	240
	(Victrex PEEK)

9.2.1.2 *Assessment of softening point*

As will be seen from curves A, B and C of *Figure 9.1*, the ‘softening point’ of an amorphous polymer, i.e. the temperature at which the modulus drops catastrophically, is closely associated with the T_g . (Such softening does not of course occur in highly cross-linked polymers, as in type D, unless degradation also takes place.)

In the case of crystalline polymers such as types E and F the situation is somewhat more complicated. There is some change in modulus around the T_g which decreases with increasing crystallinity and a catastrophic change around the T_m . Furthermore there are many polymers that soften progressively between the T_g and the T_m due to the wide melting range of the crystalline structures, and the value determined for the softening point can depend very considerably on the test method used.

Two particular test methods have become very widely used. They are the *Vicat softening point test* (VSP test) and the *heat deflection temperature under load test* (HDT test) (which is also widely known by the earlier name of *heat distortion temperature test*). In the *Vicat test* a sample of the plastics material is heated at a specified rate of temperature increase and the temperature is noted at which a needle of specified dimensions indents into the material a specified distance under a specified load. In the most common method (method A) a load of 10 N is used, the needle indenter has a cross-sectional area of 1 mm², the specified penetration distance is 1 mm and the rate of temperature rise is 50°C per hour. For details see the relevant standards (ISO 306; BS 2782 method 120; ASTM D1525 and DIN 53460). (ISO 306 describes two methods, method A with a load of 10 N and method B with a load of 50 N, each with two possible rates of temperature rise, 50°C/h and 120°C/h. This results in ISO values quoted as A50, A120, B50 or B120. Many of the results quoted in this book predate the ISO standard and unless otherwise stated may be assumed to correspond to A50.)

In the *deflection temperature under load test* (heat distortion temperature test) the temperature is noted at which a bar of material subjected to a three-point bending stress is deformed a specified amount. The load (F) applied to the sample will vary with the thickness (t) and width (w) of the samples and is determined by the maximum stress specified at the mid-point of the beam (P) which may be either 0.45 MPa (66 lbf/in²) or 1.82 MPa (264 lbf/in²).

The formula used for the calculation is:

$$F = 2Pwt^2/3L$$

Where L is the distance between the outer supports (loading points). For details see the relevant standards (ISO 75; BS 2782 method 121; ASTM D648; DIN 53461).

Whilst the Vicat test usually gives the higher values the differences are quite modest with many polymers (e.g. those of types A, B and C). For example, in the case of the polycarbonate of bis-phenol A (Chapter 20) the heat distortion temperatures are 135–140°C and 140–146°C for the high and low stress levels respectively and the Vicat softening point is about 165°C. In the case of an acetal homopolymer the temperatures are 100, 170 and 185°C respectively. With nylon 66 the two ASTM heat distortion tests give values as different as 75 and 200°C. A low-density polyethylene may have a Vicat temperature of 90°C but a heat distortion temperature below normal ambient temperatures.

The differences in the assessment of softening point between the tests is clearly largely a matter that the 'end point' of the test measures a different modulus. Reference to *Figure 9.1* shows that with some materials (e.g. of type A) this will not be of great importance but with other types (e.g. types E or F) the difference could be very large.

At the risk of oversimplification it might be said that the Vicat test gives a measure of the temperature at which a material loses its 'form stability' whilst the higher stress level heat distortion temperature (1.82 MPa) test provides a measure of the temperature at which a material loses its load-bearing capacity. The lower stress (0.45 MPa) heat distortion temperature test gives some rather intermediate figures and it is perhaps not surprising that it is today less often quoted than the other two tests.

Some interesting differences are noted between amorphous and crystalline polymers when glass fibre reinforcement is incorporated into the polymer. In *Figure 9.2* (ref. 10) it will be seen that incorporation of glass fibre has a minimal effect on the heat deflection temperature of amorphous polymers (polystyrene,

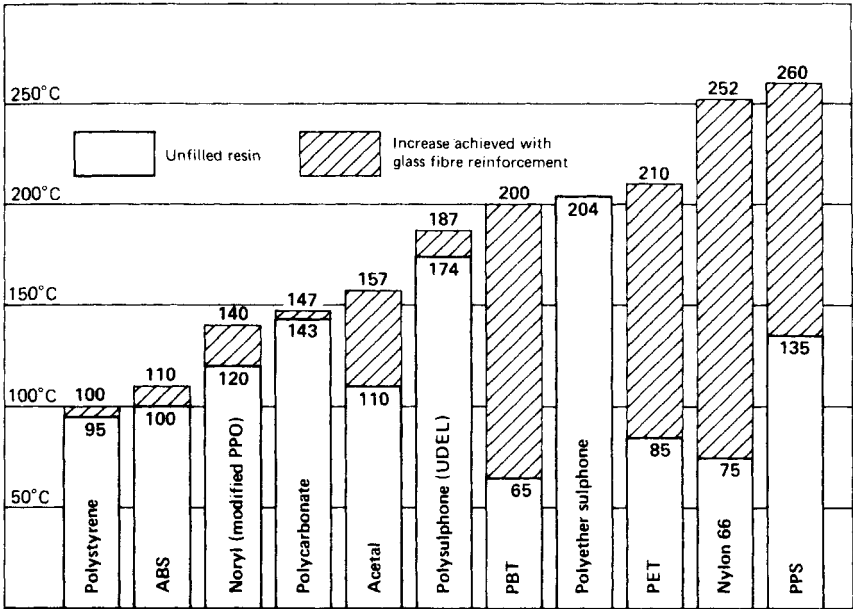


Figure 9.2. Heat deflection temperatures under a load of 1.82 MPa for selected polymers. Note that incorporation of glass fibre has a much greater effect with crystalline polymers than with amorphous ones (after Whelan and Craft courtesy of *British Plastics and Rubber*)

ABS, polycarbonate and polysulphone) but large effects on crystalline polymers. It is particularly interesting, as well as being technically important, that for many crystalline polymers the unfilled polymer has a heat deflection temperature (at 1.82 MPa stress) similar to the T_g , whereas the filled polymers have values close to the T_m (*Table 9.2*).

Other tests occasionally quoted are the BS softening point test and the Martens test. These involve the bending under load of samples held at one end as they are subjected to a rise in temperature.

Table 9.2 Comparison of T_g , T_m and heat deflection temperatures of polymers with and without glass fibre reinforcement (All values in °C)

Polymer	T_g	T_m	Heat deflection temperature	
			(unfilled)	(filled)
Polyether ether ketone	143	334	150	315
Polyether ketone	165	365	165	340
Polyphenylene sulphide	85	285	135	260
Polyethylene terephthalate	70	255	85	210
Polybutylene terephthalate	22–43	225	54	210

9.3 TOUGHNESS

For many applications the resistance to impact is the most important property of a plastics material. It is also notoriously one of the most difficult to assess.

If a polymer with no secondary transitions is struck a blow at some temperature well below its glass transitions temperature, deformation will be very limited before fracture occurs. Nevertheless because of the high modulus quite high tensile strengths will be recorded, of the order of 8000 lbf/in² (55 MPa). The energy to break will be given by the area under the stress–strain curve and will not be very large (see *Figure 9.3*).

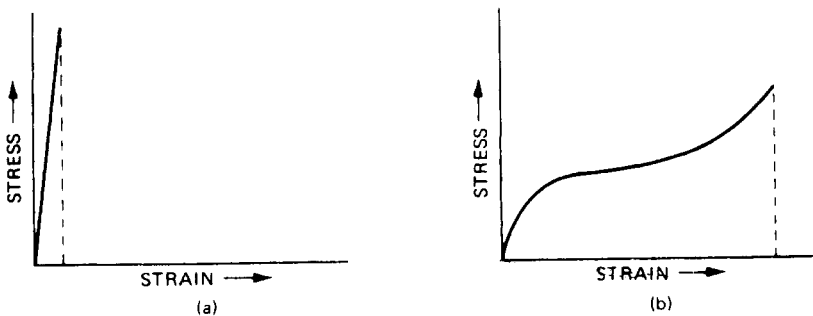


Figure 9.3. Stress–strain curves for (a) rigid amorphous plastics material showing brittle fracture and (b) rubbery polymer. The area under the curve gives a measure of the energy required to break the test piece.

On the other hand, if an amorphous polymer is struck above the T_g , i.e. in the rubbery state, large extensions are possible before fracture occurs and, although the tensile strength will be much lower, the energy to break (viz. the area under the curve) will be much more, so that for many purposes the material will be regarded as tough.

A common requirement is to produce a rigid plastics material with the toughness of a rubber. This can be achieved in a number of ways:

- (1) By the use of a moderately crystalline polymer with a T_g well below the expected service temperature (e.g. polyethylene).

- (2) By block copolymerisation so that one component of the block copolymer has a T_g well below the expected service temperature range (e.g. polypropylene with small blocks of polyethylene or preferably polypropylene with small amorphous blocks of ethylene-propylene copolymer).
- (3) By blending with semi-compatible materials which have a T_g well below the expected service temperature range (e.g. high-impact polystyrene—as described in Chapter 3).
- (4) By the use of a polymer which has effective transitions at or below the expected service temperature range and which is able to respond to stress by extensive deformation (e.g. polycarbonates).
- (5) By plasticisation. This in effect reduces the T_g and in the case of nylon which has absorbed small quantities of water the toughening effect can be quite substantial. It should, however, be noted that in the case of PVC small amounts of plasticiser actually reduce the impact strength.

The above procedures will vary in their efficiency with the extent to which they are employed. For example, too little of a stereoblock in case (2) or too little rubber in case (3) may not be enough to make the material tough and there is thus a somewhat critical *tough–brittle transition* range. In terms of a stress–strain curve a brittle material may be considered to be one that breaks without a yield whilst a tough material yields to give a substantial energy to break. (It is perhaps worth noting that if a material has not broken after being struck simply because it yielded irreversibly the product may still be useless.)

What is important to realise is that a polymer may be tough when exposed to tensile load but brittle when assessed by an Izod-type test where a notched sample is subjected to a bending load. *Table 9.3* attempts to summarise the behaviour of typical polymers to different stresses.

Table 9.3

<i>Type of stress</i>	<i>Polymers ductile at 25°C and at 1 min⁻¹ strain rate</i>
1. Around Izod notch	Low-density polyethylene Ethylene–propylene block copolymers Cellulose nitrate and propionate ABS and high-impact polystyrene Bis-phenol A polycarbonate
2. Tension	Above materials plus: High-density polyethylene Polypropylene Acetal polymers Aliphatic polyamides (nylons) PPO Poly(ethylene terephthalate) Polysulphones
3. Simple shear	Above materials plus: Poly(methyl methacrylate)
4. Compression	Above materials plus: Polystyrene

Toughness is not simply a function of polymer structure or the mode of stressing. It clearly will also depend on the temperature and the rate of striking but more important still it will depend on the product design and method of manufacture.

Consider two products A and B (*Figure 9.4*) where the molecules are randomly disposed as in A and aligned as in B. In A there will be no planes of weakness whereas if B is struck a blow at point P failure is much more likely to occur along XY than at any angle to this line (or plane if we consider a three-dimensional system). For optimum toughness the aim of the processor must therefore be to minimise such orientation. (It should be noted that in Chapter 3 it was found that the impact strength increased to a limit with increasing biaxial orientation. This would only apply when the impact blow was made at approximately right angles to the plane of orientation.)

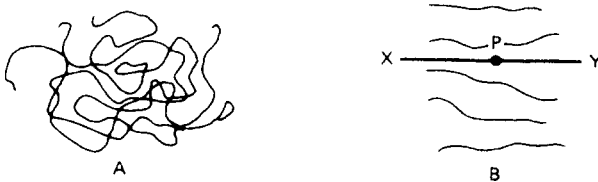


Figure 9.4

The presence of notches or sharp angles or of a few holes, voids, particle inclusions or small inserts tends to concentrate the stress. Different polymers vary in their 'notch sensitivity' and this is presumably a reflection of how close they are to their tough–brittle transitions. The aim of the designer and processor must be to reduce such stress concentration to a minimum.

9.3.1 The Assessment of Impact Strength¹

It is probably most useful to consider toughness as a property of a plastics part under some specified conditions of service. Whilst it is possible to devise impact tests and to rank a series of plastics materials according to the results obtained in such tests it remains almost impossible to use such tests to try to predict whether or not an article made from a specific material will or will not be satisfactory in service.

Amongst the factors that will influence service performance are the effect of additives and impurities, temperature, detailed geometric size and shape, orientation and morphology, surface condition, energy and speed of any impacting blow, the shape of the impacting instrument, the environment, and strains in the article due to external loads. For this reason it is desirable, but not always feasible, to test prototype articles under conditions as close to service conditions as possible.

Impact tests are, however, used to try to compare the impact strength of different materials. Of these tests four require specific mention. These are the Izod test, the Charpy test, the falling weight tests and the tensile impact test.

Of these the most well known is the *Izod test*. This consists of a bar, one end of which is held in a vice, the sample being held vertically. The bar is then struck by a striking device under controlled conditions at a specified point above the vice. The energy required to break the sample is noted. It is common to have a notch in the bar which is located during the test at the top of the vice and on the

same side as the bar is struck. As a result of the stress concentrations around the notch much lower impact strengths are recorded with notched specimens than with unnotched specimens.

Whilst Izod tests are, perhaps surprisingly, generally reproducible it has been found impossible to scale up the results and thus predict the energy required to break a bar of large cross-section from results obtained with a bar of smaller cross-section. This has led to some uncertainty in the method of quoting results and the following approaches are used:

- (1) Energy to break. This is quoted usually in joules or in ft lbf. The result will only apply to one set of sample dimensions and it is not possible to allow for any change in specimen dimensions.
- (2) Energy to break per unit width of sample. (In notched specimens this is taken as the energy to break unit width of notch. In this case the results are quoted in such units as ft lb per inch of notch or joules per millimetre. The values obtained depend on the notch width. For example, it has been found that on reducing the notch width from $\frac{1}{2}$ " to $\frac{1}{8}$ " the impact strength of a polycarbonate increased by a factor of 5.4 and that of unplasticised PVC by 3.1.)
- (3) The energy to break per fractured area. This will be the cross-sectional area of the sample less the area of the notch (as projected on the cross-section). The units used in this method are most commonly kJ/m^2 , kgf cm cm^{-2} and ft lbf in^{-2} . These are related by the factors

$$1 \text{ kJ/m}^2 = 1.02 \text{ kgf cm cm}^{-2} = 0.476 \text{ ft lbf in}^{-2}$$

Because of the diversity of the sources for this book the Izod data frequently referred to are expressed in a variety of units according to the test method used and no attempt has been made to convert the data to the use of a common unit.

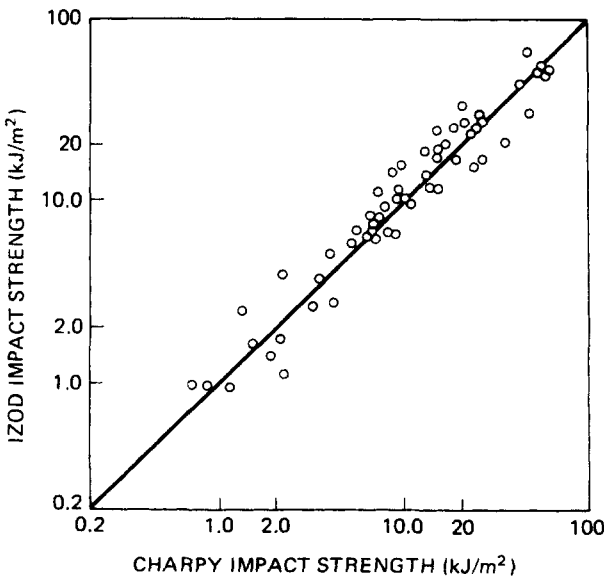


Figure 9.5. Graph showing that there is an approximate correlation between Izod and Charpy impact test results. (After Vincent¹)

An alternative to the Izod test is the *Charpy test* in which a sample supported, but not gripped, at each end is subject to an impact in the centre. According to the test a notch may be present in the centre of the sample on the face opposite to that subjected to impact. In spite of the differences between the tests there is a surprisingly good correlation between Izod and Charpy test results as shown by *Figure 9.5* based on tests on several thermoplastics.¹

The presence of notches, sharp angles, voids, particle inclusions and small inserts tends to concentrate stress on impact. One way of studying the sensitivity of a polymer or polymer compound to stress concentration is to carry out a series of tests with different notch angles or notch tip radii. Materials vary enormously in their notch sensitivity as is shown in *Figure 9.6*¹ with materials like unplasticised PVC, nylon, the polyacetals and the polycarbonates (not shown in the diagram) being very sensitive to sharp notches. It is interesting to note that the ABS material, although good at high stress concentrations, does not perform so well, relatively, as PVC, nylon and the polyacetal material with the blunter notched samples.

Other impact tests widely used are the falling weight tests where a weight is allowed to fall onto a supported flat or domed surface and tensile impact tests in which a sample is subjected to a sudden shock in tension. Whilst the

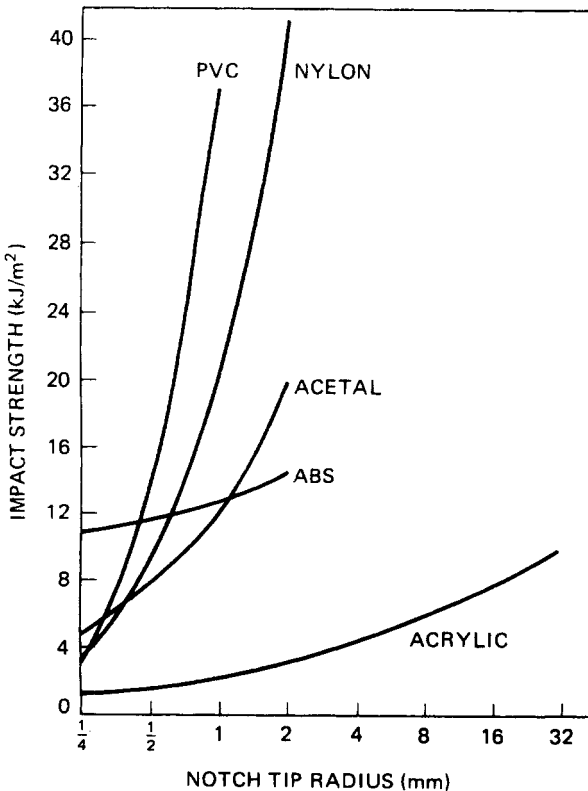


Figure 9.6. Impact strength as a function of notch tip radius for samples of five different polymers (after Vincent¹)

last named test provides results more amenable to theoretical study, plastics products are not commonly subjected to this type of impact and publisher data are limited.

9.4 STRESS–STRAIN–TIME BEHAVIOUR

When a polymer mass is stressed, the resultant deformation D_{total} may be considered as the sum of three separate deformations:

- (1) A deformation due to bond bending and stretching which is effectively instantaneous and independent of temperature (ordinary elastic deformation, D_{OE}).
- (2) A deformation due to chain uncoiling which is not instantaneous and whose rate depends on temperature (high elastic deformation, D_{HE}).
- (3) A deformation due to slippage of polymer molecules past one another (viscous deformation D_{visc}). It is often assumed that such viscous deformation rates do not change with time if the applied stress is constant. However, in long-term deformations chemical and morphological changes may occur which affect the rate of chain slippage.

It is thus seen that the simple relationship

$$D_{\text{total}} = D_{\text{OE}} + D_{\text{HE}} + D_{\text{visc}} \quad (9.2)$$

can be used to analyse the deformation under a given stress.

In *Figure 9.7* stresses are imposed on a body showing ordinary elastic deformation only, a second body showing high elastic deformation only and a third body showing viscous deformation only. The stress is imposed at time t_0 and held at a constant value until time t_1 , when it is removed. Deformation

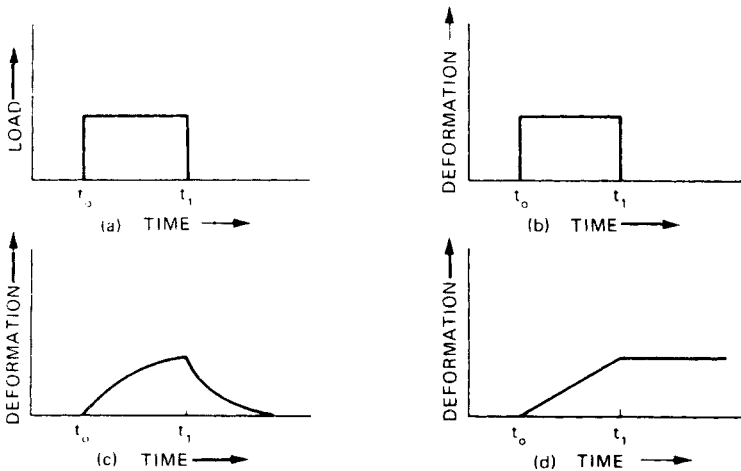


Figure 9.7. Types of deformational response as a result of a fixed load being imposed between times t_0 and t_1 (a). (b) Ordinary elastic material. (c) Highly elastic material. (d) Viscous material

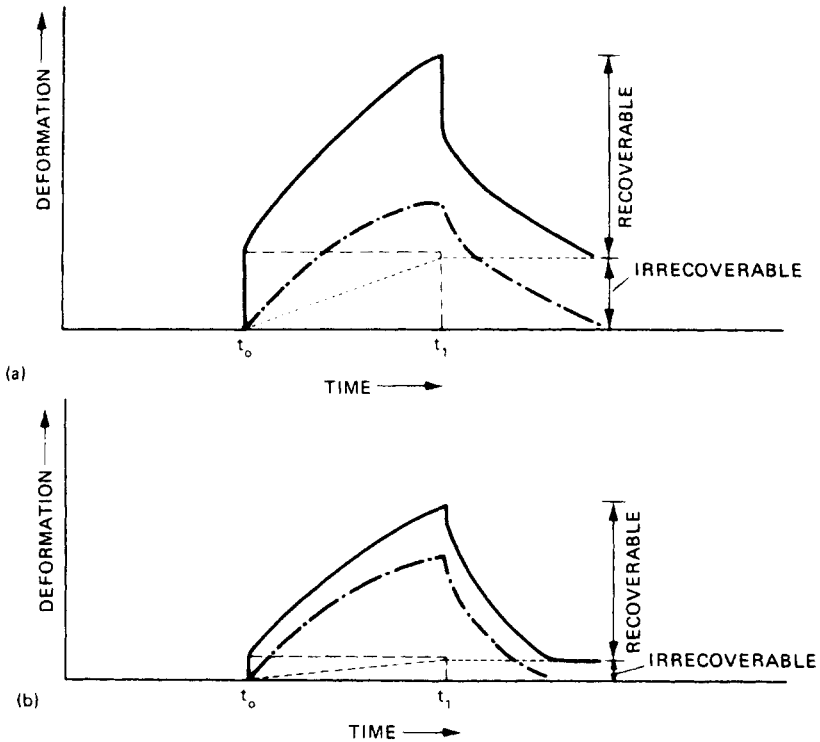


Figure 9.8. Deformation–time curves. (a) Material showing substantial ordinary elastic, high elastic and viscous components of deformation. (b) Material in which high elastic deformation predominates

responses are shown. Real polymers exhibit deformation–time curves which are a combination of the three basic responses although the balance differs widely among polymers. Figure 9.8 shows typical deformation–time curves.

It will be noticed that, given sufficient time, D_{HE} will reach a constant value whilst D_{visc} continues to increase with time. On release of stress D_{HE} will eventually disappear but D_{visc} will remain constant.

One of the most important conclusions from this is that since both the viscous and the high elastic components of deformation depend on both time and temperature, the total deformation will depend on time and temperature. Since this fact has been shown to be an important factor affecting many polymer properties it is proposed to consider the background to this in greater detail in the following section.

9.4.1 The WLF Equations

In order for molecules or segments of molecules to move from place to place it is necessary that there should be some holes in the mass of material into which these molecules or segments may move—and simultaneously leave other spaces into which other molecules or segments may occupy. One interpretation of the glass transition temperature is that it is a temperature below which the ‘free volume’ is really too small for much molecular movement. However, at and

above the T_g there is sufficient energy for molecular movement, jostling occurs and the free volume increases quite sharply with an increase in temperature. This increase in the temperature dependence of the volume naturally causes an increase in the coefficient of thermal expansion and it is usual to express the temperature coefficient of the free volume as being the difference between the thermal expansion coefficients above and below the T_g . This may be expressed mathematically by the equation

$$f = f_g + (a_r - a_g)(T - T_g) \approx f_g + a_2(T - T_g) \quad (9.3)$$

where f is the fractional free volume at temperature T , f_g the fractional free volume at T_g and a_r and a_g the coefficients of thermal expansion above and below the T_g respectively. The value of a_2 is simply $a_r - a_g$.

Now it has been argued that the viscosity is related to the fractional free volume by an expression of the form

$$\frac{1}{\eta_T} = K e^{-A/f} \quad (9.4a)$$

so that

$$\frac{1}{\eta_{T_g}} = K e^{-A/f_g} \quad (9.4b)$$

where K and A are constants. Combining these we obtain

$$\log_e \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{1}{f} - \frac{1}{f_g} \quad (9.5)$$

Substituting for f from equation (9.3) this expression leads to

$$\log_{10} \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{-(T - T_g)}{2.303 f_g [(f_g/a_2) + (T - T_g)]} \quad (9.6)$$

Data on a large range of polymers obtained by experimental methods have indicated the approximate general validity of the equation

$$\log_{10} \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (9.7)$$

known as the Williams, Landel and Ferry equation (WLF equation). By solving the pair of simultaneous equations (9.6) and (9.7) we obtain

$$f_g = 0.025$$

and

$$a_2 = 4.8 \times 10^{-4} \text{ deg}^{-1}$$

Equation (9.7) implies that if we know the viscosity at some temperature T we can estimate the viscosity at the T_g and hence in turn estimate the viscosity at another temperature T_1 , i.e. the WLF equation gives the effect of temperature on viscosity.

There are further ramifications of this observation. In essence if the value of a material property changes with temperature and this change arises from changes in the viscosity of the system then it may well be possible to apply the WLF equation.

One example of this occurs with stress relaxation. If a polymer is deformed to a fixed strain at constant temperature the force required to maintain that strain will decay with time owing to viscous slippage of the molecules. One measure of this rate of decay or stress relaxation is the relaxation time θ , i.e. the time taken for the material to relax to $1/e$ of its stress on initial application of strain.

In this case it is found that

$$\log_{10} \left(\frac{\theta_T}{\theta_{T_g}} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (9.8)$$

which is of the same form as equation (9.7).

For an experiment carried out in shear it is possible to define a shear relaxation modulus at some time t as

$$G_{rt} = \frac{f_t}{S_0} \quad (9.9)$$

where f_t is the force required to maintain the strain at time t after the initial stretching operation to the strain S_0 .

Clearly related to stress relaxation is creep, when a material is kept under constant load and because of molecular slippage the material deforms continuously with time of loading.

For small shear strains we can define a time-dependent compliance J_t (reciprocal modulus) by the equation

$$J_t = \frac{S_t}{f_0} \quad (9.10)$$

where S_t is the strain at time t under the load f_0 . There is a clear but rather complicated relation between G_{rt} and J_t but if the slope of $\log G_{rt}$ against $\log t$ is $-m$ then

$$G_{rt} J_t = \frac{\sin m\pi}{m\pi} \quad (9.11)$$

is a good approximation where $m < 0.8$.

Not only are the creep compliance and the stress relaxation shear modulus related but in turn the shear modulus is related to the tensile modulus which itself is related to the stress relaxation time θ . It is therefore in theory possible to predict creep-temperature relationships from WLF data although in practice these are still best determined by experiment.

9.4.2 Creep Curves

Major polymer manufacturers can usually supply creep data on those of their polymers which are likely to be subjected to long-term loads. A typical set of such curves is given in *Figure 9.9*. Sections through the creep curves at constant

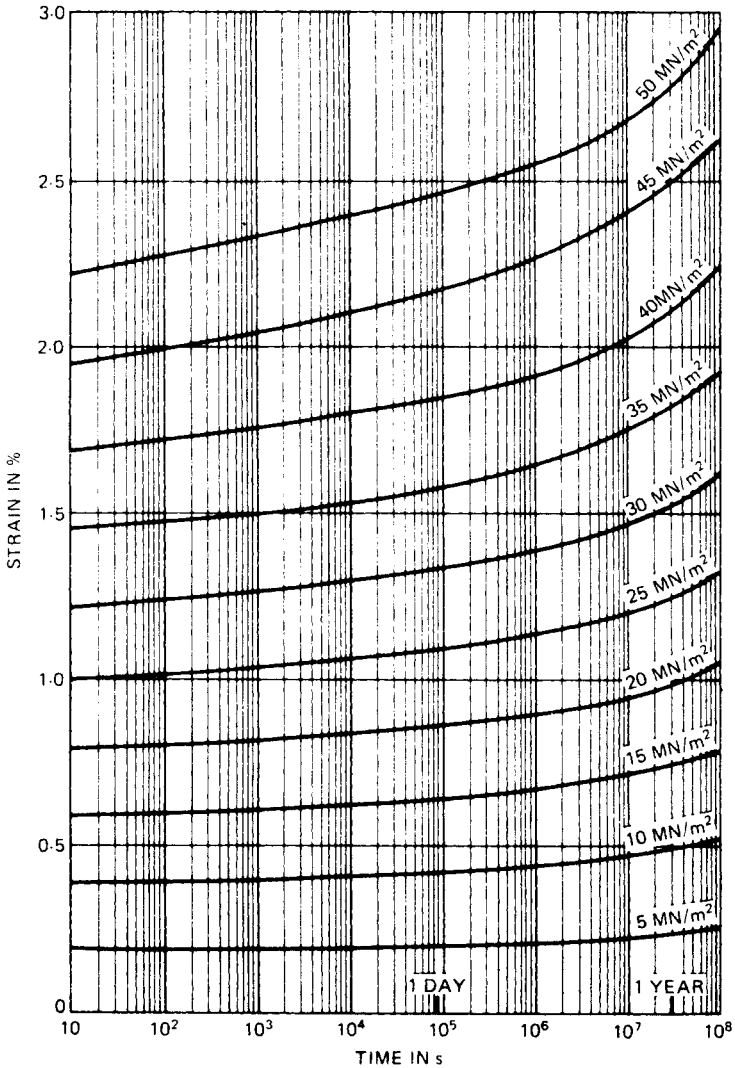


Figure 9.9. Curves for creep in tension of a commercial polysulphone (Polyethersulphone 300P-ICI) at 20°C. (From ICI Technical Service Note PES 101, reproduced permission of ICI Plastics Division)

strain and constant time can give respectively isometric stress-log time curves and isochronous stress-strain curves (Figure 9.10). Whilst not providing any new information, such alternative presentations of the data may be preferred for certain purposes.

The creep curves will depend not only on stress but also on:

- (1) Temperature.
- (2) Humidity (in the case of hygroscopic plastics materials).
- (3) Presence of solvents in the atmosphere.

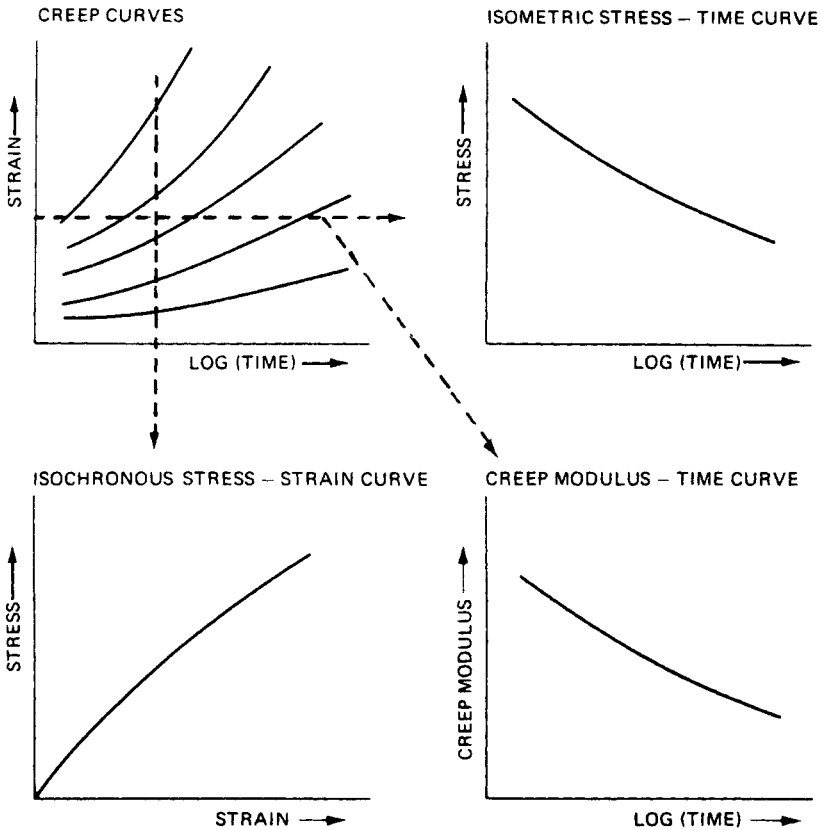


Figure 9.10. Presentation of creep data: sections through the creep curves at constant time and constant strain give curves of isochronous stress-strain, isometric stress-log (time) and creep modulus-log (time). (From ICI Technical Service Note PES 101, reproduced by permission of ICI Plastics Division)

- (4) Type of stress. A uniaxial tensile creep test would not be expected to give the required data if the designer was concerned with torsional or compressive creep.

9.4.3 Practical Assessment of Long-term Behaviour

The theory relating stress, strain, time and temperature of viscoelastic materials is complex. For many practical purposes it is often better to use an *ad hoc* system known as the *pseudo-elastic design approach*. This approach uses classical elastic analysis but employs time- and temperature-dependent data obtained from creep curves and their derivatives. In outline the procedure consists of the following steps:

- (1) Details of the function and service conditions of the component part are ascertained, this including the expected lifetime and maximum service temperature.

- (2) Before commencing calculations the 'worst case' is assumed. For example it is assumed that the component operates continuously at the maximum temperature and under the maximum load encountered in its service life.
- (3) The appropriate formula is selected from classical elastic analysis.
- (4) The appropriate figure for stress, modulus etc. is taken from the creep curve or a derivative curve. This is then inserted into the formula.

The following problem provides a simple illustration of the approach.

A blow-moulded container, cylindrical in shape but with one spherical end, is prepared from the polysulphone whose creep curves at 20°C are illustrated in *Figure 9.9*. The cylindrical part of the container has an outside diameter of 200 mm and is required to withstand a constant internal pressure of 7 MPa at 20°C. It is estimated that the required service lifetime of the part will be one year and the maximum allowable strain is 2%. What will be the minimum wall thickness for satisfactory operation?

The appropriate formula from classical elastic analysis is

$$t = \frac{pd}{2\sigma}$$

where t is the thickness
 p the internal pressure
 d the outside diameter
 σ the hoop stress

Figure 9.9 shows that the stress that will lead to a creep strain of 2% after one year is about 39 MPa. Substituting this into the equation as the hoop stress will give

$$t = \frac{7 \times 200}{2 \times 38} = 18.4 \text{ mm}$$

9.5 RECOVERY FROM DEFORMATION

In *Figure 9.8* it was seen that on release of stress some deformation may be recoverable. How much will depend largely on the relative contributions of viscous, ordinary elastic and high elastic components in the original deformation. Generally speaking the higher the value of $D_{\text{visc}}/D_{\text{total}}$ the less will be the recoverable strain. Since D_{visc} generally increases more steeply with increasing load and increasing time than the other deformation components, high loads and long loading times tend to increase the irrecoverable strain.

For data presentation it is usual to use the following terms:

$$\text{Fractional recovered strain} = \frac{\text{Strain recovered}}{\text{Creep strain when load is removed}}$$

$$\text{Reduced time} = \frac{\text{Recovery time}}{\text{Duration of creep period}}$$

These are commonly presented graphically as fractional recovered strain against log (reduced time) curves as typified in *Figure 9.11*. In the case of the acetal

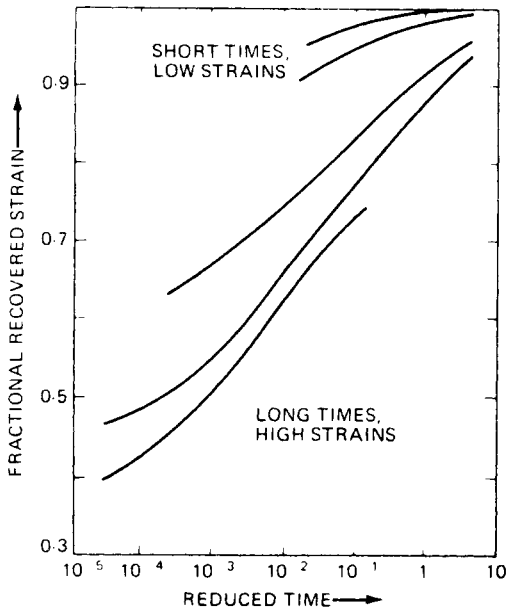


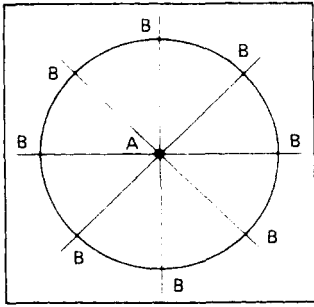
Figure 9.11. Recovery from tensile creep of an acetal copolymer at 20°C and 65% relative humidity. (From ICI Technical Service Note G117, reproduced by permission of ICI Plastics Division²)

copolymers most of the deformation in a short-time low-strain test will be of the D_{OE} type (i.e. due to bond bending and stretching). In medium-term tests there will be some more chain uncoiling which occurs very slowly and, as a corollary, re-coiling on release of stress will also be slow so that overall recovery takes longer. It is doubtful whether in this case viscous flow is at all significant except at very heavy loadings for very long periods of time.

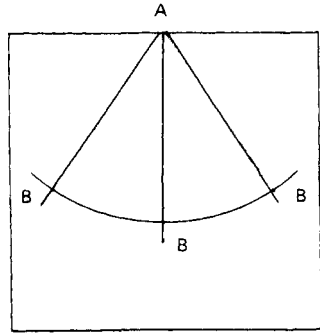
9.6 DISTORTION, VOIDS AND FROZEN-IN STRESS

A characteristic feature of thermoplastics shaped by melt processing operations is that on cooling after shaping many molecules become 'frozen' in an oriented conformation. Such a conformation is unnatural to the polymer molecule, which continually strives to take up a randomly coiled state. If the molecules were unfrozen a stress would be required to maintain their oriented conformation. Another way of looking at this is to consider that there is a frozen-in stress corresponding to a frozen-in strain due to molecular orientation.

One consequence of this is that in a thermoplastic injection moulding the molecular orientations will vary from place to place according to the flow pattern. This may well set up sufficient stresses in the moulding to cause it to distort from its intended shape. Factors affecting the amount of orientation were discussed briefly in the previous chapter and by the author elsewhere.³ Sometimes the conditions required to minimise distortion may be such that the moulding cycle becomes too long to be economic. In these cases it may be necessary to modify the moulding or at least the position and number of feed



CENTRE-GATED MOULDING



EDGE-GATED MOULDING

Figure 9.12. Moulding shrinkage along flow lines is greater than on arc perpendicular to flow line, and this will cause warping or bowing of moulding. The fault will be minimised by the use of a single gate along one edge, by the use of several gates along one edge or by designing a slight dome on the moulding if this is acceptable to the customer. (From ICI Technical Service Note G117, reproduced by permission of ICI Plastics Division)

points (gates) to the mould cavity in order that there be an appropriate symmetry and balance of flow times and molecular orientation to avoid distortion (Figure 9.12).

Resistance to distortion may also be increased by enhancing the stiffness of the product either by introduction of doubly curved surfaces or by the use of ribs (Figure 9.13(a)). In turn this can lead to other problems since the cooling of the melt in the rib section is accompanied by a contraction that pulls in material from the original flat surface, causing sink marks at A. This may be obviated by the use of narrower deeper ribs, or by building a step into the design of the moulding at that point (Figure 9.13(b)).

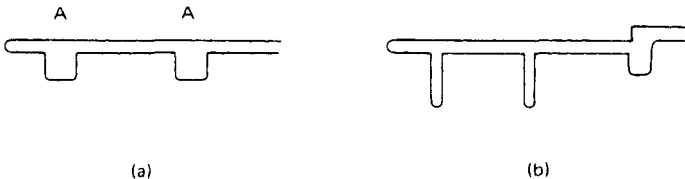


Figure 9.13

Distortion in mouldings can be worse in crystalline polymers than in amorphous plastics. This is because additional stresses may be set up as a result of varying crystallinity from point to point in the moulding so that the shrinkage on cooling from the melt also varies from point to point. This uneven shrinkage sets up stresses which may lead to distortion.

Another common problem on moulding is voids. These occur when a moulding or extrudate cools and hardens rapidly on the surface. On further cooling the moulding or extrudate cannot shrink inward because the outside dimensions are fixed and therefore the molecules are pulled towards the surface of the product, generating internal voids. At the same time molecules in the inner

layers tend to be oriented at right angles to the surface in contradistinction to molecules adjacent to the surface which as a result of the original shaping process have tended to be oriented parallel to the surface.

9.7 CONCLUSIONS

This chapter has attempted to describe briefly some properties of polymers relevant to product design in terms of molecular behaviour. For in depth consideration the reader should consult more detailed reviews (e.g. refs 4, 5 and 6). There also exist specialist monographs concerned with practical aspects of product design (e.g. refs 7 and 11). Mention should also be made of excellent booklets by materials suppliers (e.g. refs 2 and 8) concerned with design aspects. Some material manufactures now supply comprehensive data books backed by computer data bases for multi-point engineering data (e.g. ref. 12).

References

1. VINCENT, P. I., *Impact Tests and Service Performance of Plastics*, Plastics Institute, London (1971)
2. I.C.I. Plastics Division, Technical Science Note G 117 (1970)
3. BRYDSON, J. A., *Flow Properties of Polymer Melts* (2nd Edn), Geo. Godwin, London (1981)
4. NIELSEN, L. E., *Mechanical Properties of Polymers*, Reinhold, New York (1962)
5. JENKINS, A. D. (Ed.), *Polymer Science* Vol. 1 (particularly Chapters 10 and 11), North-Holland, Amsterdam (1972)
6. TURNER, S., *Mechanical Testing of Plastics*, Iliffe, London (1973)
7. BECK, R. D., *Plastic Product Design*, Van Nostrand-Reinhold, New York (1970)
8. General Electric Company (U.S.A.), *Lexan Polycarbonate—Design*
9. WILLIAMS, J. G., *Stress Analysis of Polymers*, Longman, London (1973)
10. WHELAN, A. and CRAFT, J. L., *British Plastics and Rubber*, p. 29 (Nov. 1982)
11. MORTON-JONES, D. H. and ELLIS, J. W., *Polymer Products—Design, Materials and Processing*, Chapman and Hall, London (1986)
12. GENERAL ELECTRIC COMPANY (USA), *Materials Profile*, in conjunction with the computer-based Engineering Design Database (1992)

Bibliography

- BECK, R. D., *Plastic Product Design*, Van Nostrand-Reinhold, New York (1970)
- COLLYER, A. A., *A Practical Guide to the Selection of High Temperature Engineering Thermoplastics*, Elsevier Advanced Technology, London (1990)
- LUCKETT, F. J., *Engineering Design Basis for Plastics Products*, HMSO, London (1981)
- MACDERMOTT, C. P., *Selecting Thermoplastics for Engineering Applications*, Marcel Dekker, New York and Basel (1984)
- MARGOLIS, J. M. (Ed.), *Engineering Thermoplastics*, Marcel Dekker, New York and Basel (1985)
- MORTON-JONES, D. H. and ELLIS, J. W., *Polymer Products—Design, Materials and Processing*, Chapman and Hall, London (1986)
- POWELL, P. C., *Engineering with Polymers*, Chapman and Hall, London (1983)

Polyethylene

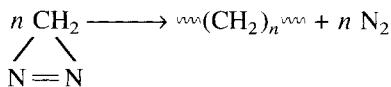
10.1 INTRODUCTION

There are at least three reasons why it is appropriate that the first chapter reviewing individual plastics materials should be concerned with polyethylene. It has the simplest basic structure of any polymer, it is the largest tonnage plastics material, and it is a polymer about which more has probably been written than any other. The main attractive features of polyethylene, in addition to its low price, are excellent electrical insulation properties over a wide range of frequencies, very good chemical resistance, good processability, toughness, flexibility and, in thin films of certain grades, transparency.

It may come as a surprise to the reader that this material which has basically the simplest molecular structure of all polymers should not have an agreed name. In most (English language) scientific publications it is known as polyethylene—an indication that it is a polymer of ethylene. Although it is a specially allowed description, the word ethylene does not accord with the terminology for alkenes (olefins) adopted by the International Union of Pure and Applied Chemistry and which would indicate the word ethene. For this reason the word polyethene is sometimes used, rather more in chemistry text books than in industry. More recently the IUPAC Commission on Macromolecular Nomenclature have recommended that the nomenclature of single-strand organic polymers should be based on the constitutional repeating unit in the structure rather than on the monomer used, and in an Appendix to their rules they recommend the term poly(methylene). As will be seen this has already by common usage come to mean a rather specific polymer obtained from diazomethane. Finally, it is probably still true that many people in the United Kingdom still refer to the material as polythene, the name promoted by the first manufacturers, ICI. For consistency the most widely used term, polyethylene, will be used in this text.

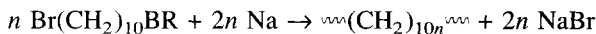
Although polyethylene is virtually defined by its very name as a polymer of ethylene produced by addition polymerisation, linear polymers with the formula $(\text{CH}_2)_n$ have also been prepared by condensation reactions. For example in 1898 von Pechmann¹ produced a white substance from an ethereal solution of

diazomethane on standing. In 1900 Bamberger and Tschirner² analysed a similar product, found it to have the formula $(\text{CH}_2)_n$ and termed it 'polymethylene'. The reaction can be considered to be fundamentally



Since 1900 other methods have been devised for producing 'polymethylene', including the use of boron trifluoride–diethyl ether catalysts at 0°C. Some of these methods give unbranched linear polymers, often of very high molecular weight, which are useful for comparing commercial polyethylenes which have molecules that are branched to varying extents.

Another condensation method was investigated by Carothers and co-workers³ and reported in 1930. They reacted decamethylene dibromide with sodium in a Wurtz-type reaction but found it difficult to obtain polymers with molecular weights above 1300.



Other routes have also been devised which are sometimes useful for research purposes and include:

- (1) Modified Fischer–Tropsch reduction of carbon monoxide with hydrogen.⁴
- (2) Reduction of poly(vinyl chloride) with lithium aluminium hydride.
- (3) Hydrogenation of polybutadiene.

Commercially, polyethylene is produced from ethylene, the polymer being produced by this route in March 1933 and reported verbally by Fawcett in 1935.⁵ The basic patent relating to the polymerisation of ethylene was applied for by ICI⁶ on 4th February 1936 and accepted on 6th September 1937.

Until the mid-1950s all commercial polyethylene was produced by high-pressure processes developed from those described in the basic patent. These materials were somewhat branched materials and of moderate number average molecular weight, generally less than 50 000. However, about 1954 two other routes were developed, one using metal oxide catalysts (e.g. the Phillips process) and the other aluminium alkyl or similar materials (the Ziegler process).⁷ By these processes polymers could be prepared at lower temperature and pressures and with a modified structure. Because of these modifications these polymers had a higher density, were harder and had high softening points. These materials are known as high-density polyethylenes (HDPE), while the earlier materials are known as low-density polyethylenes (LDPE).

At the end of the 1970s considerable interest developed in what became known as linear low density polyethylenes (LLDPE) which are intermediate in properties and structure to the high pressure and low pressure materials. While strictly speaking these are copolymers it is most convenient to consider them alongside the homopolymers. The LLDPE materials were rapidly accepted by industry particularly in the manufacture of film. The very low density polyethylenes (VLDPE) introduced by Union Carbide in 1985 were closely related.

During the 1990s there was enormous activity in the development of a further type of polyethylene based on metallocene catalysis methods. One patent search

revealed that over 950 patent applications had been filed on the subject by the summer of 1996 and has since shown no signs of abating. Commercial production commenced in the late 1990s and it is estimated that in 2000 metallocene-catalysed polyethylenes will comprise about 2% of the total polyethylene market. This is somewhat less spectacular than achieved by LLDPE and reflects the fact that although these materials may have many superior properties in the finished product they are more expensive than the traditional materials and in some respects more difficult to process. Whereas the metallocene polymers can be of LDPE, LLDPE and HDPE types it is anticipated that LLDPE types (referred to as mLLDPE) will take over 50% of the market; mainly for film application.

By the mid-1990s capacity for polyethylene production was about 50 000 000 t.p.a, much greater than for any other type of plastics material. Of this capacity about 40% was for HDPE, 36% for LDPE and about 24% for LLDPE. Since then considerable extra capacity has been or is in the course of being built but at the time of writing financial and economic problems around the world make an accurate assessment of effective capacity both difficult and academic. It is, however, apparent that the capacity data above is not reflected in consumption of the three main types of material where usage of LLDPE is now of the same order as the other two materials. Some 75% of the HDPE and LLDPE produced is used for film applications and about 60% of HDPE for injection and blow moulding.

Polymers of low molecular weight and of very high molecular weight are also available but since they are somewhat atypical in their behaviour they will be considered separately.

10.2 PREPARATION OF MONOMER

At one time ethylene for polymerisation was obtained largely from molasses, a by-product of the sugar industry. From molasses may be obtained ethyl alcohol and this may be dehydrated to yield ethylene. Today the bulk of ethylene is obtained from petroleum sources. When supplies of natural or petroleum gas are available the monomer is produced in high yield by high-temperature cracking of ethane and propane. Good yields of ethylene may also be obtained if the gasoline ('petrol') fraction from primary distillation of oil is 'cracked'. The gaseous products of the reaction include a number of lower alkanes and olefins and the mixture may be separated by low-temperature fractional distillation and by selective absorption. Olefins, in lower yield, are also obtained by cracking gas oil. At normal pressures (760 mmHg) ethylene is a gas boiling at -103.71°C and it has a very high heat of polymerisation (3350–4185 J/g). In polymerisation reactions the heat of polymerisation must be carefully controlled, particularly since decomposition reactions that take place at elevated temperatures are also exothermic and explosion can occur if the reaction gets out of control.

Since impurities can affect both the polymerisation reaction and the properties of the finished product (particularly electrical insulation properties and resistance to heat aging) they must be rigorously removed. In particular, carbon monoxide, acetylene, oxygen and moisture must be at a very low level. A number of patents require that the carbon monoxide content be less than 0.02%.

It was estimated in 1997 that by the turn of the century 185 million tonnes of ethylene would be consumed annually on a global basis but that at the same time production of polyethylene would be about 46 000 000 t.p.a., i.e. about 25% of the total. This emphasises the fact that although polyethylene manufacture is a large outlet for ethylene the latter is widely used for other purposes.

10.3 POLYMERISATION

There are five quite distinct routes to the preparation of high polymers of ethylene:

- (1) High-pressure processes.
- (2) Ziegler processes.
- (3) The Phillips process.
- (4) The Standard Oil (Indiana) process.
- (5) Metallocene processes.

10.3.1 High-pressure Polymerisation

Although there are a number of publications dealing with the basic chemistry of ethylene polymerisation under high pressure, little information has been made publicly available concerning details of current commercial processes. It may however be said that commercial high polymers are generally produced under conditions of high pressure (1000–3000 atm) and at temperatures of 80–300°C. A free-radical initiator such as benzoyl peroxide, azodi-isobutyronitrile or oxygen is commonly used. The process may be operated continuously by passing the reactants through narrow-bore tubes or through stirred reactors or by a batch process in an autoclave. Because of the high heat of polymerisation care must be taken to prevent runaway reaction. This can be done by having a high cooling surface–volume ratio in the appropriate part of a continuous reactor and in addition by running water or a somewhat inert liquid such as benzene (which also helps to prevent tube blockage) through the tubes to dilute the exotherm. Local runaway reactions may be prevented by operating at a high flow velocity. In a typical process 10–30% of the monomer is converted to polymer. After a polymer–gas separation the polymer is extruded into a ribbon and then granulated. Film grades are subjected to a homogenisation process in an internal mixer or a continuous compounder machine to break up high molecular weight species present.

Although in principle the high-pressure polymerisation of ethylene follows the free-radical-type mechanism discussed in Chapter 2 the reaction has two particular characteristics, the high exothermic reaction and a critical dependence on the monomer concentration.

The highly exothermic reaction has already been mentioned. It is particularly important to realise that at the elevated temperatures employed other reactions can occur leading to the formation of hydrogen, methane and graphite. These reactions are also exothermic and it is not at all difficult for the reaction to get out of hand. It is necessary to select conditions favourable to polymer formation and which allow a controlled reaction.

Most vinyl monomers will polymerise by free-radical initiation over a wide range of monomer concentration. Methyl methacrylate can even be polymerised

by photosensitised catalysts in the vapour phase at less than atmospheric pressure. In the case of ethylene only low molecular weight polymers are formed at low pressures but high molecular weights are possible at high pressures. It would appear that growing ethylene polymer radicals have a very limited life available for reaction with monomer. Unless they have reacted within a given interval they undergo changes which terminate their growth. Since the rate of reaction of radical with monomer is much greater with higher monomer concentration (higher pressure) it will be appreciated that the probability of obtaining high molecular weights is greater at high pressures than at low pressures.

At high reaction temperatures (e.g. 200°C) much higher pressures are required to obtain a given concentration or density of monomer than at temperatures of say 25°C and it might appear that better results would be obtained at lower reaction temperatures. This is in fact the case where a sufficiently active initiator is employed. This approach has an additional virtue in that side reactions leading to branching can be suppressed. For a given system the higher the temperature the faster the reaction and the lower the molecular weight.

By varying temperature, pressure, initiator type and composition, by incorporating chain transfer agents and by injecting the initiator into the reaction mixture at various points in the reactor it is possible to vary independently of each other polymer characteristics such as branching, molecular weight and molecular weight distribution over a wide range without needing unduly long reaction times. In spite of the flexibility, however, most high-pressure polymers are of the lower density range for polyethylenes (0.915–0.94 g/cm³) and usually also of the lower range of molecular weights.

10.3.2 Ziegler Processes

As indicated by the title, these processes are largely due to the work of Ziegler and coworkers. The type of polymerisation involved is sometimes referred to as co-ordination polymerisation since the mechanism involves a catalyst–monomer co-ordination complex or some other directing force that controls the way in which the monomer approaches the growing chain. The co-ordination catalysts are generally formed by the interaction of the alkyls of Groups I–III metals with halides and other derivatives of transition metals in Groups IV–VIII of the Periodic Table. In a typical process the catalyst is prepared from titanium tetrachloride and aluminium triethyl or some related material.

In a typical process ethylene is fed under low pressure into the reactor which contains liquid hydrocarbon to act as diluent. The catalyst complex may be first prepared and fed into the vessel or may be prepared *in situ* by feeding the components directly into the main reactor. Reaction is carried out at some temperatures below 100°C (typically 70°C) in the absence of oxygen and water, both of which reduce the effectiveness of the catalyst. The catalyst remains suspended and the polymer, as it is formed, becomes precipitated from the solution and a slurry is formed which progressively thickens as the reaction proceeds. Before the slurry viscosity becomes high enough to interfere seriously with removing the heat of reaction, the reactants are discharged into a catalyst decomposition vessel. Here the catalyst is destroyed by the action of ethanol, water or caustic alkali. In order to reduce the amount of metallic catalyst fragments to the lowest possible values, the processes of catalyst decomposition, and subsequent purification are all important, particularly where the polymer is intended for use in high-frequency electrical insulation.

A number of variations in this stage of the process have been described in the literature.

The Ziegler polymers are intermediate in density (about 0.945 g/cm^3) between the high-pressure polyethylenes and those produced by the Phillips and Standard Oil (Indiana) processes. A range of molecular weights may be obtained by varying the Al-Ti ratio in the catalyst, by introducing hydrogen as a chain transfer agent and by varying the reaction temperature.

Over the years, considerable improvements and extensions of the Ziegler process have taken place. One such was the advent of metallocene single-site catalyst technology in the late 1980s. In these systems the olefin only reacts at a single site on the catalyst molecules and gives greater control over the process. One effect is the tendency to narrower molecular weight distributions. In a further extension of this process Dow in 1993 announced what they refer to as *constrained geometry homogeneous catalysts*. The catalyst is based on Group IV transition metals such as titanium, covalently bonded to a monocyclopentadiene group bridged with a heteroatom such as nitrogen. The catalyst is activated by strong Lewis acid systems. These systems are being promoted particularly for use with linear low-density polyethylene (see Section 10.3.5).

10.3.3 The Phillips Process

In this process ethylene, dissolved in a liquid hydrocarbon such as cyclohexane, is polymerised by a supported metal oxide catalyst at about $130\text{--}160^\circ\text{C}$ and at about $200\text{--}500 \text{ lbf/in}^2$ ($1.4\text{--}3.5 \text{ MPa}$) pressure. The solvent serves to dissolve polymer as it is formed and as a heat transfer medium but is otherwise inert.

The preferred catalyst is one which contains 5% of chromium oxides, mainly CrO_3 , on a finely divided silica-alumina catalyst (75–90% silica) which has been activated by heating to about 250°C . After reaction the mixture is passed to a gas-liquid separator where the ethylene is flashed off, catalyst is then removed from the liquid product of the separator and the polymer separated from the solvent by either flashing off the solvent or precipitating the polymer by cooling.

Polymers ranging in melt flow index (an inverse measure of molecular weight) from less than 0.1 to greater than 600 can be obtained by this process but commercial products have a melt flow index of only 0.2–5 and have the highest density of any commercial polyethylenes ($\sim 0.96 \text{ g/cm}^3$).

The polymerisation mechanism is largely unknown but no doubt occurs at or near the catalyst surface where monomer molecules are both concentrated and specifically oriented so that highly stereospecific polymers are obtained. It is found that the molecular weight of the product is critically dependent on temperature and in a typical process there is 40-fold increase in melt flow index, and a corresponding decrease in molecular weight, in raising the polymerisation temperature from 140°C to just over 170°C . Above 400 lbf/in^2 (2.8 MPa) the reaction pressure has little effect on either molecular weight or polymer yield but at lower pressures there is a marked decrease in yield and a measurable decrease in molecular weight. The catalyst activation temperature also has an effect on both yield and molecular weight. The higher the activation temperature the higher the yield and the lower the molecular weight. A number of materials including oxygen, acetylene, nitrogen and chlorine are catalyst poisons and very pure reactants must be employed.

In a variation of the process polymerisation is carried out at about $90\text{--}100^\circ\text{C}$, which is below the crystalline melting point and at which the polymer has a low

solubility in the solvent. The polymer is therefore formed and removed as a slurry of granules each formed around individual catalyst particles. High conversion rates are necessary to reduce the level of contamination of the product with catalyst and in addition there are problems of polymer accumulation on reactor surfaces. Because of the lower polymerisation temperatures, polymers of higher molecular mass may be prepared.

10.3.4 Standard Oil Company (Indiana) Process

This process has many similarities to the Phillips process and is based on the use of a supported transition metal oxide in combination with a promoter. Reaction temperatures are of the order of 230–270°C and pressures are 40–80 atm. Molybdenum oxide is a catalyst that figures in the literature and promoters include sodium and calcium as either metals or as hydrides. The reaction is carried out in a hydrocarbon solvent.

The products of the process have a density of about 0.96 g/cm³, similar to the Phillips polymers. Another similarity between the processes is the marked effect of temperature on average molecular weight. The process is worked by the Furukawa Company of Japan and the product marketed as Staflen.

10.3.5 Processes for Making Linear Low-density Polyethylene and Metallocene Polyethylene

Over the years many methods have been developed in order to produce polyethylenes with short chain branches but no long chain branches. Amongst the earliest of these were a process operated by Du Pont Canada and another developed by Phillips, both in the late 1950s. More recently Union Carbide have developed a gas phase process. Gaseous monomers and a catalyst are fed to a fluid bed reactor at pressures of 100–300 lbf/in² (0.7–2.1 MPa) at temperatures of 100°C and below. The short branches are produced by including small amounts of propene, but-1-ene, hex-1-ene or oct-1-ene into the monomer feed. Somewhat similar products are produced by Dow using a liquid phase process, thought to be based on a Ziegler-type catalyst system and again using higher alkenes to introduce branching.

As mentioned in Section 10.3.2, there has been recent interest in the use of the Dow constrained geometry catalyst system to produce linear low-density polyethylenes with enhanced properties based, particularly, on ethylene and oct-1-ene.

LLDPE materials are now available in a range of densities from around 0.900 g/cm³ for VLDPE materials to 0.935 g/cm³ for ethylene–octene copolymers. The bulk of materials are of density approx. 0.920 g/cm³ using butene in particular as the comonomer.

In recent years the market for LLDPE has increased substantially and is now more than half the total for LDPE and for HDPE.

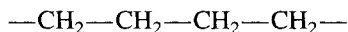
Mention has already been made in this chapter of metallocene-catalysed polyethylene (see also Chapter 2). Such metallocene catalysts are transition metal compounds, usually zirconium or titanium, incorporated into a cyclopentadiene-based structure. During the late 1990s several systems were developed where the new catalysts could be employed in existing polymerisation processes for producing LLDPE-type polymers. These include high pressure autoclave and

solution processes as well as gas phase processes. At the present time it remains to be seen what methods will become predominant.

Mention may also be made of catalyst systems based on iron and cobalt announced in 1998 by BP Chemicals working in collaboration with Imperial College London and, separately, by DuPont working in collaboration with the University of North Carolina. The DuPont/UNC catalysts are said to be based on tridentate pyridine *bis*-imine ligands coordinated to iron and cobalt. These are capable of polymerising ethylene at low pressures (200–600 psi) yielding polymers with very low branching (0.4 branches per 1000 carbon atoms) and melting points as high as 139°C. The BP/ICL team claim that their system provides many of the advantages of metallocenes but at lower cost.

10.4 STRUCTURE AND PROPERTIES OF POLYETHYLENE

The relationship between structure and properties of polyethylene is largely in accord with the principles enunciated in Chapters 4, 5 and 6. The polymer is essentially a long chain aliphatic hydrocarbon of the type



and would thus be thermoplastic. The flexibility of the C—C bonds would be expected to lead to low values for the glass transition temperature. The T_g , however, is associated with the motion of comparatively long segments in amorphous matter and since in a crystalline polymer there is only a small number of such segments the T_g has little physical significance. In fact there is considerable argument as to the position of the T_g , and amongst the values quoted in the literature are -130°C , -120°C , -105°C , -93°C , -81°C , -77°C , -63°C , -48°C , -30°C , -20°C and $+60^\circ\text{C}$! In one publication Kambour and Robertson and the author* independently concluded that -20°C was the most likely value for the T_g . Such a value, however, has little technological significance. This comment also applies to another transition at about -120°C which is currently believed to arise from the Schatzki crankshaft effect. Far more important is the crystalline melting point T_m , which is usually in the range $108\text{--}132^\circ\text{C}$ for commercial polymers, the exact value depending on the detailed molecular structure. Such low values are to be expected of a structure with a flexible backbone and no strong intermolecular forces. Some data on the crystalline structure of polyethylene are summarised in *Table 10.1*. There are no strong intermolecular forces and most of the strength of the polymer is due to the fact that crystallisation allows close molecular packing. The high crystallinity also leads to opaque structures except in the case of rapidly chilled film where the development of large crystalline structures is prevented.

Polyethylene, in essence a high molecular weight alkane (paraffin), would be expected to have a good resistance to chemical attack and this is found to be the case.

The polymer has a low cohesive energy density (the solubility parameter δ is about $16.1 \text{ MPa}^{1/2}$) and would be expected to be resistant to solvents of solubility parameter greater than $18.5 \text{ MPa}^{1/2}$. Because it is a crystalline material and does

* JENKINS, A. D. (Ed.), *Polymer Science*, North-Holland, Amsterdam (1972).

Table 10.1 Crystallinity data for polyethylene

Molecular disposition	planar zigzag
Unit cell dimensions	$a = 7.36 \text{ \AA}$ $b = 4.92 \text{ \AA}$ $c = 2.54 \text{ \AA}$
Cell density (unbranched polymer) (25°C)	1.014
Amorphous density (20°C)	0.84

not enter into specific interaction with any liquids, there is no solvent at room temperature. At elevated temperatures the thermodynamics are more favourable to solution and the polymer dissolves in a number of hydrocarbons of similar solubility parameter.

The polymer, in the absence of impurities, would also be expected to be an excellent high-frequency insulator because of its non-polar nature. Once again, fact is in accord with prediction.

At the present time there are available many hundreds of grades of polyethylene, most of which differ in their properties in one way or another. Such differences arise from the following variables:

- (1) Variation in the degree of short chain branching in the polymer.
- (2) Variation in the degree of long chain branching.
- (3) Variation in the average molecular weight.
- (4) Variation in the molecular weight distribution (which may in part depend on the long chain branching).
- (5) The presence of a small amount of comonomer residues.
- (6) The presence of impurities or polymerisation residues, some of which may be combined with the polymer.

Further variations can also be obtained by compounding and cross-linking the polymer but these aspects will not be considered at this stage.

Possibilities of *branching* in high-pressure polyethylenes were first expressed when investigation using infrared spectroscopy indicated that there were about 20–30 methyl groups per 1000 carbon atoms. Therefore in a polymer molecule of molecular weight 26 000 there would be about 40–60 methyl groups, which is of course far in excess of the one or two methyl groups to be expected from normal chain ends. More refined studies have indicated that the methyl groups are probably part of ethyl and butyl groups. The most common explanation is that these groups arise owing to a ‘back-biting’ mechanism during polymerisation (*Figure 10.1*).

Polymerisation could proceed from the radical in the normal way or alternatively chain transfer may occur by a second back-biting stage either to the butyl group (*Figure 10.2(a)*) or to the main chain (*Figure 10.2(b)*).

According to this scheme a third back-bite is also possible (*Figure 10.3*). In the first stage a tertiary radical is formed which could then depolymerise by β -scission. This will generate vinylidene groups, which have been observed and found to provide about 50% of the unsaturation in high-pressure polymers, the rest being about evenly divided by vinyl and in-chain *trans* double bonds. (There may be up to about three double bonds per 1000 carbon atoms.)

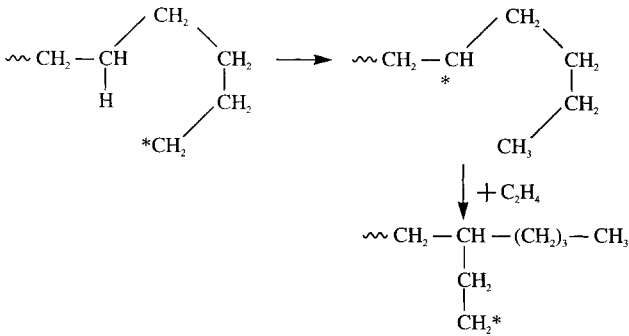


Figure 10.1

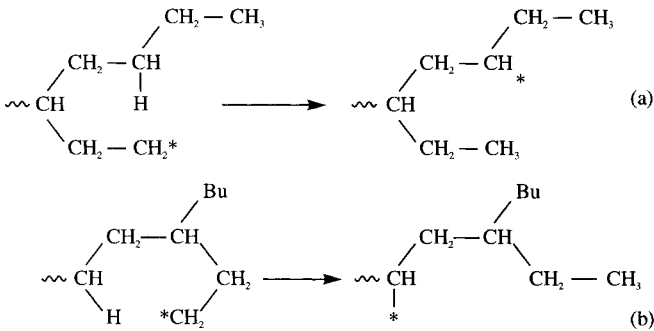


Figure 10.2. (a) Transfer to the butyl group. (b) Transfer to the main chain

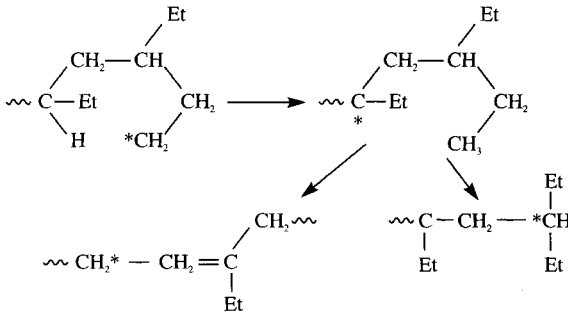


Figure 10.3

Short chain branching is negligible with Ziegler and Phillips homopolymers although it is possible to introduce deliberately up to about seven ethyl side chains per 1000 carbon atoms in the Ziegler polymers.

The presence of these branch points is bound to interfere with the ease of crystallisation and this is clearly shown in differences between the polymers. The branched high-pressure polymers have the lowest density (since close-packing due

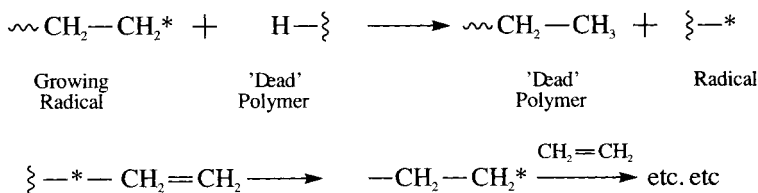


Figure 10.4

to crystallisation is reduced), the least opacity (since the growth of large crystalline structures is impeded) and a lower melting point, yield point, surface hardness and Young's modulus in tension (these properties being dependent on the degree of crystallinity). In addition the more the branching and the lower the crystallinity, the greater will be the permeability to gases and vapours. For general technological purposes the *density* of the polyethylene (as prepared from the melt under standard conditions) is taken as a measure of short chain branching.

In addition to the short chain branches there is some evidence in high-pressure polyethylenes for the presence per chain of a few long branches which are probably several tens of carbon atoms long. These probably arise from the transfer mechanism during polymerisation shown in Figure 10.4. Such side chains may be as long as the original main chain and like the original main chain will produce a wide distribution of lengths. It is therefore possible to obtain fairly short chains grafted on to short main chains, long side chains on to long main chains and a wide variety of intermediate situations.

In addition, subsequent chain transfer reactions may occur on side chains and the larger the resulting polymer, the more likely will it be to be attacked. These features tend to cause a wide molecular weight distribution for these materials and it is sometimes difficult to check whether an effect is due inherently to a wide molecular weight distribution or simply due to long chain branching.

One further effect of long chain branches is on flow properties. Unbranched polymers have higher melt viscosities than long-branched polymers of similar weight average molecular weight. This would be expected since the long-branched molecules would be more compact and be expected to entangle less with other molecules.

The more recently developed so-called linear low-density polyethylenes are virtually free of long chain branches but do contain short side chains as a result of copolymerising ethylene with a smaller amount of a higher alkene such as oct-1-ene. Such branching interferes with the ability of the polymer to crystallise as with the older low-density polymers and like them have low densities. The word linear in this case is used to imply the absence of long chain branches.

For reference purposes the polymer produced from diazomethane is particularly useful in that it is free from both long and short branches and apart from the end groups consists only of methylene groups. This material is generally known as polymethylene, which is also the name now being recommended by IUPAC to describe polyethylenes in general. The diazomethane polymer has the highest density of this family of materials, it being about 0.98 g/cm^3 . Copolymerisation with diazoethane and higher homologues provides an alternative method for producing a polymer with short chains but with no long ones.

Differences in *molecular weight* will also give rise to differences in properties. The higher the molecular weight, the greater the number of points of attraction and

entanglement between molecules. Whereas differences in short chain branching and hence degree of crystallinity largely affect properties characterised by small solid displacement, molecular weight differences will affect properties that involve large deformations such as ultimate tensile strength, elongation at break, melt viscosity and low-temperature brittle point. There is also an improvement in resistance to environmental stress cracking with increase in molecular weight.

Before the advent of Ziegler and Phillips polymers it was common practice to characterise the molecular weight for technological purposes by the *melt flow index* (MFI), the weight in grams extruded under a standard load in a standard plastometer at 190°C in 10 minutes. This test had also proved useful for quality control and as a very rough guide to processability. From measurements of MFI various workers have calculated the apparent viscosity of the polymer and correlated these figures with both number average and weight average molecular weight. (It should be noted that estimation of apparent viscosities from melt flow index data is rather hazardous since large corrections have to be made for end effects, pressure losses in the main cylinder and friction of the plunger. It would be better to use a high shear viscometer designed to minimise the sources of error and to compare results at equal shear rate.) Suffice it to say that the higher the melt flow index, the lower the molecular weight.

With the availability of the higher density polymers the value of the melt flow index as a measure of molecular weight diminishes. For example, it has been found⁸ that with two polymers of the same weight average molecular weight (4.2×10^5), the branched polymer (density = 0.92 g/cm³) had only 1/50 the viscosity of the more or less unbranched polymer (density = 0.96 g/cm³). This is due to long chain branches as explained above.

Commercial polyethylenes also vary in their *molecular weight distribution* (MWD). Whilst for some purposes a full description of the distribution is required, the ratio of weight average molecular weight to number average molecular weight ($\overline{M}_w/\overline{M}_n$) provides a useful parameter. Its main deficiency is that it provides no information about any unusual high or low molecular weight tail which might have profound significance. For polymethylenes the ratio is about 2 whilst with low-density polymers values varying from 1.9 to 100 have been reported with values of 20–50 being said to be typical. High-density polymers have values of 4–15.

The very high figures for low-density materials are in part a result of long chain branching and, as has already been stated, it is sometimes not clear if an effect is due to branching or to molecular weight distribution. It is generally considered, however, that with other structural factors constant a decrease in $\overline{M}_w/\overline{M}_n$ leads to an increase in impact strength, tensile strength, toughness, softening point and resistance to environmental stress cracking. There is also a pronounced influence on melt flow properties, the narrower distribution materials being less sensitive to shear rate but more liable to sharkskin effects.

The general principles outlined in the previous paragraph (which has been unchanged since the first edition of this book) have been found to be particularly relevant for the metallocene polyethylenes being introduced in the late 1990s. These have $\overline{M}_w/\overline{M}_n$ ratios in the range 2–3 and while they do exhibit enhanced toughness they show higher melt viscosities at high shear rates than corresponding traditional polymers and suffer from problems with melt defects.

Much of recent development in polymerisation technology has been devoted to establishing control of the MWD of LLDPE polymers. With such polymers, narrowing the MWD confers higher toughness, greater clarity, lower heat seal

initiation temperatures and, where this is important, higher cross-link efficiency. As with LDPE there is lower melt shear sensitivity and poorer melt strength. Catalyst systems have been used which result in polymers with a bimodal (double-peaked) molecular weight distribution in an attempt to improve flow properties, whilst another approach combines the use of polymers with narrow molecular weight distribution but with a broad side-chain length distribution.

A number of *comonomers* have been used in conjunction with ethylene. Such comonomers are either hydrocarbons such as propylene or but-1-ene non-hydrocarbons such as vinyl acetate. Small amounts of a second alkene are sometimes used to produce a controlled degree of short chain branching and some retardation in the growth of large crystal structures. As will be described in the next chapter, copolymers of this type produced by the Phillips process have better creep, environmental stress cracking and thermal cracking resistance than the corresponding homopolymer. The use of hydrocarbon comonomers such as oct-1-ene became very common with the development of LLDPE and this approach is also being used with metallocene polyethylenes. Properties of metallocene polyethylenes such as low density (cf. standard homopolymers), lower melt temperatures, clarity and heat sealability would be expected to be more related to the presence of copolymers than the narrow molecular weight distribution (which has a more significant effect on toughness and melt flow properties). Small amounts of vinyl acetate also impede crystallisation and, as with the alkene copolymers, substantial amounts of the second comonomer lead to rubbery materials.

The final variable to be mentioned here is the presence of impurities. These may be metallic fragments residual from Ziegler-type processes or they can be trace materials incorporated into the polymer chain. Such impurities as catalyst fragments and carbonyl groups incorporated into the chain can have a serious adverse influence on the power factor of the polymer, whilst in other instances impurities can have an effect on aging behaviour.

10.5 PROPERTIES OF POLYETHYLENE

Polyethylene is a wax-like thermoplastic softening at about 80–130°C with a density less than that of water. It is tough but has moderate tensile strength, is an excellent electrical insulator and has very good chemical resistance. In the mass it is translucent or opaque but thin films may be transparent.

10.5.1 Mechanical Properties

The mechanical properties are very dependent on the molecular weight and on the degree of branching of the polymer. As with other polymers these properties are also dependent on the rate of testing, the temperature of test, the method of specimen preparation, the size and shape of the specimen and, to only a small degree with polyethylene, the conditioning of samples before testing. The data in *Table 10.2*, although not all obtained from the same source, has been obtained using only one test method for each property. The figures given show clearly the general effects of branching (density) and molecular weight on some polymer properties but it should be remembered that under different test conditions different results may be obtained. It should also be remembered that polymers of different density but with the same melt flow index do not have the same molecular weight. The general effects of changing rate of testing, temperature

Table 10.2 Effect of molecular weight and density (branching) on some mechanical and thermal properties of polyethylene

Property	Test	Density $\approx 0.92 \text{ g/cm}^3$ (high-pressure polymers)					Density $\approx 0.94 \text{ g/cm}^3$ high-pressure polymers	Density $\approx 0.95 \text{ g/cm}^3$ Ziegler-type polymers			Density $\approx 0.96 \text{ g/cm}^3$ Phillips-type polymers	Density $\approx 0.98 \text{ g/cm}^3$ polymethylene
		0.3	2	7	20	70		0.02	0.2	1.5		
Melt flow index	BS2782	0.3	2	7	20	70	0.7	0.02	0.2	1.5	—	—
Tensile strength (lbf/in ²)	BS903	2200	1800	1500	1300	—	3000	3200†	3350†	3350†	~4000	~5000
(MPa)		15.3	12.5	10.2	8.9	—	20.7	22.0	23.0	23.0	~27.5	~34.5
Elongation at break (%)	BS903	620	600	500	300	150	—	>800	380	20	500	~500
Izod impact strength (ft lbf)	BS2782	~10	~10	~10	~10	~10	—	3.2	2.0	1.5	5.0	—
(J)		~13.5	~13.5	~13.5	~13.5	~13.5	—	4.3	2.7	2.0	6.8	—
Vicat softening point (°C)	BS2782	98	90	85	81	77	116	124	122	121	—	—
Softening temperature (°C)	BS1493	—	—	—	—	—	—	110	110	106	122	—
Crystalline melting point (°C)	—	~108	~108	~108	~108	~108	125	~130	~130	~130	~133	136
Number average molecular weight	—	48 000	32 000	28 000	24 000	20 000	—	—	—	—	—	—
CH ₃ groups per 1000 C atoms	—	20	23	28	31	33	—	5-7	5-7	5-7	<1.5	unbranched

† Yield strength

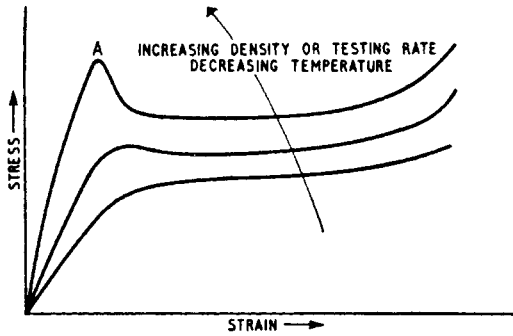


Figure 10.5. Effect of polymer density, testing rate and temperature on the shape of the stress-strain curve for polyethylene⁹

and density on the tensile stress-strain curves are shown schematically in *Figure 10.5*. It is seen in particular that as the test temperature is lowered or the testing rate increased, a pronounced ‘hump’ in the curve becomes apparent, the apex of the hump A being the yield point. Up to the yield point deformations are recoverable and the polymer is almost Hookean in its behaviour. The working of the sample, however, causes ‘strain softening’ by, for example, spherulite breakdown or in some cases by crystal melting so that the polymer extends at constant stress. This cold drawing, however, causes molecular orientation and induces crystallisation so that there is a stiffening of the sample and an upward sweep of the stress-strain curve. The effect of temperature on a sample of low-density polyethylene with an MFI of 2 is shown in *Figure 10.6*. The varying influence of rate of strain on tests results can be clearly shown from figures obtained with two commercial polyethylene samples (*Table 10.3*). It is seen that in one case an increase in rate of strain is accompanied by increase in tensile strength and in the other case, reduction.

Table 10.3 Effect of straining rate on the measured tensile strength and elongation at break of two samples of polyethylene

Rate of strain (in/min)	Tensile strength (MPa)	
	Polymer A	Polymer B
6	18.48	11.03
12	18.96	10.90
18	20.00	10.34
30	22.07	9.66
	Elongation at break (%)	
6	380	450
12	300	490
18	200	490
30	180	500

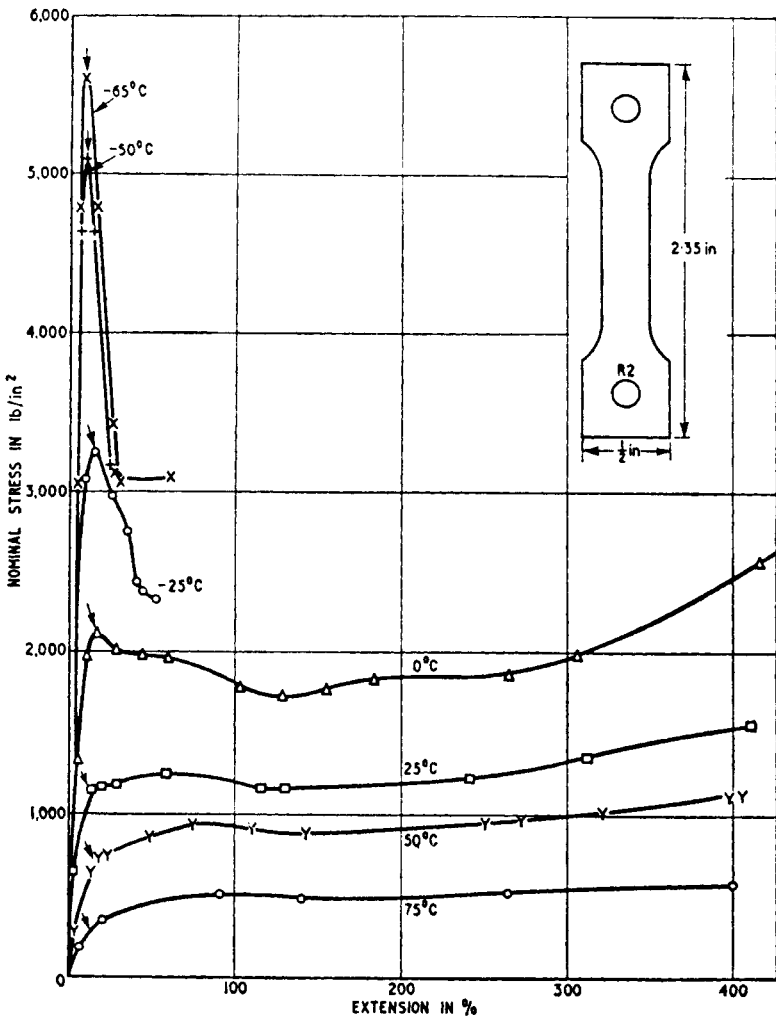


Figure 10.6. Effect of temperature on the tensile stress-strain curve for polyethylene. (Low-density polymer $\sim 0.92 \text{ g/cm}^3$, MFI = 2.) Rate of extension 190% per minute¹⁰

The elongation at break of polyethylene is strongly dependent on density (Figure 10.7), the more highly crystalline high-density materials being less ductile. This lack of ductility results in high-density polymers tending to be brittle, particularly with low molecular weight materials. The tough-brittle dependence on melt flow index and density is shown in Figure 10.8.

Under load polyethylene will deform continuously with time ('creep'). A knowledge of creep behaviour is important when considering load-bearing applications, water piping being a case in point with polyethylene. In general there will be an increase in creep with increased load, increased temperature and decreased density. A large amount of creep data has been made available in specialised monographs and in trade literature.

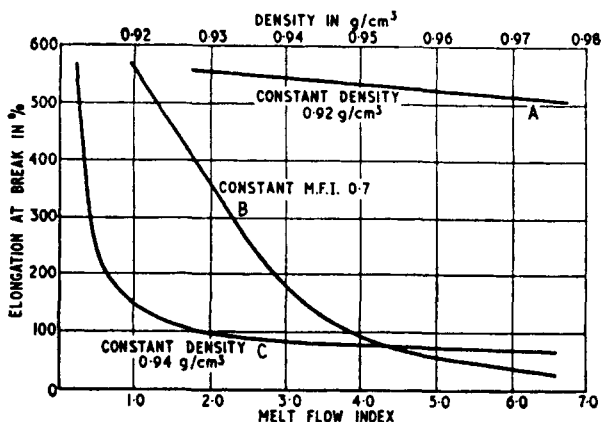


Figure 10.7. Effect of density and melt flow index on elongation at break. (Separation rate 45 cm/min on specimen of 1 in gauge length.) A, constant density (0.92 g/cm^3). B, constant MFI (0.7). C, constant density (0.94 g/cm^3).⁹ (Reproduced by permission of ICI)

10.5.2 Thermal Properties

As mentioned in Section 10.4 there are conflicting data on the position of the T_g of polyethylene. It is the author's belief that a transition at about -20°C is probably the true T_g but another transition at about -120°C is also to be observed. Tough at room temperature, the polymers become brittle on cooling but some specimens do not appear to become brittle until temperatures as low as -70°C have been reached. In general the higher the molecular weight and the more the branching the lower the brittle point. Measured brittle points also depend on the method of sample preparation, thus indicating that the polymer is notch sensitive, i.e. sensitive to surface imperfections.

The specific heat of polyethylene is higher than for most thermoplastics and is strongly dependent on temperature. Low-density materials have a value of about 2.3 J/g at room temperature and a value of 2.9 J/g at $120\text{--}140^\circ\text{C}$. A somewhat schematic representation is given in Figure 10.9. The peaks in these curves may

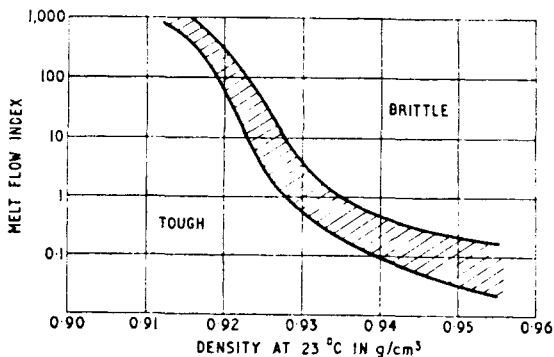


Figure 10.8. Effects of melt flow index and density on the room temperature tough-brittle transition of polyethylene.⁹ (Reproduced by permission of ICI)

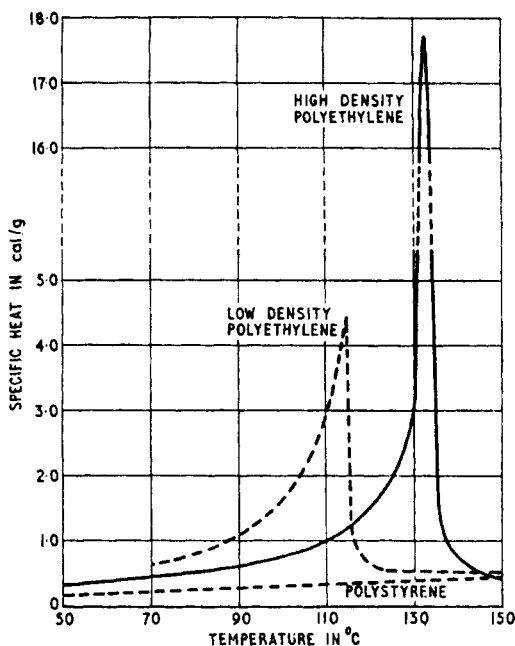


Figure 10.9. Specific heat-temperature relationships for low-density polyethylene, high-density polyethylene and polystyrene.¹¹ (The Distillers Company Ltd.)

be considered to be due to a form of latent heat of fusion of the crystalline zones. Melting point (T_m) data are given in Table 10.2 and the T_m is seen to vary with density.

Flow properties of polyethylene have been widely studied. Because of the wide range of average molecular weights amongst commercial polymers the viscosities vary widely. The most commonly used materials, however, have viscosities lower than for unplasticised PVC and poly(methyl methacrylate) and higher than for the nylons.

Typical of thermoplastics (see Chapter 8) the melts are pseudoplastic and also in common with most thermoplastics the zero shear rate apparent viscosity of linear polyethylene is related to the weight average molecular weight by the relationship

$$\log (\eta_{a,0}) = K + 3.4 \log \bar{M}_w$$

for polymers with a molecular weight in excess of about 5000.

Polymers with long branches do *not* fit these equations and different relations exist with polymers of different degrees of long branching. In many cases the equation

$$\log (\eta_{a,0}) = A + B\bar{M}_n^{1/2}$$

gives a good fit to the data.

It is interesting to note that so-called linear low-density polyethylenes are said to be less pseudoplastic than conventional low-density polyethylenes. Thus on

comparing the two materials at the same melt flow index the ‘linear’ polymer will be found to be more viscous at the higher shear rates usually encountered during processing.

As usual, an increase in temperature reduces melt viscosity and equations of the type discussed in Chapter 8 fit data very well. Melt processing is usually carried out in the range 150–210°C but temperatures as high as 300°C may be used in some paper-coating applications. In an inert atmosphere the polymer is stable at temperatures up to 300°C so that the high processing temperatures do not lead to severe problems due to degradation, providing contact of the melt with oxygen is reduced to a minimum.

The elastic melt effects mentioned briefly in Chapter 8 are commonly encountered with polyethylene. Some typical experimental results on die swell are shown in *Figure 8.8*. The phenomenon of elastic turbulence (waviness, bambooning, melt fracture) is also observed in low-temperature processes (e.g. bottle blowing) and when extruding at very high rates (wire covering). This situation is generally aggravated by high molecular weights and low temperature but reduced by long chain branching and increasing the molecular weight distribution.

Table 10.4 Effect of polymer structure on flow properties

<i>Effect of increase of</i>	<i>On viscosity</i>	<i>On flow behaviour index</i>	<i>On critical shear rate</i>	<i>On sharkskin</i>
Branching (long)	decreases	little effect	increases	?
Molecular weight	increases	slightly decreases	decreases	?
Mol. Wt. distribution	decreases	decreases	increases	decreases

In addition to elastic turbulence (characterised by helical deformation) another phenomenon known as ‘sharkskin’ may be observed. This consists of a number of ridges transverse to the extrusion direction which are often just barely discernible to the naked eye. These often appear at lower shear rates than the critical shear rate for elastic turbulence and seem more related to the linear extrudate output rate, suggesting that the phenomenon may be due to some form of slip-stick at the die exit. It appears to be temperature dependent (in a complex manner) and is worse with polymers of narrow molecular weight distribution.

Melt elasticity is of considerable importance in understanding much of the behaviour of polyethylene when processing by film extrusion techniques and when blow moulding. The complex relationships observed experimentally here have been summarised by the author elsewhere.¹²

10.5.3 Chemical Properties

The chemical resistance of polyethylene is, to a large measure, that expected of an alkane. It is not chemically attacked by non-oxidising acids, alkalis and many aqueous solutions. Nitric acid oxidises the polymer, leading to a rise in power factor and to a deterioration in mechanical properties. As with the simple alkanes, halogens combine with the hydrocarbon by means of substitution mechanisms.

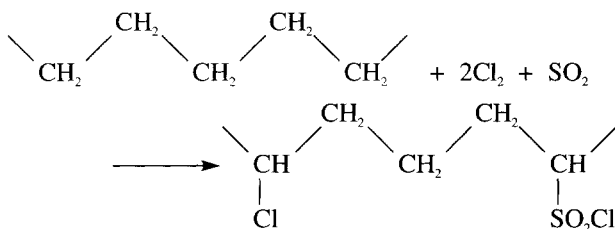


Figure 10.10

When polyethylene is chlorinated in the presence of sulphur dioxide, sulphonyl chloride as well as chlorine groups may be incorporated into the polymer (Figure 10.10). This reaction is used to produce a useful elastomer (Hypalon, see Chapter 11).

Oxidation of polyethylene which leads to structural changes can occur to a measurable extent at temperatures as low as 50°C. Under the influence of ultraviolet light the reaction can occur at room temperature. The oxidation reactions can occur during processing and may initially cause a reduction in melt viscosity. Further oxidation can cause discolouration and streaking and in the case of polymers rolled for 1–2 hours on a two-roll mill at about 150°C the product becomes ropey and incapable of flow. It is rare that such drastic operating conditions occur but it is found that at a much earlier stage in the oxidation of the polymer there is a serious deterioration in power factor and for electrical insulation applications in particular it is necessary to incorporate antioxidants. It is to be expected that the less branched high-density polyethylene, because of the smaller number of tertiary carbon atoms, would be more resistant to oxidation. That this is not always the case has been attributed to residual metallic impurities, since purer samples of high-density polymers are somewhat superior to the low-density materials.

Since polyethylene is a crystalline hydrocarbon polymer incapable of specific interaction and with a melting point of about 100°C, there are no solvents at room temperature. Low-density polymers will dissolve in benzene at about 60°C but the more crystalline high-density polymers only dissolve at temperatures some 20–30°C higher. Materials of similar solubility parameter and low molecular weight will, however, cause swelling, the more so in low-density polymers (Table 10.5).

Low-density polyethylene has a gas permeability in the range normally expected with rubbery materials (Table 5.11). This is because in the amorphous zones the free volume and segmental movements facilitate the passage of small molecules. Polymers of the Phillips type (density 0.96 g/cm³) have a permeability of about one-fifth that of the low-density materials.

Exposure of polyethylene to ultraviolet light causes eventual embrittlement of the polymer. This is believed to be due to the absorption of energy by carbonyl groups introduced into the chain during polymerisation and/or processing. The carbonyl groups absorb energy from wavelengths in the range 220–320 nm. Fortunately very little energy from wavelengths below 300 nm strikes the earth's surface and so the atmosphere offers some protection. However, in different climates and in different seasons there is some variation in the screening effect of the atmosphere and this can give rise to considerable variation in the outdoor weathering behaviour of the polymer.

Table 10.5 Absorption of liquids by polyethylenes of density 0.92 and 0.96 g/cm³ at 20°C after 30 days immersion

Solvent	Solubility parameter δ MPa ^{1/2}	% increase in weight in polymers	
		0.92 g/cm ³	0.96 g/cm ³
Carbon tetrachloride	17.5	42.4	13.5
Benzene	18.7	14.6	5.0
Tetrahydrofuran	19.4	13.8	4.6
Petrol (BP 60–100°C)	—	12.8	5.8
Diethyl ether	15.1	8.5	2.6
Lubricating oil	—	4.9	0.95
Cyclohexanone	20.3	3.9	2.4
Ethyl acetate	18.6	2.9	1.6
Oleic acid	—	1.81	1.53
Acetone	20.4	1.24	0.79
Acetic acid	—	1.01	0.85
Ethanol	26.0	0.7	0.4
Water	48.0	<0.01	<0.01

When polyethylene is subjected to high-energy irradiation, gases such as hydrogen and some lower hydrocarbons are evolved, there is an increase in unsaturation and, most important, cross-linking occurs by the formation of C—C bonds between molecules. The formation of cross-link points interferes with crystallisation and progressive radiation will eventually yield an amorphous but cross-linked polymer. Extensive exposure may lead to colour formation and in the presence of air surface oxidation will occur. Oxygen will cause polymer degradation during irradiation and this offsets the effects of cross-linking. Long exposure to low radiation doses on thin film in the presence of oxygen may lead to serious degradation but with short exposure, high radiation doses and thicker specimens the degradation effects become less significant. Since cross-linking is accompanied by a loss of crystallisation, irradiation does not necessarily mean an increased tensile strength at room temperature. However, at temperatures about 130°C irradiated polymer still has some strength (it is quite rubbery), whereas the untreated material will have negligible tenacity. It is found that incorporation of carbon black into polyethylene which is subsequently irradiated can give substantial reinforcement whereas corresponding quantities in the untreated product lead to brittleness.

If polyethylene is exposed to a mechanical stress in certain environments, fracture of the sample occurs at stresses much lower than in the absence of the environment. As a corollary if a fixed stress, or alternatively fixed strain, is imposed on a sample the time for fracture is much less in the 'active environment' than in its absence. This phenomenon is referred to as *environmental stress cracking*. An example of this effect can be given by considering one of the tests used (the Bell Telephone Laboratory Test) to measure the resistance of a specific polymer to this effect. A small moulded rectangle is nicked to a fixed length and depth with a sharp blade and the nicked sample is then bent through 180 degrees so that the nick is on the outside of the bend and at right angles to the line of the bend. The bent sample is held in a jig and immersed in a specific

detergent, usually an alkyl aryl polyethylene glycol ether (e.g. Igepal CA) and placed in an oven at 50°C. Low-density polymers with an MFI of 20 and above will often be observed to crack in an hour or two. Amongst materials which appear to be active environments are alcohols, liquid hydrocarbons, organic esters, metallic soaps, sulphated and sulphonated alcohols, polyglycol ethers and silicone fluids. This is rather a formidable list and at one time it was thought that this would lead to some limitation in the use of polyethylene for bottles and other containers. However, for a number of reasons this has not proved a problem except with high-density homopolymers and the main reason for concern about the cracking phenomenon is in fact associated with cables when the polyethylene insulator is in contact with greases and oils.

The reason for the activity of the above named classes of liquids is not fully understood but it has been noted that the most active liquids are those which reduce the molecular cohesion to the greatest extent. It is also noticed that the effect is far more serious where biaxial stresses are involved (a condition which invariably causes a greater tendency to brittleness). Such stresses may be frozen in as a result of molecular orientation during processing or may be due to distortion during use.

Different polyethylenes vary considerably in the environmental stress cracking resistance. It has been found that with low-density polymers the Bell Test generally shows that the higher the molecular weight the greater the resistance, low-density polymers with a melt flow index of 0.4 being immune to the common detergents. Narrow molecular weight distributions considerably improve resistance of a polymer of given density and average molecular weight. Large crystalline structures and molecular orientations appear to aggravate the problem. The effect of polymer density is somewhat complicated. The Bell Test is performed at constant strain and hence much higher stresses will be involved in the high-density polymers. It is thus not surprising that these materials often appear to be inferior by this test but in constant stress tests different results may be expected. Paradoxically, Phillips-type homopolymers have often been less satisfactory in service than indicated by the Bell Test.

It may seem surprising that low-density, comparatively low molecular weight (MFI 20) materials have been successfully used for detergent bottles in view of the stress cracking phenomenon. (Nevertheless higher molecular weight materials are usually used here, i.e. with an MFI <0.7.) The reason for this lies in the fact that good processing conditions and good design result in low stresses being imparted to the products. Under these conditions stress cracking times are invariably longer than the required service life of the product.

10.5.4 Electrical Properties

The insulating properties of polyethylene compare favourably with those of any other dielectric material. As it is a non-polar material, properties such as power factor and dielectric constant are almost independent of temperature and frequency. Dielectric constant is linearly dependent on density and a reduction of density on heating leads to a small reduction in dielectric constant. Some typical data are given in *Table 10.6*.

Oxidation of polyethylene with the formation of carbonyl groups can lead to a serious increase in power factor. Antioxidants are incorporated into compounds for electrical applications in order to reduce the effect.

Table 10.6 Electrical properties of polyethylene

Volume resistivity	$>10^{22} \Omega \text{ m}$
Dielectric strength	700 kV/mm
Dielectric constant	
density = 0.92 g/cm ³	2.28
density = 0.96 g/cm ³	2.35
Power factor	$\sim 1-2 \times 10^{-4}$

10.5.5 Properties of LLDPE and VLDPE

As with LDPE and HDPE materials, there is a wide range of linear low-density polyethylenes (LLDPEs). Primarily competitive with LDPE, the 'linear low' materials have found rapid acceptance because of their high toughness (at low, normal and high temperatures), tensile strength, elongation at break and puncture resistance compared to LDPE materials of similar melt flow index and density. More specifically the improved resistance to environmental stress cracking has been emphasised by suppliers as also has the ability to use dishwashers to clean LLDPE kitchen utensils, a consequence of the higher heat deformation resistance.

The very low density materials (VLDPEs) introduced in the mid-1980s are generally considered as alternatives to plasticised PVC (Chapter 12) and ethylene-vinyl acetate (EVA) plastics (see Chapter 11). They have no volatile or extractable plasticisers as in plasticised PVC nor do they have the odour or moulding problems associated with EVA. Whilst VLDPE materials can match the flexibility of EVA they also have better environmental stress cracking resistance, improved toughness and a higher softening point.

Some comparative data for a VLDPE copolymer based on ethylene and oct-1-ene and an EVA material (91% ethylene, 9% vinyl acetate) are given in *Table 10.7*.

Table 10.7 Comparison of VLDPE and EVA (9%VA)

	VLDPE	EVA
Density (g/cm ³)	0.910	0.926
MFI	7	9
Tear strength (N/mm ²)	11.4	6.1
Elongation at break (%)	710	475
Vicat temperature (°C)	78	51
Low-temperature brittle point (°C)	-135	-130
Hardness (Shore D)	42	32
Stress crack time (h)	600	240

10.5.6 Properties of Metallocene-catalysed Polyethylenes

Metallocene-catalysed polyethylenes exhibit the general characteristics of polyethylene as noted in the introductory paragraph of Section 10.5. Furthermore

they are more like low density polyethylenes (LDPE and LLDPE) than HDPE. As with LLDPE they are usually copolymers containing small quantities of a low molecular weight α -olefin such as but-1-ene, hex-1-ene and oct-1-ene. The property differences largely arise from the narrow molecular weight distribution, the more uniform incorporation of the α -olefin and the low level of polymerisation residues (about one-tenth that of Ziegler–Natta catalysed LLDPE).

It is generally claimed that metallocene polyethylenes (often abbreviated to m-PE) exhibit superior mechanical and optical properties as well as better organoleptic properties (resulting from the lower residue levels). As an example m-LLDPE is particularly favoured as a stretch film for wrapping because of the good prestretchability, high puncture resistance and tear strength, all of which are claimed to be better than with conventional LLDPE.

As previously mentioned, narrow molecular weight distribution polymers such as m-PE are less pseudoplastic in their melt flow behaviour than conventional polyethylenes so that given an m-LLDPE and a conventional LLDPE of similar melt index (measured at low shear rates), the m-LLDPE will have a much higher melt viscosity at the high shear rates involved in film processing. The polymers are also more susceptible to melt fracture and sharkskin. This difference requires that such steps be taken as to use more highly powered extruders, to use special processing aids such as fluoroelastomers or to make compromises in the polymer structure which may, however, reduce the advantages of m-PE materials. One obvious approach would be to produce bi-, tri- or other polymodal blends (see the Appendix to Chapter 2 for explanations) to overcome the inherent disadvantages of narrow molecular weight distribution polymers. It is of interest that ‘bimodal’ polymers produced by a two-reactor system have become available which have enhanced resistance to cracking and are rapidly finding use in pipe applications.

Metallocene-catalysed very low density polyethylene (m-VLDPE) has become available with densities of as low as 0.903. This is of use for sealing layers of multi-layer films since sealing can commence at lower temperatures than with conventional materials such as LLDPE and EVA (see Section 11.6) with the polymer seal exhibiting both cold strength and hot tack strength.

10.6 ADDITIVES

Although polyethylene can be, and indeed often is, used without additives a number may be blended into the polymer for various reasons. These additives can be classified as follows:

- (1) Fillers.
- (2) Pigments.
- (3) Flame retarders.
- (4) Slip agents.
- (5) Blowing agents.
- (6) Rubbers.
- (7) Cross-linking agents.
- (8) Antioxidants.
- (9) Carbon black.
- (10) Antistatic additives.

Fillers, important constituents of many plastics materials, are rarely used with polyethylene since they interfere with the crystallinity of the polymer and often give rather brittle products of low ductility. Carbon black has some reinforcing effect and is of use in cross-linked polymers. It is also of some use in introducing a measure of conductivity to the polymer. Somewhat better results with non-black fillers may be achieved with the use of silane and titanate coupling agents and compounds with increased rigidity and tensile strength compared with unfilled polymer may be obtained. However, unlike polypropylene, mineral-filled polyethylene has remained unimportant. A number of *pigments* are available for use in polyethylene. The principal requirements of a pigment are that it should have a high covering power/cost ratio and that it should withstand processing and service conditions. In the case of polyethylene special care should be taken to ensure that the pigment does not catalyse oxidation, an effect observed with a number of pigments based on cobalt, cadmium and manganese. Other adverse effects have also been reported with hydrated chromic oxide, iron blues, ultramarine and anatase titanium dioxide. For electrical insulation applications pigments such as cobalt blues, which cause a rapid rise of power factor on aging, should be avoided.

Polyethylene burns readily and a number of materials have been used as *flame retarders*. These include antimony trioxide and a number of halogenated materials.

Layers of low-density polyethylene film often show high cohesion, or 'blocking', a feature which is often a nuisance on both processing and use. One way of overcoming this defect is to incorporate *anti-blocking* agents such as fine silicas. In addition *slip agents* may be added to reduce the friction between layers of film. Fatty acid amides such as oleamide and, more importantly, erucamide, are widely used for this purpose. Polymers with densities of above 0.935 g/cm^3 show good slip properties and slip agents are not normally required for these products.

Products with very low dielectric constant (about 1.45) can be obtained by the use of cellular polymers. *Blowing agents* such as 4,4'-oxybisbenzenesulphonylhydrazide and azocarbonamide are incorporated into the polymer. On extrusion the blowing agent decomposes with the evolution of gas and gives rise to a cellular extrudate. Cellular polyethylene is a useful dielectric in communication cables.

Although many *rubbery materials* show varying compatibility with polyethylene the only elastomeric materials used in commercial compounds are polyisobutylene (PIB) and butyl rubber. Polyisobutylene was originally used as a 'plasticiser' for polyethylene but was later found also to improve the environmental stress cracking resistance. Ten per cent PIB in polyethylene gives a compound resistant to stress cracking as assessed by the severe BTL test. It has been shown¹³ that within broad limits the higher the molecular weight of the PIB the greater the beneficial effect. Very high molecular weight polyisobutylenes are, however, less effective, possibly due to the difficulty in obtaining satisfactory blends. PIB may or may not increase the 'ease of flow' of polyethylene, this depending on the molecular weights of the two polymers. Because of its lower cost butyl rubber is preferred to polyisobutylene at the present time, use of the latter in polyethylene being largely restricted to cable applications.

Polyethylene is sometimes blended with ethylene-propylene rubber (see Chapter 11). In this application it is most commonly used as an additive to the rubber, which in turn is added to polypropylene to produce rubber-modified

polypropylenes. In addition up to 20% of ethylene-propylene rubber may be used in blown film applications.

Vulcanised (cross-linked) polyethylene is being used for cable application where service temperatures up to 90°C are encountered. Typical *cross-linking agents* for this purpose are peroxides such as dicumyl peroxide. The use of such agents is significantly cheaper than irradiation processes for the cross-linking of the polymer. An alternative process involves the use of vinyl silanes (see Section 10.9).

When polyethylene is to be used in long-term applications where a low power factor is to be maintained and/or where it is desired to provide thermal protection during processing, *antioxidants* are incorporated into the polymers. These were discussed extensively in Chapter 7 but a few particular points with regard to their use in polyethylene should be made. Although amines have been used widely in the past phenols are now used almost exclusively.

For protection against degradation during processing 4-methyl-2,6-t-butylphenol is widely used. It causes only a low level of staining and is also used in non-toxic formulations. Its volatility restricts its use for long-term and/or high-temperature work. For service use 1,1,3-tris-(4-hydroxy-2-methyl-5-t-butylphenyl)butane (Topanol CA) and bis-[2-hydroxy-5-methyl-3-(1-methylcyclohexyl)phenyl]methane (Nonox WSP) are widely used. Only small amounts (of the order of 0.1%) are required of these chain-breaking antioxidants, which may be used in conjunction with a peroxide-decomposing antioxidant such as dilauryl- β,β' -thiodipropionate (DLTP). The phenols show little tendency to bloom, bleed, discolour or stain but Topanol CA/DLTP blends cause some discolouration which can be minimised by incorporation of certain phosphorus compounds (e.g. 0.1–0.2% of Phosclere T268).

In the presence of carbon black the phenols and phenol/DLTP combinations are much less effective whilst some phenolic sulphides (e.g. Santonox) show positive synergism with carbon black. However, in general terms the phenol systems tend to be reduced to about the same levels as to those to which the phenol sulphide systems are raised. Some typical figures are given in *Table 10.8*.

Table 10.8 Comparison of antioxidants in polyethylene in both the absence and presence of copper powder and carbon black (data based on ICI literature). Induction time assessed from oxygen uptake measurements using a Barcroft manometer

<i>Chain-breaking antioxidant</i>	<i>DLTP</i>	<i>Carbon black</i>	<i>Copper powder</i>	<i>Induction period at 140°C (h)</i>
Phenol alkane (0.1%)	—	—	—	60
Phenol alkane (0.05%)	0.05%	—	—	300
Phenol alkane (0.1%)	0.1%	—	—	450
Phenol alkane (0.1%)	0.1%	3%	—	310
Phenol alkane (0.1%)	0.1%	—	0.1%	100
Phenol sulphide (0.1%)	—	—	—	110
Phenol sulphide (0.1%)	0.1%	—	—	240
Phenol sulphide (0.2%)	—	3%	—	190
Phenol sulphide (0.1%)	0.1%	—	0.1%	8–16
Phenol sulphide (0.1%)	0.1%	3%	—	No data supplied

Phenol alkane—Topanol CA (TcT).

Phenol sulphide—4,4'-thiobis-(3-methyl-6-t-butylphenol).

Carbon black—Kosmos CB9.

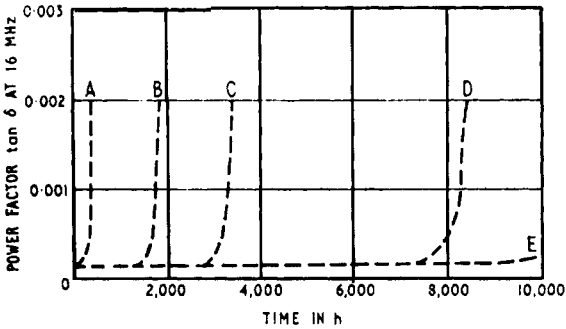


Figure 10.11. Oxidation of polyethylene in air at 105°C. Effect of adding 0.1% antioxidant on power factor.¹ A, blank. B, *N,N'*-diphenyl-*p*-phenylenediamine. C, 4,4'-thiobis-(6-butyl-*m*-cresol). D, Nonox WSP. E, *N,N'*-di-β-naphthyl-*p*-phenylenediamine

A number of tests have been devised for measuring the efficiency of antioxidants. Samples may be aged by hot rolling at about 160°C, by air oven aging or by aging in aerated water. Changes in the polymer can be noted by measurements of such properties as carbonyl content (by infrared measurements), gel content, melt flow index, oxygen uptake and power factor. Since the *raison d'être* for incorporating antioxidants is often to prevent an increase in power factor on aging, power factor measurements are widely used. In addition the property is very sensitive to oxidation. Figure 10.11 shows the change in power factor of polyethylenes containing various antioxidants after air aging. Figure 10.12 shows the effect of varying the antioxidant concentration. The sharp increase in power factor after an induction time during which little change occurs is to be noted in particular. In practice about 0.1% of antioxidant is employed in electrical grade compounds.

The weathering properties of polyethylene are improved by the incorporation of *carbon blacks*. Maximum protection is obtained using blacks with a particle size of 25 μm and below. In practice finely divided channel or furnace blacks are used at 2–3% concentration and to be effective they must be very well dispersed into the polymer. The use of more than 3% black leads to little improvement in weathering resistance and may adversely affect other properties.

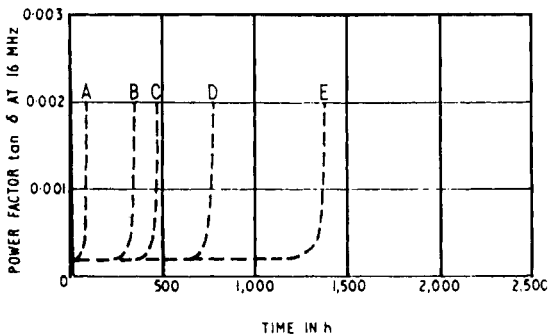


Figure 10.12. Oxidation of polyethylene in air at 105°C. Effect of antioxidant concentration (*N,N'*-diphenyl-*p*-phenylenediamine). A, blank. B, 50 ppm. C, 100 ppm. D, 500 ppm. E, 1000 ppm

Antistatic additives are widely used to reduce dust attraction and also in films to improve handling behaviour on certain types of bag making and packaging equipment. Whilst at one time it was more common to apply an antistatic agent to the surface by wiping, dipping or spraying, increasing use is now being made of antistatic agents which are incorporated into the polymer mass during normal compounding and which migrate to the surface with the passage of time. This approach has the advantage that the extra coating process is avoided and also that any layer of material removed by normal handling will be replaced by material which will migrate out of the mass. The selection of such 'antistats' is critical and will depend particularly on the polymers used and on the thermal stability required. For a given polymer the agent should have a limited compatibility and a high diffusion rate in order to produce an antistatic layer as soon as possible after manufacture. Whereas quaternary ammonium compounds are widely used for polystyrene, polyethylene glycol alkyl esters would appear to be preferred in polyethylene compositions. The actual chemical composition of the rather small number of antistatic agents so far found suitable is rarely disclosed by the suppliers.

Polyethylene can be compounded on any of the standard types of mixing equipment used for visco-elastic materials. For laboratory purposes a two-roll mill is suitable; operating temperatures varying from about 90°C to about 140°C according to the type of polymer. On the industrial scale, compounding is undertaken either in internal mixers, or more particularly, extrusion compounders.

10.7 PROCESSING

Although plastics materials may in principle be processed in a variety of physical states (in solution, in emulsion, as a paste or as a melt), melt processing is used almost exclusively with polyethylene. The main features to be borne in mind when processing the polymers are:

- (1) The low water absorption of the polymer avoids the necessity of predrying before processing except where hygroscopic additives are present.
- (2) The tendency of the material to oxidise in air particularly at melt temperatures means that the melt should come in contact with air as little as possible.
- (3) Although processing temperatures are low compared with many plastics the specific heat, which varies with temperature, is high. As a consequence, as was shown in Chapter 8, more heat needs to be put in and taken out of polyethylene during processing than for other major thermoplastics. This means higher energy costs to raise the temperature and longer cooling times after shaping.
- (4) The melt viscosity is highly non-Newtonian in that the apparent viscosity drops considerably with increasing shear rate. Melt viscosities are about the average encountered with plastics materials but there is a considerable variation between grades.
- (5) The high degree of crystallisation, which leads, among other things, to a high shrinkage on cooling.
- (6) The short polymer relaxation times.
- (7) A rather sharp melting point.

Polyethylene is processed by a wide variety of techniques, most of which were outlined briefly in Chapter 8. There is insufficient space here to deal adequately with the principles and practice of these processes or even with the particular characteristics of polyethylene being fabricated by these processes. For this reason a list of books giving further details is given at the end of Chapter 8.

Compression moulding is used only occasionally with polyethylene. In this process the polymer is heated in a mould at about 150°C, compressed to shape and cooled. The process is slow since heating and cooling of the mould must be carried out in each cycle and it is employed only for the manufacture of large blocks and sheets, for relatively strain-free objects such as test-pieces and where alternative processes cannot be used because of lack of equipment.

A very large number of products are produced by *injection moulding*. In this process the polymer is melted and injected into a mould which is at a temperature below the freezing point of the polymer so that the latter can harden. For mouldings with a minimum frozen-in strain, operating conditions should be so selected that the mould cavity pressure drops to zero as the material sets. Because of the tendency of the material to crystallise, high shrinkage values are observed, ranging from 0.015–0.050 cm/cm with low-density materials to 0.025–0.060 cm/cm with high-density polymers. High mould temperatures, desirable to reduce strains through freezing of oriented molecules, lead to increased shrinkage since there is more time available for crystallisation. High cavity pressures reduce shrinkage since during much of the cooling part of the cycle there is only pressure reduction in the polymer and not physical contraction. High cavity pressures also reduce packing near to the point of entry into the mould which can occur as the material in the cavity shrinks. Since it is partially solidified material which is packed into the mould, and which often freezes while the molecules are oriented, a weakness of the part around the gate can occur and so 'packing' should be reduced as far as possible. Melt temperatures are of the order of 160–190°C for low-density polymers and up to 50°C higher with high-density materials. In order to achieve these melt temperatures cylinder temperatures may be anything from 30 to 100°C higher.

Many articles, bottles and containers in particular, are made by *blow moulding* techniques of which there are many variations. In one typical process a hollow tube is extruded vertically downwards on to a spigot. Two mould halves close on to the extrudate (known in this context as the 'parison') and air is blown through the spigot to inflate the parison so that it takes up the shape of the mould. As in injection moulding, polymers of low, intermediate and high density each find use according to the flexibility required of the finished product.

Another moulding process based on the extruder is '*extrusion moulding*'. Molten polymer is extruded into a mould where it sets. Since satisfactory mouldings can be produced using low moulding pressures, cheap cast moulds can be used. The process has been used to produce very large objects from polyethylene. The techniques of screw-preplasticising with injection moulding can be considered as a development of this process.

Approximately three-quarters of the polyethylene produced is formed into products by means of *extrusion* processes. These processes will differ according to the product being made, i.e. according to whether the end-product is film, coated paper, sheet, tube, rod or wire covering. In principle the extrusion process consists of metering polymer (usually in granular form) into a heated barrel in which a screw is rotating. The rotation of the screw causes the granules to move up the barrel, where they are compacted and plasticised. The resultant melt is

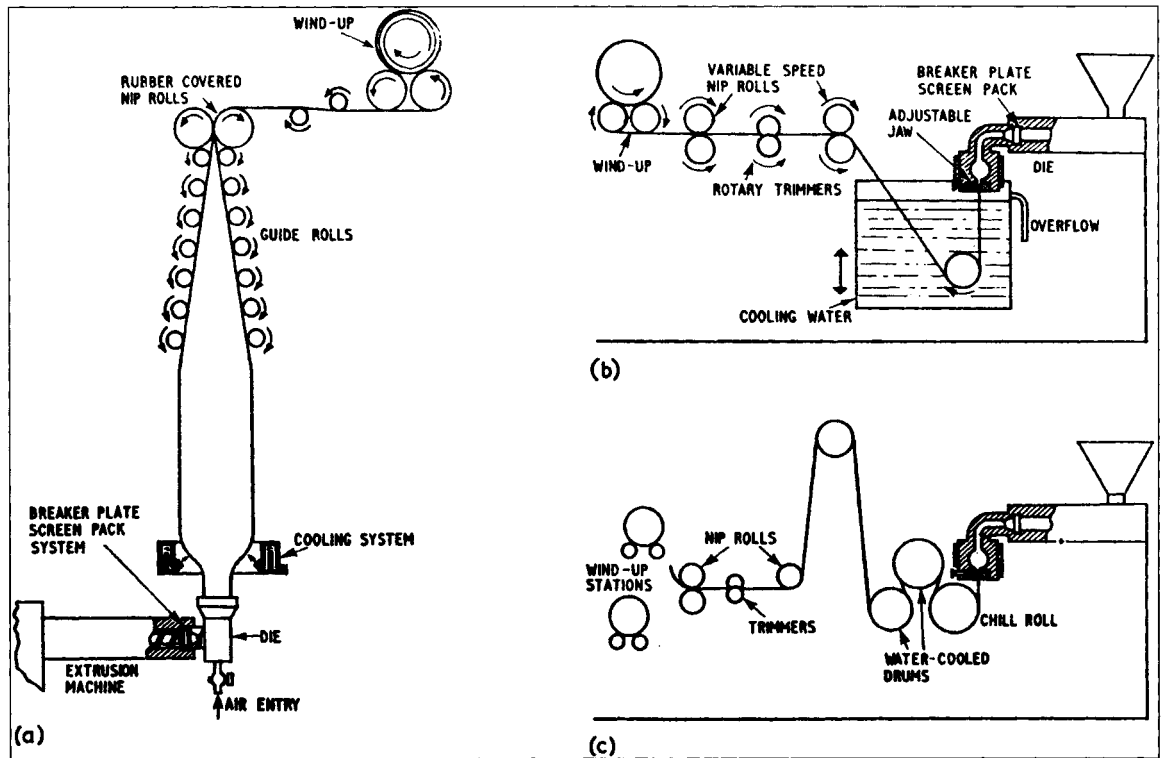


Figure 10.13. Methods of producing polyethylene film: (a) tubular process using air cooling; (b) flat film process using water bath cooling; (c) flat film process using chill roll cooling¹⁰

then forced under pressure through an orifice to give a product of constant cross-section. Although the polymer may be processed on a variety of different machines, screws usually have a length–diameter ratio in excess of 16:1 and a compression ratio of between 2.5:1 and 4:1. (The compression ratio can be considered as the volume of one turn of the screw channel at the feed end to the volume of one turn at the delivery end of the barrel.) Since well over half the polyethylene extruded is converted into film, film extrusion processes will be considered in somewhat greater detail. There are basically two processes, the tubular process and the flat film process, which are shown schematically in *Figure 10.13*.

In the tubular process a thin tube is extruded (usually in a vertically upward direction) and by blowing air through the die head the tube is inflated into a thin bubble. This is cooled, flattened out and wound up. The ratio of bubble diameter to die diameter is known as the *blow-up ratio*, the ratio of the haul-off rate to the natural extrusion rate is referred to as the *draw-down ratio* and the distance between the die and the frost line (when the extrudate becomes solidified and which can often be seen by the appearance of haziness), the *freeze-line distance*.

The properties of the film are strongly dependent on the polymer used and on processing conditions. The higher the density the lower the flexibility, the greater the brittleness and to some extent, up to densities of about 0.94 g/cm^3 , the greater the clarity (in the absence of sharkskin effects) and the lower the tensile strength at rupture. High-density materials are also less susceptible to ‘blocking’. The higher the molecular weight the greater the melt viscosity, tensile strength and resistance to film brittleness at low temperatures but the lower the transparency and the less the ability of the melt to draw down. Wide molecular weight distributions have been claimed to improve the resistance to film brittleness but this view is not universally accepted.

For general purpose work, polymers with a density of about 0.923 g/cm^3 , a melt flow index of about 2, a reasonably wide molecular weight distribution, and which are free from high molecular weight oxidised ‘blobs’, are most commonly used. The requirements of a film, however, differ according to the application. Whereas in some instances toughness may be of greater importance, in other cases high optical clarity may be the paramount requirement. The choice of both polymer and processing conditions can greatly influence the properties of the product.

There has been extensive investigation¹⁴ into the effect of processing conditions on clarity, haze and gloss of polyethylene film. It can easily be demonstrated that the presence of haze and lack of clarity of low- and intermediate-density polymers is due to surface irregularities which can arise either as a melt roughness (which tends to disappear after extrusion if the polymer remains molten) or due to crystallisation (which though not developing structures large enough to impede the passage of light tends to cause surface distortions).

The effects of melt roughness and surface crystallisation are shown more clearly in *Figure 10.14*, in which haze is plotted against freeze-line distance, all other operating variables being constant. It will be observed that initially as the freeze-line distance increases there is a reduction in haze since the extra period that the polymer is molten allows a reduction in melt roughness. Eventually, however, there is an increase in haze because the longer cooling times allow larger crystal structures to build up and distort the surface. An increase in

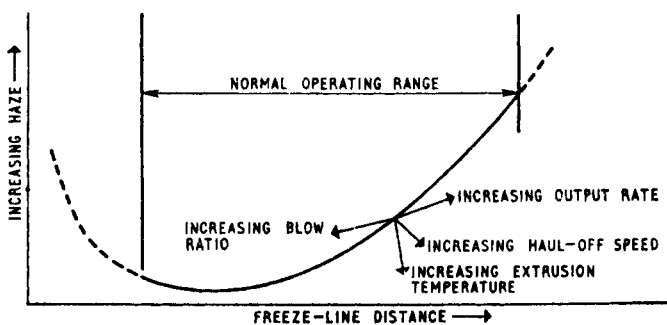


Figure 10.14. Effect of freeze-line distance and other operating variables on the haze of low-density polyethylene film.⁹ (Reproduced by permission of ICI)

extrusion temperature reduces haze because there is a reduction in melt imperfections and because the time available for crystallisation is reduced (although the total cooling time is the same, the polymer will be above its melting point for a longer fraction of this time). An increased output rate with constant freeze-line distance would increase melt imperfections but reduce surface crystallinity effects and thus shift the curve to the right. The effects of most other operating variables can also be explained in terms of melt roughness and surface crystallinity.

The effect of extrusion conditions on the impact strength of tubular film has also been studied and found to be related to molecular orientation. Polyethylene molecules in the melt have a very short relaxation time (a measure of the time taken for molecules to coil after release of an orienting stress). Thus in the tubular film process only molecules that have been oriented just before the melt freezes will remain in the oriented state. Because of this the order in which drawing down and transverse stretching of the film occur will affect the impact strength. These factors can be adjusted by varying freeze-line distance, blow ratio and output rate, the shape of the bubble giving a guide to the sequence of events. In recent years the technology of film manufacture has been extended by the appearance of ethylene-propylene rubber modified LDPE and also linear low-density polyethylene. Both materials can show high levels of toughness.

Considerable amounts of polyethylene film are produced using coaxial extrusion processes in which two or more melt streams are combined in the die to produce extruded film of two or more layers of plastics materials. Layers in such a composite may be included, for example, to improve barrier properties, to enhance sealability or even simply to act as an adhesive between dissimilar layers.

[NB Some technical reviews refer to polymer composites being used in film manufacture when it is not always obvious whether the reference is to the use of a physical blend of the component polymers or whether the polymers are separated in layers (as in coaxial extrusion) or in some combination. Clearly the effects can be quite different.]

Although a large proportion of polyethylene film is made by the tubular process some film is produced by extruding flat film from a slit die either into a water bath or on to a chilled casting roll. Although extrusion directly into water results in the most rapid quenching and tends to give products of highest clarity, the presence of antistatic and slip additives tends to cause water to carry over

from the cooling bath and become trapped in the rolled film. For this reason the chill-roll process is usually preferred. Because of the higher cooling rates that are possible with chill-roll processes higher linear output rates can be achieved than with tubular processes. In addition since high melt temperatures can be used (which reduce melt roughness) and quenching is carried out within an inch or two of the die lips (which reduces surface effects due to crystallinity) products of high clarity may be obtained. In comparison the principal advantages of the tubular process are the ease with which bags and sacks may be made from the extruded tube and the ability to make wide sheet from fairly simple dies.

Calendering processes, of great importance in the production of sheet materials from PVC compounds, are little used with polyethylene because of the difficulty in obtaining a smooth sheet. Commercial products have, however, been made by calendering low-density polymer containing a small amount of a peroxide such as benzoyl peroxide to give a stiff but crinkly sheet (Crinothene) which was suitable for lampshades and other decorative applications.

Although the tonnage consumption is small compared with the amount of polyethylene consumed in injection moulding or extrusion, polyethylene is widely processed using a powder as the starting material. This powder can be made either by precipitating the polymer by cooling a solution or by grinding processes. The former method gives the finest powder whilst the latter is more economic.

The oldest-established of the *powder processes* is fluidised-bed coating. In the process a metal object which is to be coated with polyethylene is heated to about 160–250°C and then suspended in a fluidised bed of powdered polymer. Fluidisation is brought about by blowing air through a porous base in the powder container so that in effect the individual particles are lubricated with a thin film of air. Particles coming into contact with the hot metal fuse and adhere to the metal part. This, together with the adhering particles, is then transferred to a second oven where the particles fuse together to give an even coating. In a variation of this process the fluidised powder particles are electrically charged whilst the object to be coated is earthed. This can then attract the charged particles without the need for preheating the part.

Larger objects may be coated by spraying techniques of which there are two basic variants, flame spraying and electrostatic spraying. In the first process the powder is sprayed on to preheated metal with a flame spray gun and the coating is then heated to fuse the particles. With electrostatic spraying the particles are charged as they leave the spray gun and are attracted to the object to be coated, which is earthed. It is claimed that thinner coatings are possible using electrostatic spraying techniques so that the method may in future years become a serious competitor of present-day techniques of applying surface coatings.

Whereas dipping and spraying techniques require the use of fine powder, the coarser ground powders may be tolerated in powder moulding techniques. Once again there are a number of variants of the techniques such as the Engel process but in principle they involve pouring powder into a heated low-cost mould. Some of the powder close to the mould fuses and sinters on to the mould, while the excess is poured out. The mould and the adhering powder are then heated until the powder forms a smooth continuous layer, the assembly is cooled and the resultant moulding removed from the mould. This process is very suitable for large objects but because of the long process time is less suitable for small articles. One important variation of the process is *rotational moulding*. In this

case the required amount of powder is added to the mould, which is completely closed and then rotated in an oven about two axes. The powder melts and is distributed over the walls of the mould. The mould is then cooled whilst the moulds are rotating.

Powdered polyethylene is also used to bond cloth interliners to garments. Automobile carpets are often made with a polyethylene rather than a latex backing because the polyethylene-backed carpet can be heat-formed so that the carpet will fit the shape of the car floor and cutting and sewing operations are consequently eliminated.

It is common practice to print upon certain products such as films and bottles. Because polyethylene is chemically inert it is not possible to obtain a good ink adhesion directly on to the polymer surface. To overcome this problem the surface of the polymer is usually modified in order to provide an oxidised layer that will enable the ink to adhere. Modification may be carried out either by treatment with a naked flame or, more commonly, by subjecting the surface to a high-voltage discharge. The presence of slip agents and antistats may complicate the process and in the case of polyethylene film the modification is usually carried out immediately after extrusion before the wind-up stage and before an appreciable concentration of slip agent or antistatic additive has migrated to the surface. Once the surface has been modified it is possible to print on to the film without undue difficulty.

10.8 POLYETHYLENES OF LOW AND HIGH MOLECULAR WEIGHT

The most common commercial grades of polyethylene have number average molecular weights of the order of 10 000–40 000 (with corresponding \bar{M}_w values in the range 50 000–300 000). There are, however, a number of special purpose grades on either side of this range.

Most low molecular weight materials have molecular weights in the range 1000–10 000 with viscosities of about 1–2 poise at 150°C (c.f. 10^4 – 10^6 poise for conventional polymers) and melting points in the range 80–110°C. Such materials do not exhibit the tenacity and toughness of high polymers and are essentially wax-like. They are, however, tougher than conventional waxes and also show very good water and chemical resistance. Because of these characteristics such low molecular weight polyethylenes are used in wax formulations, wax-paper coatings and as lubricants in, for example, PVC.

Very high molecular weight polyethylenes (\bar{M}_w in the range 1 – 6×10^6) prepared by the Ziegler process have also become available. As might be expected from consideration of *Figure 3.1* these polymers cannot be processed easily in the molten state without decomposition and it is therefore often necessary to process in the rubbery phase.

The polymers are linear in nature but, because of the difficulties large molecules have in crystallising, the densities are only of the order of 0.94 g/cm^3 and properties that are primarily dependent on percentage crystallinity (density), for example yield strength and stiffness, are slightly worse than those obtained with linear polyethylenes of conventional molecular weight. The main advantages claimed for the very high molecular weight polymers are high abrasion resistance and impact strength, very good stress-cracking resistance and low creep.

10.9 CROSS-LINKED POLYETHYLENE

Cross-linking of a crystalline thermoplastic polymer has, in general, two distinct effects. Firstly it interferes with molecular packing, reducing the level of crystallisation, and consequently the polymer has a lower modulus, hardness and yield strength than the corresponding non-cross-linked material. More importantly, because the network structure still exists above the crystalline melting point the material retains a measure of strength, typical of a rubber material. Polyethylene is typical in such behaviour and because of the enhanced heat resistance (in terms of resistance to melt flow), cross-linked or vulcanised polyethylene finds application in the cable industry both as a dielectric and a sheathing material.

Three main approaches are used for cross-linking polyethylene:

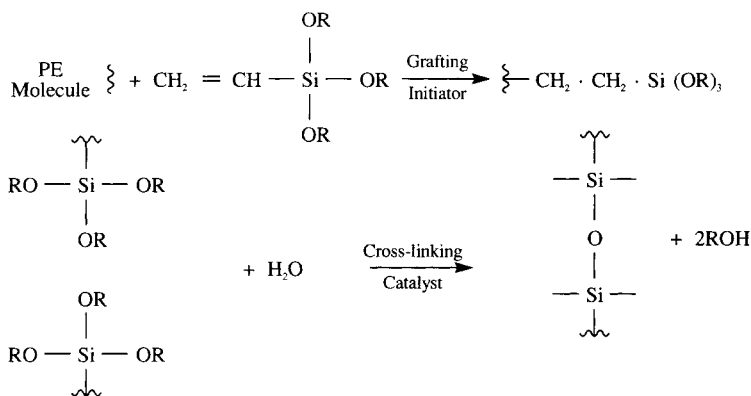
- (1) Radiation cross-linking;
- (2) Peroxide cross-linking;
- (3) Vinyl silane cross-linking.

Radiation cross-linking requires expensive equipment and extensive protective measures. The technique is being used commercially and is most suitable with thin sections. Equipment requirements for peroxide curing are somewhat simpler but the method requires close control. At elevated temperatures the peroxide molecules break up, producing free radicals. These abstract hydrogen from the polymer chain to produce a polymer free radical. In the case of polyethylene the most likely reaction is that two radicals will combine and thus cross-link two chains but other reactions may lead to chain scission. It is important that the peroxide be sufficiently stable thermally to withstand compounding and shaping operations without degradation in order to avoid premature cross-linking. Dicumyl peroxide is frequently used for low-density polyethylene but more stable peroxides are necessary for higher density materials. For cable covering, high production rates require high curing temperatures in the absence of oxygen and this normally involves the use of high-pressure steam in a long curing tube set into the extrusion line. Large amounts of carbon black may be incorporated into polyethylene that is to be cross-linked. The carbon black is believed to take part in the cross-linking process and the compounded product has superior mechanical properties in many respects to the unfilled material. It is also to be noted that copolymers of ethylene with small amounts of vinyl acetate are often preferred for peroxide cross-linking.

The third process for cross-linking is the Sioplas process developed by Dow. The first stage of this involves the grafting of an easily hydrolysable trialkoxyvinylsilane onto the polyethylene chain, the site activation having been achieved with the aid of a small amount of peroxide. The compound is then extruded onto the wire, which is collected on a drum. The drum is then exposed to hot water, or, more commonly, low-pressure steam. The water hydrolyses the alkoxy groups, which then condense to form a siloxane cross-link.*

The cross-linking stage is facilitated by the use of a cross-linking catalyst, which is typically an organo-tin compound. A number of variations of this process exist and in one of these compounding, grafting and extrusion onto wire are carried out in the same extruder.

* For an introduction to the nomenclature of organosilicon compounds see Chapter 29.



There has been interest, particularly in Japan, in the production of cross-linked low-density polyethylene foam. Some processes, such as the Furukawa process and the Hitachi process, use chemical cross-linking techniques whilst others, such as the Sekisui process, involve radiation cross-linking.

These cross-linked cellular materials have been used in the automotive industry for carpeting, boot mats and sound deadening. They have also found use for pipe insulation and as flotation media for oil-carrying and dredging hose.

10.10 CHLORINATED POLYETHYLENE

The first patent on the chlorination of polyethylene was taken out by ICI in 1938. In the 1940s scientists of that company carried out extensive studies on the chlorination process. The introduction of chlorine atoms onto the polyethylene backbone reduces the ability of the polymer to crystallise and the material becomes rubbery at a chlorine level of about 20%, providing the distribution of the chlorine is random. An increase in the chlorine level beyond this point, and indeed from zero chlorination, causes an increase in the T_g so that at a chlorine level of about 45% the polymer becomes stiff at room temperature. With a further increase still, the polymer becomes brittle.

Chlorination may be carried out with both high-density and low-density polyethylene. When carried out in solution the chlorination is random but when carried out with the polymer in the form of a slurry the chlorination is uneven and due to residual crystalline zones of unchlorinated polyethylene the material remains a thermoplastic.

Thermoplastic chlorinated polyethylenes are seldom used on their own but primarily in blends with other polymers, particularly PVC. If chlorination is taken to a level at which the polymer is only semi-compatible with the PVC, a blend with high impact strength may be obtained. In these circumstances the material is classified as an impact modifier.

There have been some attempts to develop chlorinated polyethylene elastomers. The rubbers possess such attractive properties as very good oil, heat, flame, ozone, and weathering resistance and are also available in a convenient powder form. In spite of being marketed at competitive prices, the chlorinated polyethylene rubbers (designated as CM rubbers by ASTM) took

some time to become established, probably largely as a result of difficulties in curing the materials. Today, however, they are of importance for cable sheathing and are now also being investigated more generally in technical goods such as hydraulic and radiator hoses, gaskets, seal caps, membranes and spark plug caps. The major competition for these materials is in the chemically closely related chlorosulphonated polyethylenes (Hypalon – Du Pont) described in the next chapter.

10.11 APPLICATIONS

Polyethylene was introduced initially as a special purpose dielectric material of particular value for high-frequency insulation. With increasing availability the polymer subsequently began to be used for chemical plant and, to a small extent, for water piping. Since World War II there has been a considerable and continuing expansion in polyethylene production and this, together with increasing competition between manufacturers, has resulted in the material becoming available in a wide range of grades, most of which are sold in the lowest price bracket for plastics materials. The present position of polyethylene as a general purpose thermoplastic material is due in no small measure to the low cost and easy processability of the polymer.

The characteristics of polyethylene which lead to its widespread use may be summarised as follows:

- (1) Low cost.
- (2) Easy processability.
- (3) Excellent electrical insulation properties.
- (4) Excellent chemical resistance.
- (5) Toughness and flexibility even at low temperatures.
- (6) Reasonable clarity of thin films.
- (7) Freedom from odour and toxicity.
- (8) A sufficiently low water vapour permeability for many packaging, building and agricultural applications.

To these could also be added the fact that a great quantity of information is available concerning the processing and properties of this material and that its properties are reasonably well known and understood by the public at large.

The limitations of the polymer are:

- (1) The low softening point.
- (2) The susceptibility of low molecular weight grades to environmental stress cracking.
- (3) The susceptibility to oxidation (however, polyethylene is better in this respect than many other polymers).
- (4) The opacity of the material in bulk.
- (5) The wax-like appearance.
- (6) The poor scratch resistance.
- (7) The lack of rigidity (a limitation in some applications but a virtue in others).
- (8) The low tensile strength.
- (9) The high gas permeability.

For many purposes these limitations are not serious whilst in other cases the correct choice of polymer, additives, processing conditions and after-treatment can help considerably.

As mentioned in the introduction to the chapter, world capacity to produce polyethylene was of the order of so *c.* 50×10^6 t.p.a. in the late 1990s although production to that level is not expected until about 2002. By type, this market is shared between LDPE, HDPE and LLDPE approximately in the ratio 40:36:24.

In the early 1990s it was estimated that the geographical breakdown for production capacity was Western Europe 26%, North America 33%, Japan 8%, Eastern Europe 8% and Rest of the World 25%.

Major applications for LDPE film include heavy duty sacks, refuse sacks, carrier bags and for general packaging. Many of these uses may now be considered to be mature and future growth will become more closely tied to national economic situations. Similar comments may also be made about the extensive use of polyethylene film in the building industry. Areas expected to be capable of further development are shrink film for food wrapping and film for agricultural purposes. One technical development in this area is the increased use of up to 20% of ethylene-propylene rubber (see Chapter 11) in LDPE film formulations. This arises from the improved low-temperature properties and higher impact strength of the blends compared with corresponding unblended LDPE.

The LDPE film market has now been partly eroded by LLDPE. Polymerisation plants for LLDPE are cheaper to build, easier to operate and maintain, have lower energy requirements and are more versatile than the high-pressure plants. For these reasons manufacturing costs are reduced. There are also some technical advantages to the user since films from LLDPE have a higher impact strength, tensile strength and extensibility. Such properties allow the possibility of making film of lower gauge but with the same mechanical performance. LLDPE materials show lower gloss, greater haze, are less suitable for shrink film and have a narrower heat sealing range.

There are two main classes of HDPE now on the market:

- (1) High molecular weight, broad MWD polymer—used primarily for blow moulding and pipe.
- (2) Low molecular weight, narrow MWD polymer—used widely for injection moulding and rotational moulding.

Each type is available in varying densities. Bimodal MWD polymers have become established in some markets. The high molecular weight component confers impact strength, toughness, stiffness and good environmental stress cracking resistance, whilst the lower molecular weight peak improves flow behaviour.

High-density polyethylene film is being increasingly used for carrier bags. It is also finding rapid acceptance as a wrapping material instead of paper for food products, probably largely a consequence of its crisp feel and greaseproof nature. HDPE film is also of some interest in some pseudo-fibre applications. If extruded sheet is embossed with a regular pattern and the embossed sheet biaxially stretched under controlled conditions of temperature, the sheet breaks up into a net-like form. Such a process, developed by Smith and Nephew in England, is now used to make nets varying in appearance from a fine web to coarse open structures. HDPE film is also used in monoaxially stretched form, when it is slit into tape, and also to some extent in the manufacture of fibrillated tape. It is, however, generally inferior to polypropylene for these applications, which will thus be dealt with in the next chapter.

Table 10.9 Usage of polyethylene in Western Europe and USA 1997 (Based on data in *Modern Plastics International*)

	Western Europe						USA					
	LDPE		LLDPE		HDPE		LDPE		LLDPE		HDPE	
	1000 t	%	1000 t	%	1000 t	%	1000 t	%	1000 t	%	1000 t	%
Film and sheet	3297	73	1382	83.2	706	18.4	1535	44	1701	47.3	1131	18.5
Extrusion coating	454	10	5	0.3	0	0	430	12	9	0.2	0	0
Injection moulding	188	4	101	6.0	831	21.6	134	4	268	7.4	1023	16.8
Blow moulding	51	1	6	0.4	1403	36.4	31	1	11	0.3	1829	30.0
Pipe and conduit	106	2	31	1.9	556	14.4	*	*	*	*	448	7.2
Wire and cable	206	4.5	26	1.6	48	1.2	71	2	80	2.2	55	0.9
Other	255	5.5	111	6.6	306	8.0	1345	37	1531	42.6	1622	26.6
Total	4557		1662		3850		3518		3600		6108	

* USA and Western European data were presented differently in the original source material. Pipe and conduit tonnages and also export sales as well as sales to compounders are included under 'Other' for USA data.

Polyethylene is an important injection moulding material. Whilst the percentage of LDPE used for injection moulding is only about 5% the actual tonnage is substantial although it has lost some of the market to HDPE, polypropylene and ethylene–vinyl acetate copolymers in recent years. In addition there is considerable use of blends of LDPE and HDPE. A very wide range of products are made, including toys, chemical plant, electrical fittings, seals, bushes and many industrial items, including several at one time made from rubber. Injection moulding is somewhat more important with HDPE both in percentage and absolute terms. Uses include industrial containers, cases, crates, pails, food tubs, containers, closures and caps, housewares, toys and a multiplicity of other applications. For many of these applications the material is in close competition with polypropylene and to some extent high-impact polystyrene, which will be discussed in Chapters 11 and 16.

Partly because LLDPE is now cheaper than LDPE, the former is now becoming the preferred material for low-stiffness injection mouldings.

Blow moulding is widely used for HDPE. One large application area is that of bottles for milk and other foodstuffs, household chemicals, personal toiletries and drug packaging. These take about 70% of the blow moulding market but other important areas include drums, pails and toys. In some cases the selection between blow moulding and rotational moulding requires careful consideration but at the present time the tonnage rotationally moulded is only about one-thirtieth of that blow moulded. Blow moulding of LDPE is largely confined to squeeze bottles, particularly for detergents, and in this case is a less important process than rotational moulding.

Another substantial use area for polyethylene is for pipe. Uses include domestic water and gas piping, agricultural piping and, on a smaller scale ink tubes for ball point pens. In this field of application there has recently been particular interest in ‘bimodal’ polymers, because of their resistance to cracking, in water piping with diameters up to 1000 mm and capable of withstanding pressures of 6–10 bar. Such pipes have been used for relining ageing concrete and cast iron drinking water distribution networks.

High molecular weight HDPE (HMW-HDPE) is used for blown film and for demanding moulding and structural uses. Examples are blow moulded drums for packing dangerous chemicals and pressure piping.

Very high (ultra-high) molecular weight polyethylenes (VHMWPE or UHMWPE) of molecular weights in the range $3\text{--}6 \times 10^6$, with their outstanding abrasion resistance, low-temperature toughness and low coefficient of friction, are used in severe operating conditions such as ore handling and food processing. Such materials are sometimes cross-linked with peroxides to further improve the abrasion resistance.

VLDPEs, with their very good low-temperature impact properties, are of interest in frozen food packaging. By 1998 the market for UHMWPE materials was estimated at 65 000 t.p.a. of which Ticona had about half the market share.

The excellent electrical insulation properties of polyethylene have led to extensive use in cable and other wire-covering applications. Spectacular early uses included undersea cables and airborne radar and the materials continue to be used in substantial quantities. One particular trend is the increasing use of cross-linked polyethylene for this area of use. Such materials have improved heat resistance and in addition have given generally better resistance to stress cracking. Cellular polyethylene is used as the insulator for television downlead aerials.

The development of the all-polyethylene sack has somewhat reduced the relative importance of extrusion coating. At one time paper-polyethylene laminates were widely used for sacks but their use has declined. However, techniques have been developed for coating a wide range of substrates to provide a useful range of materials of interest to the packaging industry.

Although the above applications consume over 90% of the polyethylene produced there are a number of other important end-uses. Filament for ropes, fishing nets and fabrics are an important outlet for high-density polyethylene; powdered polymers are used for dip coating, flame spraying, rotational moulding and other outlets, whilst fabricated sheet is important in chemical plant.

Mention may also be made of an application in which careful control of polymer morphology has led to the production of novel materials. By treatment of solutions of high-density polyethylene, products are obtained with a cellulose-like morphology and which are known as *fibrides* or synthetic wood pulp. They are used for finishing paper and special boards to impart such features as sealability and improved wet strength. They are also reported to be used for such diverse applications as tile adhesives, thixotropic agents, battery separators and teabags!

The greatest challenge to polyethylene is not from other materials but arises as a consequence of its own success. The vast quantities of polyethylene used each year for packaging have resulted in an undesirable level of litter. As a result of public resistance and, in some countries, legislation, growth in the use of polyethylene for packaging may be constrained in the future.

References

1. VON PECHMAN, H., *Chem. Ber.*, **31**, 2643 (1898)
2. BAMBERGER, E. and TSCHIRNER, F., *Chem. Ber.*, **33**, 955 (1900)
3. CAROTHERS, W. H., HILL, J. W., KIRBY, J. E. and JACOBSON, R. A., *J. Am. Chem. Soc.*, **52**, 5279 (1930)
4. KOCH, H. and IBING, G., *Brennstoff-Chem.*, **16**, 141 (1955)
5. FAWCETT, E. W., *Trans. Faraday Soc.*, **32**, 119 (1936)
6. *British Patent* 471590
7. ZIEGLER, K. E., *Angew. Chem.*, **67**, 426, 541 (1955)
8. PETICOLAS, W. L. and WATKINS, J. M., *Paper presented at 129th meeting of Am. Chem. Soc.*, Dallas, Texas (1956)
9. *Technical trade literature*, I.C.I. Plastics Ltd., Welwyn Garden City
10. SANDIFORD, D. J. H. and WILLBOURN, A. H., *Polythene* (Eds. RENFREW, D. AND MORGAN, P.), Iliffe, London, 2nd Edn., Chapter 8 (1960)
11. *Technical trade literature*, British Resin Products Ltd., London
12. BRYDSON, J. A., *Flow Properties of Polymer Melts (2nd edn.)*, Godwin, London (1981)
13. EXLEY, P. A. and STABLER, H. J., *A.P.I. Project Theses*
14. CLEGG, P. L. and HUCK, N. D., *Plastics*, **26** (282), 114 (1961); (283) 107 (1961)

Bibliography

- BOENIG, H. V. *Polyolefines: Structure and Properties*, Elsevier (1966)
- KRESSER, T. O. J., *Polyethylene*, Reinhold, New York (1960)
- Crystalline Olefin Polymers* (Eds. RAFF, R. A. V. and DOAK, K. W.), Interscience, New York (1964)
- Polythene—the Technology and Uses of Ethylene Polymers* (Eds. RENFREW, A. and MORGAN, P.), Iliffe, London, 2nd Edn (1960)
- RITCHIE, P. D. (Ed.), *Vinyl and Allied Polymers*, Vol. 1—*Aliphatic Polyolefins and Polydienes: Fluoro-olefin Polymers*, Iliffe, London (1968)
- SITTIG, M., *Polyolefine Resin Processes*, Gulf Publishing Co., Houston (1961)
- TOPCHIEV, A. V. and KRENTSEL, B. A., *Polyolefines*, Pergamon Press, Oxford (1962)
- VANDENBERG, E. J. (Ed), *Polythene—An ACS Symposium 1974*. Published by American Chemical Society (1975)

Reviews

GONDRO, C., *Kunststoffe*, **80** (10), 1080–5 (1990)

HATZMANN, G., JAGDMANN, S. and KLIMESCH, R. G., *Kunststoffe*, **86**, 1447–1453 (1996)

HERNER, M. and WOLTER, H.-J., *Kunststoffe*, **77**, 959–62 (1987)

KAPS, R., LECHT, R. and SCHULTE, U., *Kunststoffe*, **86**, 1454–1458 (1996)

MÜNSTEDT, H. and WOLTER, H.-J.; *Kunststoffe*, **80** (10), 1076–9 (1990)

Aliphatic Polyolefins other than Polyethylene, and Diene Rubbers

11.1 POLYPROPYLENE

Until the mid-1950s the only polyolefins (polyalkenes) of commercial importance were polyethylene, polyisobutylene and isobutylene–isoprene copolymers (butyl rubber). Attempts to produce polymers from other olefins had, at best, resulted only in the preparation of low molecular weight material of no apparent commercial value.

In 1954 G. Natta of Milan following on the work of K. Ziegler in Germany found that certain 'Ziegler-type' catalysts were capable of producing high molecular weight polymers from propylene and many other olefins. By variations on the form of the catalysts used Natta was able to produce a number of different types of high molecular weight polypropylenes which differed extensively in their properties. One form, now known as isotactic polypropylene, was in many ways similar to high-density polyethylene but with a higher softening point, rigidity and hardness, whilst another form, the atactic polymer, was amorphous and had little strength.

Commercial exploitation was very rapid, with isotactic polypropylene being marketed by Montecatini as Moplen as early as 1957. From that time on consumption growth rates have been high, with the material becoming widely used for fibres, films and injection mouldings. The expiry of the basic patents led to a surge in production capacity in the 1970s which so exceeded demand that the material became available at abnormally low prices, which in turn stimulated more growth in usage. Since that time production growth rates for polypropylene have generally been higher than for the other major tonnage plastics, and in the mid-1980s polypropylene moved into third place after polyethylene and PVC in the plastics production league. In 1998 it was estimated that global capacity was about 26.3×10^6 tonnes, with the United States and Western Europe each sharing about 25% of the market. As with other large tonnage materials, the figures for these two major production regions are somewhat lower than for ten years earlier due to the increasing share taken by the so-called developing countries and by the OPEC nations.

The application of metallocene catalysis to the preparation of polypropylenes reached a commercial stage with the production by Exxon of their Achieve range in 1996 and in 1997 by Targor, the BASF-Hoechst joint venture with the introduction of Metocene. Such metallocene polypropylenes are, however, only a small proportion of the total polypropylene market, predicted at only about 3% of the total in 2005.

With a rapidly growing market many grades of polypropylene are available but five main classes may be distinguished:

- (i) homopolymers produced by Ziegler–Natta catalysis;
- (ii) block copolymers produced by Ziegler–Natta catalysis;
- (iii) random copolymers produced by Ziegler–Natta catalysis;
- (iv) rubber-modified blends of the above;
- (v) homopolymers and copolymers produced by metallocene catalysis.

Two interesting developments should also be noted; syndiotactic polypropylene produced by a novel metallocene system and polypropylene grafted with styrene and/or maleic anhydride marketed by Montell as Hivalloy.

Mention should be made of the nomenclature for the polymer. Industrially the material is invariably known in the English-speaking world as polypropylene. However, the IUPAC name for the monomer is propene and until 1975 the recommended IUPAC name was polypropene, a term very rarely used. The latest IUPAC rules base the name of a polymer on the constitutional repeating unit, which in this case is a propylene unit (c.f. a methylene unit for polyethylene) and this leads to the name poly(propylene) (i.e. with brackets). In this volume the more common, unbracketed but still unambiguous name will be used.

11.1.1 Preparation of Polypropylene

There are many points of resemblance between the production of polypropylene and polyethylene using Ziegler-type catalysts. In both cases the monomers are produced by the cracking of petroleum products such as natural gas or light oils. For the preparation of polypropylene the C_3 fraction (propylene and propane) is the basic intermediate and this may be separated from the other gases without undue difficulty by fractional distillation. The separation of propylene from propane is rather more difficult and involves careful attention to the design of the distillation plant. For polymer preparation impurities such as water and methylacetylene must be carefully removed. A typical catalyst system may be prepared by reacting titanium trichloride with aluminium triethyl, aluminium tributyl or aluminium diethyl monochloride in naphtha under nitrogen to form a slurry consisting of about 10% catalyst and 90% naphtha. The properties of the polymer are strongly dependent on the catalyst composition and its particle shape and size.

In the suspension process, which was the first method to be commercially developed, propylene is charged into the polymerisation vessel under pressure whilst the catalyst solution and the reaction diluent (usually naphtha) are metered in separately. In batch processes reaction is carried out at temperatures of about 60°C for approximately 1–4 hours. In a typical process an 80–85% conversion to polymer is obtained. Since the reaction is carried out well below the polymer melting point the process involves a form of suspension rather than solution polymerisation. The polymer molecular weight can be controlled in a variety of

ways, for example by the use of hydrogen as a chain transfer agent or by variations in the molar ratio of catalyst components, the polymerisation temperature, the monomer pressure or the catalyst concentration.

At this stage of the process the following materials are present in the polymerisation vessel :

- (1) Isotactic polymer.
- (2) Atactic polymer.
- (3) Solvent.
- (4) Monomer.
- (5) Catalyst.

The first step in separating these ingredients involves the transfer of the reaction mixture to a flash drum to remove the unreacted monomer, which is purified (where necessary) and recycled. The residual slurry is centrifuged to remove the bulk of the solvent together with most of the atactic material which is soluble in the naphtha. The remaining material is then treated with an agent which decomposes the catalyst and dissolves the residue. A typical agent is methanol containing a trace of hydrochloric acid. The solution of residues in the methanol is removed by a centrifuging operation and the polymer is washed and dried at about 80°C. At this stage the polymer may be blended with antioxidants, extruded and cut into pellets. There are a number of variations in this basic process, many of which involve extra processes to reduce the atactic content of the polymer. A typical flow sheet for the manufacture of polypropylene is given in *Figure 11.1*.

There have also been a number of quite substantial changes in the method of polymerisation over the years. For example, newer catalyst systems, such as those containing magnesium compounds, give an appreciable improvement in the yield of isotactic material and this enables the washing stage to be dispensed with. In particular, both liquid (bulk process) and gas-phase processes have been developed, including methods which avoid the need for separate stages for the removal of catalyst residues and/or atactic material. Thermal and chemical after-treatments have also been developed to reduce the width of the molecular mass distribution.

One such system is that developed by Himont, which uses three components:

- (1) A titanium component supported on a magnesium halide.
- (2) An organo-aluminium component.
- (3) A Lewis base.

Detailed modifications in the polymerisation procedure have led to continuing developments in the materials available. For example in the 1990s greater understanding of the crystalline nature of isotactic polymers gave rise to developments of enhanced flexural modulus (up to 2300 MPa). Greater control of molecular weight distribution has led to broad MWD polymers produced by use of twin-reactors, and very narrow MWD polymers by use of metallocenes (see below). There is current interest in the production of polymers with a bimodal MWD (for explanations see the Appendix to Chapter 4).

Another technical development is that of high impact isotactic polypropylene in which rubber droplets are produced *in situ* during the polymerisation stage. After propylene homopolymerisation ethylene is added to the reacting mass in a

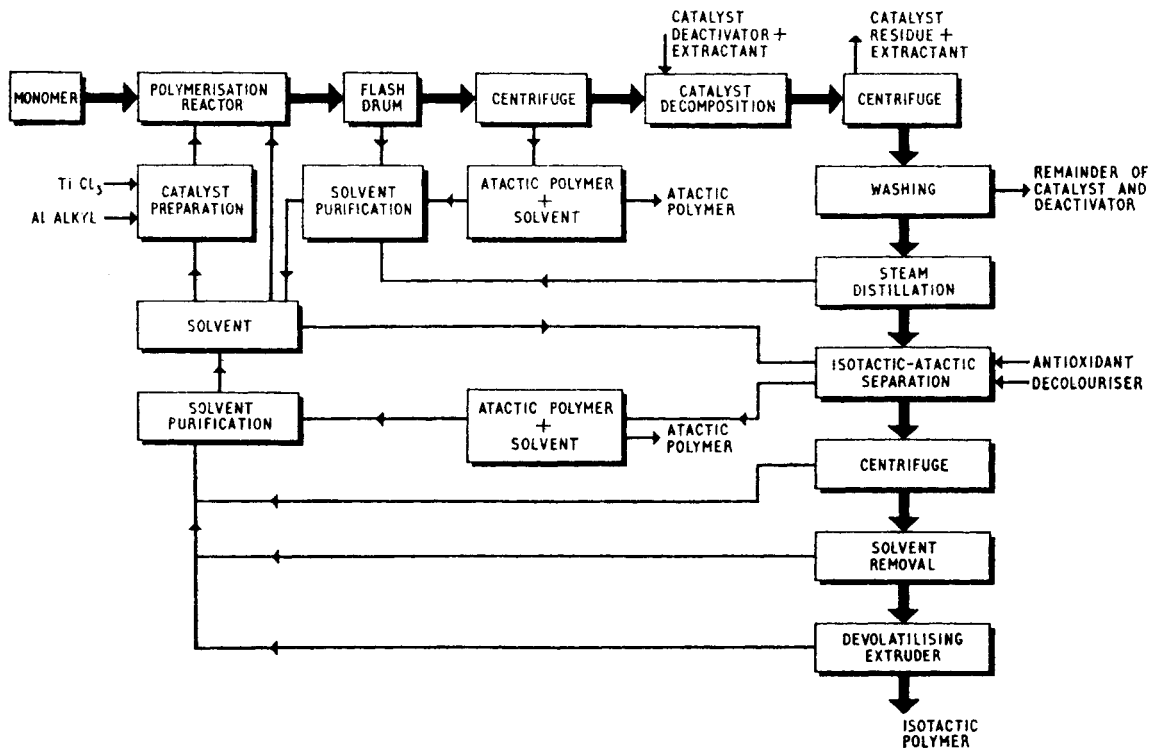


Figure 11.1. Typical flow sheet for polypropylene manufacture

second reactor and finely dispersed ethylene-propylene rubber droplets are formed by polymerisation in the porous homopolymer polypropylene pellets.

Polypropylenes produced by metallocene catalysis became available in the late 1990s. One such process adopts a standard gas phase process using a metallocene catalyst such as *rac*-dimethylsilylenebis(2-methyl-1-benz(e)indenyl)zirconium dichloride in conjunction with methylaluminoxane (MAO) as cocatalyst. The exact choice of catalyst determines the direction by which the monomer approaches and attaches itself to the growing chain. Thus whereas the isotactic material is normally preferred, it is also possible to select catalysts which yield syndiotactic material. Yet another form is the so-called *hemi-isotactic polypropylene* in which an isotactic unit alternates with a random configuration.

Metallocene catalysis can also make possible the production of copolymers of propylenes with monomers such as long-chain olefins, cyclic olefins and styrene which is not possible with more conventional Ziegler-Natta catalysts.

11.1.2 Structure and Properties of Polypropylene

Polypropylene is a linear hydrocarbon polymer containing little or no unsaturation. It is therefore not surprising that polypropylene and polyethylene have many similarities in their properties, particularly in their swelling and solution behaviour and in their electrical properties. In spite of the many similarities the presence of a methyl group attached to alternate carbon atoms on the chain backbone can alter the properties of the polymer in a number of ways. For example it can cause a slight stiffening of the chain and it can interfere with the molecular symmetry. The first effect leads to an increase in the crystalline melting point whereas the interference with molecular symmetry would tend to depress it. In the case of the most regular polypropylenes the net effect is a melting point some 50°C higher than that of the most regular polyethylenes. The methyl side groups can also influence some aspects of chemical behaviour. For example the tertiary carbon atom provides a site for oxidation so that the polymer is less stable than polyethylene to the influence of oxygen. In addition, thermal and high-energy treatment leads to chain scission rather than cross-linking.

The most significant influence of the methyl group is that it can lead to products of different tacticity, ranging from completely isotactic and syndiotactic structures to atactic molecules (see Chapter 4). The isotactic form is the most regular since the methyl groups are all disposed on one side of the molecule. Such molecules cannot crystallise in a planar zigzag form as do those of polyethylene because of the steric hindrance of the methyl groups but crystallise in a helix, with three molecules being required for one turn of the helix. Both right-hand and left-hand helices occur but both forms can fit into the same crystal structure. Commercial polymers are usually about 90–95% isotactic. In these products, atactic and syndiotactic structures may be present either as complete molecules or as blocks of varying length in chains of otherwise isotactic molecules. Stereo-block polymers may also be formed in which a block of monomer residues with a right-handed helix is succeeded by a block with a left-handed helix. The frequency with which such changes in the helix direction occur can have an important influence on the crystallisation and hence the bulk properties of the polymer. In practice it is difficult to give a full description of a specific propylene polymer although there has been marked progress in recent years. Many manufacturers simply state that their products are highly isotactic, others quote the polymer crystallinity obtained after some specified annealing

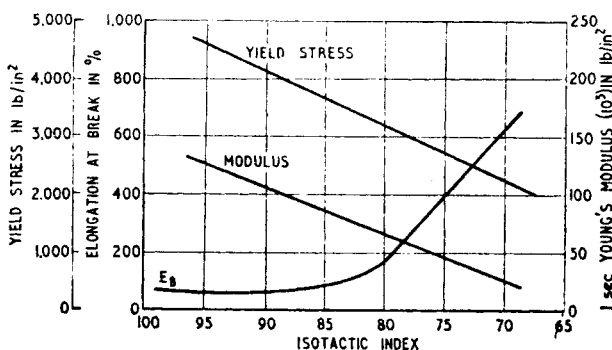


Figure 11.2. Effect of isotacticity on tensile properties. (Reproduced by permission of ICI Plastics Division)

treatment, whilst others quote the so-called 'isotactic index', the percentage of polymer insoluble in *n*-heptane. Both of these last two properties provide some rough measure of the isotacticity but are both subject to error. For example the isotactic index is affected by high molecular weight atactic polymer which is insoluble in *n*-heptane and by the presence of block copolymers of isotactic and atactic structures which may or may not dissolve, according to the proportion of each type present.

In spite of these problems the general effects of varying the degree of isotacticity are well known. Whereas the atactic polymer is an amorphous somewhat rubbery material of little value, the isotactic polymer is stiff, highly crystalline and with a high melting point. Within the range of commercial polymers, the greater the amount of isotactic material the greater the crystallinity and hence the greater the softening point, stiffness, tensile strength, modulus and hardness, all other structural features being equal (Figure 11.2).

The influence of molecular weight on the bulk properties of polypropylene is often opposite to that experienced with most other well-known polymers. Although an increase in molecular weight leads to an increase in melt viscosity and impact strength, in accord with most other polymers, it also leads to a lower yield strength, lower hardness, lower stiffness and softening point. This effect is believed to be due to the fact that high molecular weight polymer does not crystallise so easily as lower molecular weight material and it is the differences in the degree of crystallisation which affect the bulk properties. It may also be mentioned that an increase in molecular weight leads to a reduction in brittle point (see Table 11.1).

Published data on commercial polypropylenes indicate that their molecular weights are in the range $\bar{M}_n = 38\,000\text{--}60\,000$ and $\bar{M}_w = 220\,000\text{--}700\,000$, with values of \bar{M}_w/\bar{M}_n from about 5.6 to 11.9. These averages are somewhat higher than those encountered normally with polyethylene and may help to explain the difference in molecular weight dependence. It is in fact the case that the very high molecular weight polyethylenes also have some difficulty in crystallising and they too have lower tensile strength and stiffness than more conventional polymers of lower molecular weight.

Only a limited amount of information is available concerning the effects of molecular weight distribution. There is, however, evidence that the narrower the distribution the more Newtonian are the melt flow properties. It has been noted

Table 11.1 Some mechanical and thermal properties of commercial polypropylenes

Property	Test method	Homopolymers			Copolymers	
Melt flow index	(a)	3.0	0.7	0.2	3.0	0.2
Tensile strength (lbf/in ²)	(b)	5000	4400	4200	4200	3700
(MPa)		34	30	29	29	25
Elongation at break (%)	(b)	350	115	175	40	240
Flexural modulus (lbf/in ²)	-	190 000	170 000	160 000	187 000	150 000
(MPa)		1310	1170	1100	1290	1030
Brittleness temperature (°C)	ICI/ASTM D.476	+15	0	0	-15	-20
Vicat softening point (°C)	BS 2782	145-150	148	148	148	147
Rockwell hardness (R-scale)	-	95	90	90	95	88.5
Impact strength (ft lbf)	(c)	10	25	34	34	42.5
(J)		13.5	34	46	46	57.5

(a) Standard polyethylene grader: load 2.16kg at 230°C.

(b) Straining rate 18 in/min.

(c) Falling weight test on 14 in diameter moulded bowls at 20°C.

that with polymers of molecular weights suitable for moulding and extrusion, polymers of wide distribution (e.g. $\overline{M}_w/\overline{M}_n$ about 6) are stiffer and more brittle than those with a $\overline{M}_w/\overline{M}_n$ ratio of about 2.

The morphological structure of polypropylene is rather complex and at least four different types of spherulite have been observed. The properties of the polymer will depend on the size and type of crystal structure formed and this will in turn be dependent on the relative rates of nucleation to crystal growth. The ratio of these two rates can be controlled by varying the rate of cooling and by the incorporation of nucleating agents. In general the smaller the crystal structures the greater the transparency and flex resistance and the less the rigidity and heat resistance.

One unfortunate characteristic property of polypropylene is the dominating transition point which occurs at about 0°C with the result that the polymer becomes brittle as this temperature is approached. Even at room temperature the impact strength of some grades leaves something to be desired. Products of improved strength and lower brittle points may be obtained by block copolymerisation of propylene with small amounts (4-15%) of ethylene. Such materials are widely used (known variously as polyallomers or just as propylene copolymers) and are often preferred to the homopolymer in injection moulding and bottle blowing applications.

Further variations in the properties of polyethylenes may be achieved by incorporating additives. These include rubber, antioxidants and glass fibres and their effects will be discussed further in Section 11.1.4.

11.1.3 Properties of Isotactic Polypropylene

Although very similar to high-density polyethylene, isotactic polypropylene differs from the former in a number of respects of which the following are among the most important:

- (1) It has a lower density (0.90 g/cm^3).
- (2) It has a higher softening point and hence a higher maximum service temperature. Articles can withstand boiling water and be subject to many steam sterilising operations. For example mouldings have been sterilised in hospitals for over 1000 hours at 135°C in both wet and dry conditions without severe damage.
- (3) Polypropylene appears to be free from environmental stress cracking problems. The only exception seems to be with concentrated sulphuric and chromic acids and with aqua regia.
- (4) It has a higher brittle point.
- (5) It is more susceptible to oxidation.

As shown in the previous section the mechanical and thermal properties of polypropylene are dependent on the isotacticity, the molecular weight and on other structure features. The properties of five commercial materials (all made by the same manufacturer and subjected to the same test methods) which are of approximately the same isotactic content but which differ in molecular weight and in being either homopolymers or block copolymers are compared in *Table 11.1*.

The figures in *Table 11.1* show quite clearly how an increase in molecular weight (decrease in melt flow index) causes a reduction in tensile strength, stiffness, hardness and brittle point but an increase in impact strength. The general effects of isotactic index and melt flow index on some mechanical and thermal properties are also shown graphically in *Figures 11.3–11.6*.¹ Both random and block copolymers are now available and these show interesting differences as indicated in *Table 11.2*.

Many features of the processing behaviour of polypropylene may be predicted from consideration of thermal properties. The specific heat of polypropylene is lower than that of polyethylene but higher than that of polystyrene. Therefore the plasticising capacity of an injection moulding machine using polypropylene is lower than when polystyrene is used but generally higher than with a high-density polyethylene.

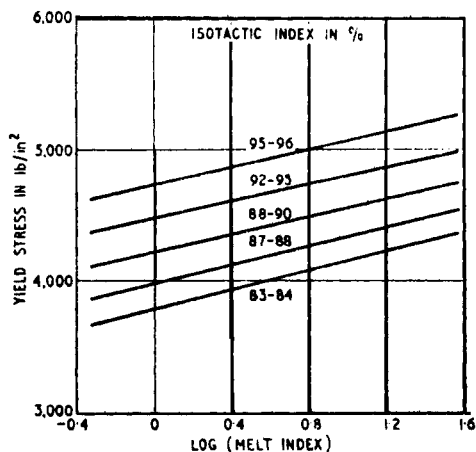


Figure 11.3. Variation of tensile yield stress with melt flow index (10 kg load at 190°C) and isotactic index. (After Crespi and Ranalli¹)

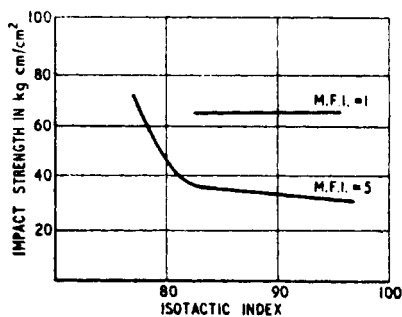


Figure 11.4. Variation of impact strength with melt flow index (10 kg at 190°C) and isotactic index. (After Crespi and Ranalli¹)

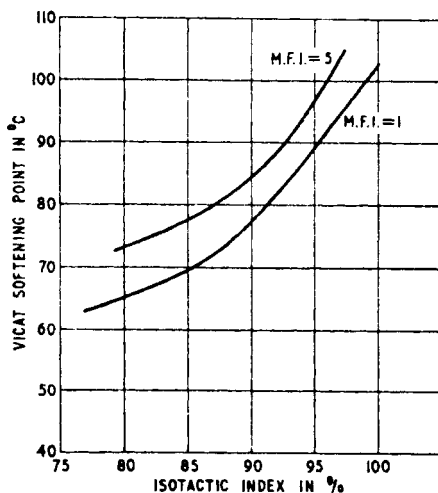


Figure 11.5. Variation of Vicat softening point (5 kg load) with isotactic index and melt flow index. (After Crespi and Ranalli¹)

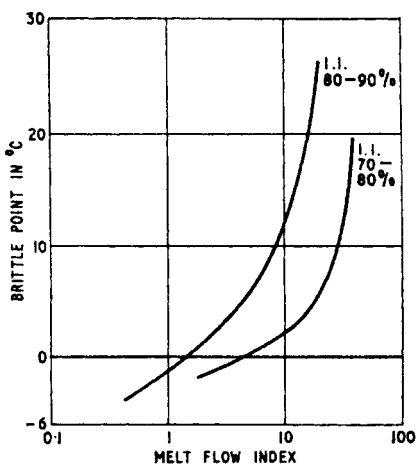


Figure 11.6. Variation of ASTM D746 brittle point with melt flow index and isotactic index (After Crespi and Ranalli¹)

Table 11.2 Comparison of random and block copolymers (data based on three grades of Novolen – Targor GmbH)

<i>Property</i>	<i>Units</i>	<i>Test method</i>	<i>Random copolymer</i>	<i>Block copolymer</i>	<i>Homopolymer</i>
Novolen grade			3348SC	2600TC	1148TC
Melt Flow Ratio 230°C/2.16 kg	g/10 min	ISO1133	30	48	48
Tensile Yield Stress	MPa	ISO527	23	19	35
Tensile Modulus	MPa	ISO527	820	950	1550
Charpy Impact 23°C	kJ/m ²	ISO179/1eU	No break	No break	103
0°C			190	170	
-20°C			50	150	
Haze	%	ASTM D1003	7	95	60

This data indicates that the random copolymer has greater transparency but inferior low temperature impact strength.

Studies of melt flow properties of polypropylene indicate that it is more non-Newtonian than polyethylene in that the apparent viscosity declines more rapidly with increase in shear rate. The melt viscosity is also more sensitive to temperature. Van der Wegt² has shown that if the log (apparent viscosity) is plotted against log (shear stress) for a number of polypropylene grades differing in molecular weight, molecular weight distribution and measured at different temperatures the curves obtained have practically the same shape and differ only in position.

The standard melt flow index machine is often used for characterising the flow properties of polypropylene and to provide a rough measure of molecular weight. Under the conditions normally employed for polyethylene (2.16 kg load at 190°C) the flow rate is too low for accurate measurement and in practice higher loads, e.g. 10 kg, and/or higher temperatures are used. It has been found³ that a considerable pressure drop exists in the barrel so that the flow towards the end of a test run is higher than at the beginning.

The moulding shrinkage of polypropylene is less than that experienced with polyethylenes but is dependent on such processing factors as mould temperature, melt temperature and plunger dwell time. In general, conditions which tend to reduce the growth of crystal structures will tend to reduce shrinkage; for example, low mould temperatures will encourage quenching of the melt. It is also found that low shrinkage values are obtained with high melt temperatures. This is probably due to the fact that high melt temperatures lead to a highly disordered melt whereas some molecular order may be present in melts which have not been heated much above the crystalline melting point. Such regions of order would provide sites for crystal nucleation and hence crystallisation would be more rapid when cooling was carried out.

The electrical properties of polypropylene are very similar to those of high-density polyethylenes. In particular the power factor is critically dependent on the amount of catalyst residues in the polymer. Some typical properties are given in *Table 11.3* but it should be noted that these properties are dependent on the antioxidant system employed as well as on the catalyst residues.

Table 11.3 Some typical electrical properties of a high heat stability grade of polypropylene⁴

Dielectric constant at 5×10^6 Hz	2.25
Volume resistivity (Ωm)	$>10^{19}$
Power factor at 10^2 Hz	0.0009
10^3 Hz	0.001
10^4 Hz	0.0009
10^5 Hz	0.006
10^6 Hz	0.0004
5×10^6 Hz	0.0005

As with electrical properties the chemical resistance of polypropylene shows many similarities to high-density polyethylene. The two polymers have similar solubility parameters and tend to be swollen by the same liquids. In both cases the absence of any possible interaction between the crystalline polymer and the liquid prevents solution of the polymers in any liquids at room temperature. In some instances polypropylene is more affected than polyethylene but in other cases the reverse is true. Similar remarks may be made concerning the permeability of the two polymers to liquids and gases. With many permeants polypropylene shows the lowest permeability but not, for example, with hexane. It may be mentioned in this context that although high-density polyethylene is usually intermediate between low-density polyethylene and polypropylene, where the permeant causes stress cracking (as with a silicone oil), the high-density polyethylenes often have the highest permeability. The fact that polypropylene is resistant to environmental stress cracking has already been mentioned.

Polypropylene differs from polyethylene in its chemical reactivity because of the presence of tertiary carbon atoms occurring alternately on the chain backbone. Of particular significance is the susceptibility of the polymer to oxidation at elevated temperatures. Some estimate of the difference between the two polymers can be obtained from *Figure 11.7*, which compares⁵ the rates of oxygen uptake of each polymer at 93°C. Substantial improvements can be made by the inclusion of antioxidants and such additives are used in all commercial compounds. Whereas polyethylene cross-links on oxidation, polypropylene degrades to form lower molecular weight products. Similar effects are noted

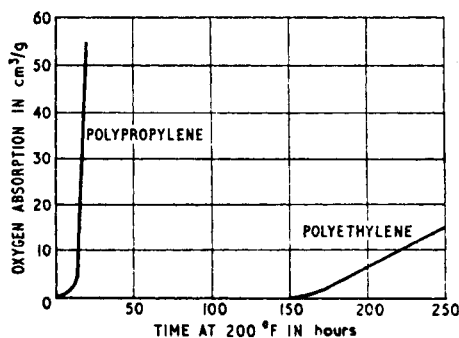


Figure 11.7. Comparison of oxidation rates of unstabilised polyethylene and polypropylene (After Kresser⁵)

Table 11.4 Effect of percentage stretch on tensile properties of polypropylene film⁷

Stretch (%)	Tensile strength		E_B (%)
	(lbf/in ²)	(MPa)	
None	5 600	39	500
200	8 400	58	250
400	14 000	97	115
600	22 400	155	40
900	23 800	165	40

when the polymer is exposed to high-energy radiation and when heated with peroxides (conditions which will cross-link polyethylene).

Although a crystalline polymer, polypropylene mouldings are less opaque when unpigmented than corresponding mouldings from high-density polyethylene. This is largely due to the fact that the differences between the amorphous and crystal densities are less with polypropylene (0.85 and 0.94 g/cm³ respectively) than with polyethylene (see Chapter 6). Clarity may also be affected by the use of nucleating agents (see also Sections 3.3 and 11.1.4). Biaxially stretched film has a high clarity since layering of the crystalline structures reduces the variations in refractive index across the thickness of the film and this in turn reduces the amount of light scattering.⁶

Biaxial stretching also leads to polymers of improved tensile strength. The effect of increasing the amount of stretching on the tensile strength and breaking elongation are given in *Table 11.4*.

There are other differences between cast, monoaxially oriented, and balanced biaxially oriented film. Typical figures illustrating these effects are given in *Table 11.5*.

When film is produced by air-cooled tubular blowing methods cooling rates are slower and larger degrees of crystallinity result. Hence tubular film is slightly

Table 11.5 Comparison of cast, monoaxially oriented and biaxially oriented polypropylene film⁹

Property	Cast polymer	Monoaxially oriented	Balanced oriented
Tensile strength (lbf/in ²)			
Machine direction	5700	8 000	26 000
Transverse direction	3200	40 000	22 000
Tensile strength (MPa)			
Machine direction	39	55	180
Transverse direction	22	280	152
Elongation at break (%)			
Machine direction	425	300	80
Transverse direction	300	40	65
ASTM D.523 gloss (45°C head)	75–80	>80	>80
Low temperature brittleness	brittle at °C	excellent	excellent
Coefficient of friction	0.4	0.4–0.5	0.8

stronger in tension but has lower impact strength, tear strength and breaking elongation. The film also has more haze and less gloss but somewhat better gas barrier properties and greater freedom from blocking.

Properties of metallocene isotactic and syndiotactic polypropylenes

Isotactic polypropylenes produced by metallocene catalysis are now being produced by a number of different manufacturers and because different systems are used there is some variation in properties. Typically however such materials have similar density, hardness and tensile strength to conventional homopolymers but differ in having

- (i) a narrower molecular weight distribution \bar{M}_w/\bar{M}_n c.1.9;
- (ii) better optical properties such as 93% ASTM D1003 transparency (cf. 40% for a conventional homopolymer) and higher specular gloss (77% cf. 57% by ISO 2813);
- (iii) lower T_m (typically about 15°C less using DSC methods);
- (iv) lower extractables;
- (v) lower toughness.

The narrow molecular weight distribution means that the melts are more Newtonian (see Section 8.2.5) and therefore have a higher melt viscosity at high shear rates than a more pseudoplastic material of similar molecular dimensions. In turn this may require more powerful extruders. They are also more subject to melt irregularities such as sharkskin and melt fracture. This is one of the factors that has led to current interest in metallocene-polymerised polypropylenes with a bimodal molecular weight distribution.

The lower melting point can be advantageous in that film sealing temperatures may be lower thus allowing faster production rates of packaging products.

The higher transparency coupled with the rigidity expected of a conventional polypropylene homopolymer is of particular interest in thin-wall moulding applications.

Syndiotactic polypropylene first became available in the 1990s (Fina, Mitsui Toastu, Sumitomo) and more recently has been marketed by Dow. Currently this polymer is more expensive than other polypropylenes both because of catalyst costs and the small scale of production.

Syndiotactic materials are generally softer, tougher and more transparent than isotactic materials but exhibit similar melting points (*Table 11.6*).

Table 11.6 Comparison of some properties of syndiotactic and isotactic polypropylenes

	<i>Syndiotactic PP</i>	<i>Isotactic PP</i>
Density (g/cm ³)	0.9	0.9
Elastic modulus (MPa)	61	16.5
Impact strength (-23°C) (kJ/m ²)	80	16
Opacity (%)	1.7	85
Crystallinity	30–40	40–60
T_m (°C)	168	163

(NB The data compares a syndiotactic material with a melt index of 30 and an isotactic material with an index of 0.3. This should however not invalidate the large differences seen in such properties as modulus, impact strength and opacity.)

11.1.4 Additives for isotactic polypropylene

Commercial grades of polypropylene may be blended with a number of other additives. Of these the most important are:

- (1) Fillers.
- (2) Rubbers.
- (3) Pigments.
- (4) Carbon black and ultraviolet absorbers.
- (5) Antioxidants.
- (6) Nucleating agents.

Whilst most of the polypropylene produced is used without mineral filler the use of such materials is more common than with polyethylene. About 3% of polypropylene compounds are filled with talc and these have found use in both injection moulding and sheet applications. The improved stiffness and heat deformation resistance has led to the use of such compounds for the manufacture of heater housings, car mounting components and several domestic appliances. Talc-filled polypropylene sheet is also used as an alternative to carton board. More recently there has been increasing interest in the use of calcium carbonate, which may be used at levels as high as 50 parts per hundred (pts phr). In comparison to the talc-filled grades the calcium-carbonate-filled grades are claimed to have higher impact strength, brighter colour, higher thermal stability, improved fatigue strength but lower stiffness. Tensile strength is markedly reduced with both fillers.

Glass fibres are used to confer enhanced strength and rigidity. Substantial improvements are, however, only realised after a coupling reaction takes place between organofunctional silanes on the glass fibre and reactive groups introduced into the polypropylene molecule. One grade containing 25% w/w of long fibres (in which the fibres were as long as the granules) had about three times the tensile strength and four times the rigidity at room temperature and four times the strength and eight times the rigidity at 100°C than a corresponding unfilled polymer. One notable use of glass-filled polypropylene has been in structural foam form in which it was used for the tank or tub of a domestic washing machine. Another interesting development has been the use of chopped strand mat (developed originally mainly for polyester laminating resins—see Chapter 25) impregnated with easy flow grades of homo- and block copolymers which may be moulded to give products of both high rigidity and impact toughness such as car underfloor panels and engine covers. Asbestos fibres have also been used but concern over health hazards and other factors have led to declining use with polypropylene.

In the early stages of development of polypropylene rubbers, particularly butyl rubber, were used to reduce the brittleness of polypropylene. Their use declined for some years with the development of the polypropylene copolymers but interest was greatly renewed in the 1970s. This interest has been centred largely around the ethylene-propylene rubbers which are reasonably compatible in all proportions with polypropylene. At first the main interest was with blends in which the rubber content exceeded 50% of the blend and such materials have been designated as *thermoplastic polyolefin elastomers* (discussed in Section 11.9.1). There is also increasing interest in compounds with less than 50% rubber, often referred to as *elastomer-modified thermoplastics*. It is of interest to note

that the rubbery component is capable of being diluted with large amounts of carbon black and mineral oils to reduce costs substantially.

In general the selection of pigments for polypropylene follows the same considerations as for polyethylene. Because of the higher processing temperatures and the lesser resistance to oxidation, selection does, however, require rather more care.

To improve the resistance to ultraviolet light carbon black is often useful as a light screen. Its use in fibres and films is clearly very restricted and in these instances ultraviolet absorbers and/or quenching agents are used. Recent developments include the greater use of hindered amine and nickel compounds.

Antioxidants are necessary components of all polypropylene compounds and the selection of such ingredients is an important factor in determining the success of a given commercial material. For optimum processing stability a single antioxidant of the phenol alkane type, for example 1,1,3-tris-(4-hydroxy-2-methyl-5-*t*-butylphenyl)butane (Topanol CA), tends to give the best results. These are usually assessed by comparing the relative rates of chain scission as indicated by relative increases in melt flow index. However, for long-term service stability at elevated temperatures it is more common to employ a synergistic mixture of a chain-breaking antioxidant and a peroxide-decomposing antioxidant, for example a phenol alkane and dilauryl thiodipropionate. Prolonged oven heating leads to embrittlement of the polymer and embrittlement time is a useful criterion for efficiency of an antioxidant with respect to service stability. Results of various synergistic ratios with two antioxidants are shown in *Figure 11.8*.

As with most polyolefins and polydienes the presence of copper has a strong adverse effect and most antioxidants are relatively ineffective. In these instances quite good results may be achieved by the use of 1% of a 50:50 phenol alkane-dilauryl thiodipropionate blend instead of the 0.1–0.2% of antioxidants more commonly used in polypropylene.

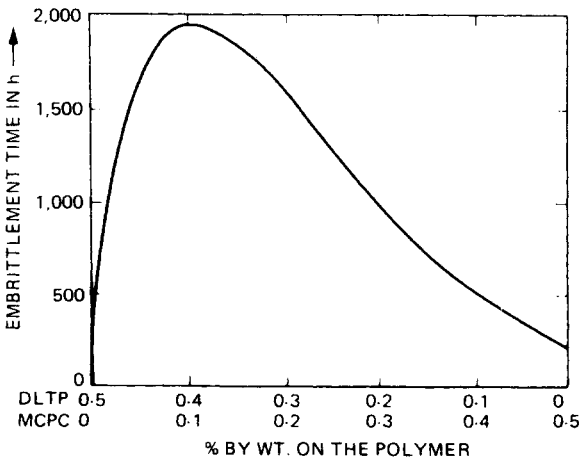


Figure 11.8. Synergistic effect of two antioxidants in polypropylene (DLTP=dilauryl thiodipropionate. MCPC=2,2'-methylenebis[6-(1-methylcyclohexyl-*p*-cresol)]). (After Leyland and Watts⁸)

11.1.5 Processing Characteristics

Polypropylene may generally be processed by methods very similar to those used with the polyethylenes, particularly high-density polyethylene. The main differences are the lower specific heat and the greater sensitivity of flow properties to temperature and shear rate. The moulding shrinkage is lower than with polyethylene but higher than with polystyrene. The effect of injection moulding variables on the shrinkage has already been discussed. Most processing operations involve the use of melt temperatures in the range 210–250°C. Because of the tendency of polypropylene to oxidise, heating times should be kept down to a minimum.

The blow moulding of polypropylene is generally considered as being more difficult than for polyethylene. However, providing sufficient care is paid to both equipment design and operating conditions good mouldings may be obtained. The basic difficulty is to reconcile the need for a homogeneous melt which requires high melt temperatures and extensive shear mixing with the tendency of these conditions to cause polymer degradation. In order to work at the lowest practical temperatures very good temperature control is necessary for all stages of the process and in addition the machine should be of robust construction. This is because at the low temperatures high pressures will be developed in the barrel and in particular the thrust bearings must be well designed. To minimise wear the extruder barrel should have a continuous hardened steel liner.

Attention also has to be paid to screw design. The screw metering zone should be long and shallow to ensure melt homogenisation but not so shallow that

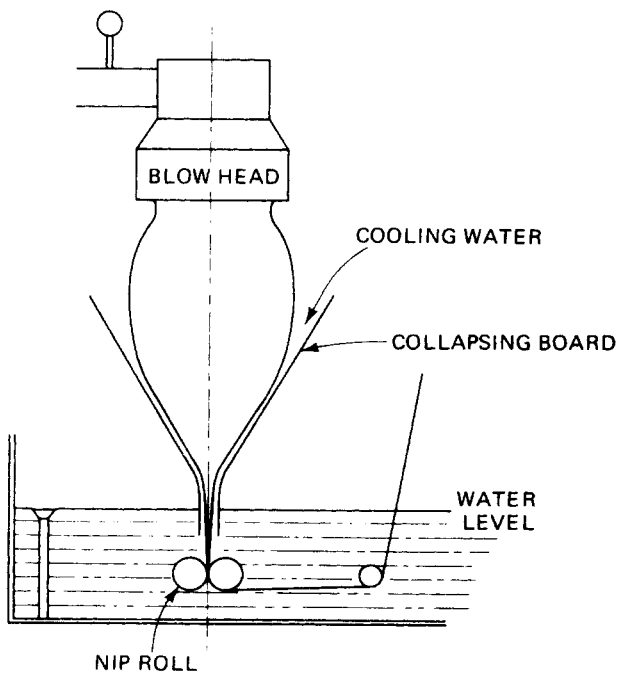


Figure 11.9. Equipment setting for TQ film extrusion. (After Gray¹⁰; reproduced with permission of The Plastics and Rubber Institute)

excessive shear and hence degradation result. Typical flight depths for a 60 mm diameter screw are about 2.25 mm and for a 90 mm screw 3.0 mm. Design and maintenance of the die is also important since where streams of molten polymer are split, for example when passing through a cross-head, subsequent fusion may be inadequate and form lines of weakness in the article. Polypropylene is more susceptible to these problems than high-density polyethylene. Mould cooling times are also a little longer and warm mouldings are also somewhat tackier than those from HDPE.

Film manufacture also requires special considerations in the case of polypropylene in order to ensure small crystal structures and hence high clarity. Chill-roll casting processes may be used and these give films of high clarity and minimal thickness variations at high rates of production. Blown film processes can, however, give superior mechanical properties and in addition equipment costs are lower, and in consequence the process is more economic for lower tonnage production.

In order to ensure the small crystal structures blown film is usually extruded downwards between two converging boards. In the Shell TQ (tubular quench) process these boards are covered with a downward flowing film of cooling water which accelerates the cooling of the polymer (*Figure 11.9*). One development of this, the Dow-Taga process has the water running out of a sizing ring above the boards (*Figure 11.10*). In a third process the extrudate passes over a mandrel before passing into the water bath.

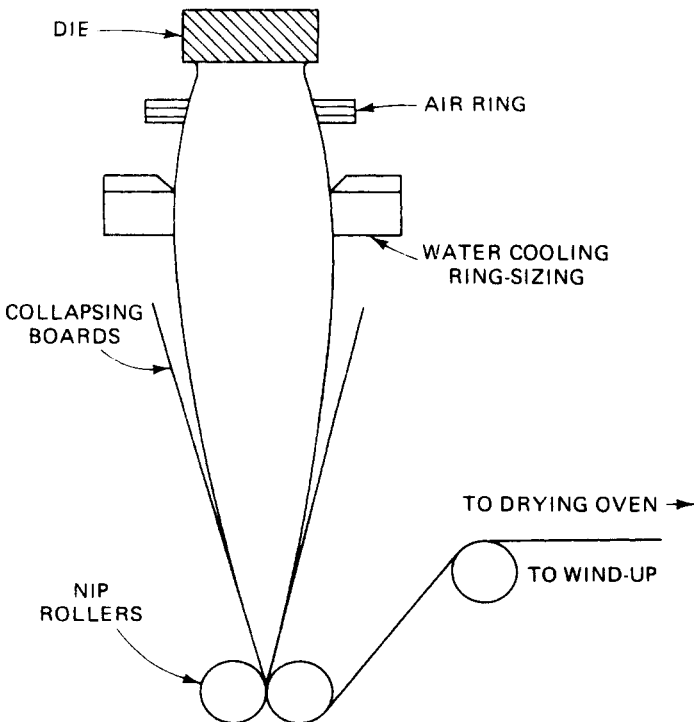


Figure 11.10. Dow-Taga process. (After Gray¹⁰; reproduced with permission of The Plastics and Rubber Institute)

The bulk of polypropylene film is used in oriented form (OPP) because of its greater strength and also its better barrier properties. Film made by chill-roll casting techniques is fed directly from the chill roll into a heated zone in which the sheet is subjected to longitudinal and transverse stretching. The longitudinal stretch is achieved by a cooling roll beyond the heating zone drawing the film at a faster rate than it emerges from the chill roll. The transverse stretching is achieved by feeding the film into a tenter frame consisting of a pair of diverging endless belts or chains fitted with clips. Transverse drawing may precede longitudinal drawing or vice versa or the two operations may be simultaneous as in *Figure 11.11*.

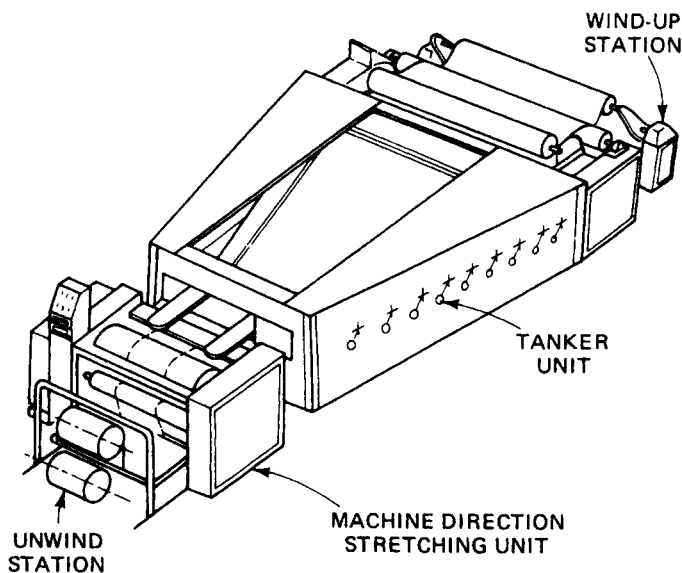


Figure 11.11. Two-stage orientation—flat films (After Gray¹⁰; reproduced with permission of The Plastics and Rubber Institute)

Tubular film may be biaxially oriented by passing cooled film through a pair of nip rolls, reheating it to a uniform temperature and then passing it between a further pair of rolls. Between the two pairs of rolls a mandrel of air is introduced in order to expand the film. The process is similar to that shown for poly(vinylidene chloride) in *Figure 17.4*.

In order to reduce the tendency of the film to shrink oriented film may be annealed at about 100°C whilst under tension immediately after drawing. The film is often coated with another polymer such as a vinylidene chloride-based copolymer. This both improves the barrier properties and improves the heat sealability.

An important application for polypropylene is film tape. This is made by slitting unoriented film (cast or blown) into tapes 2 or 3.5 mm wide and stretching under heat about seven-fold. With cast film the orientation is more completely monoaxial and there is a tendency for the film to split along its length (fibrillate). Tubular film does not self-split so easily and also has a somewhat softer feel. Such tapes may be woven into sacks and these have

found extensive acceptance particularly at the expense of those made from jute.

Film tapes may also be made drawn up to 10:1 ratios and then fibrillated by pin rollers, embossed rollers or some other technique. Fibrillated tape has been a substantial replacement for sisal.

11.1.6 Applications

Whilst it is inevitable that polypropylene will be compared more frequently with polyethylene than with any other polymer its use as an injection moulding material also necessitates comparison with polystyrene and related products, cellulose acetate and cellulose acetate-butyrates, each of which has a similar rigidity. When comparisons are made it is also necessary to distinguish between conventional homopolymers and the block copolymers. A somewhat crude comparison between these different polymers is attempted in *Table 11.7* but further details should be sought out from the appropriate chapters dealing with the other materials.

Table 11.7 Comparative ratings of various polymers in respect of some selected properties

<i>Polymer</i>	<i>Clarity of moulding</i>	<i>Temperature resistance</i>	<i>Toughness</i>
Polypropylene (homopolymer)	opaque	A	F-G
Polypropylene (copolymer)	opaque	B	D-F
Polyethylene (high density)	opaque	D	D-F
Polystyrene	clear	E	H
High-impact polystyrene	opaque	F	D-G
ABS polymers	opaque	C	A
Cellulose acetate	clear	G	B-C
CAB	clear	H	B-C

A indicates the most favourable material. H the least favourable.

Such a table must be subject to certain generalisations and in special instances there may be some variations in the above ratings. There are also many other factors which must also be taken into account and the choice of a particular polymer for a given application will depend on a careful study of the product requirements and the properties of potential materials. Polypropylene homopolymers and copolymers have found applications for mouldings where such properties as good appearance, low-density sterilisability, environment stress cracking resistance and good heat resistance are of importance. One further particularly useful property of polypropylene is the excellent resistance of thin sections to continued flexing. This has led to the introduction of a number of one piece mouldings for boxes, cases and automobile accelerator pedals in which the hinge is an integral part of the moulding. The special copolymer grades with their higher impact strength and lower brittle point have absorbed a large part of this market. Typical mouldings include hospital sterilisable equipment, luggage, stacking chairs, washing machine parts, toilet cisterns and various car parts such as dome lights, kick panels, door frame parts, accelerator pedals and car battery cases.

In broad tonnage terms the injection moulding markets for high-density polyethylene and polypropylene are very similar. The main reasons for selecting polypropylene have been given above. In favour of HDPE is the inherently better oxidation and ultraviolet resistance. Whilst these properties may be greatly improved in polypropylene by the use of additives these may increase the cost of polypropylene compounds to beyond that which is considered economically attractive. It is for this reason that HDPE has retained a substantial part of the crate market.

As already mentioned there has been considerable interest in physically modified polypropylenes for injection moulding. For example, elastomer-modified blends are widely used in the car industry for such purposes as bumpers and radiator grilles, fascia panels and protective strips. Outside of the car industry there has been interest in the material for ski boots. Talc-filled grades are used where extra rigidity and heat deformation resistance are required whilst the cheaper calcium-carbonate-filled grades have replaced polystyrene in such applications as flower pots. Further property enhancement may be obtained by the use of coupled glass fibre as a filler, on occasion in conjunction with a blowing agent to give a glass-reinforced structural foam such as that used for the outer tank of a well-known domestic washing machine.

One particular growth area for polypropylene mouldings is for thin-wall packaging such as margarine tubs. This is largely at the expense of polystyrene and arises partly from economics and partly from the wish to have a product free of residual styrene monomer.

As a blow moulding material polypropylene has never enjoyed the success of HDPE. This is in large measure because moulding of the former requires more attention to equipment design and operating conditions. Many successful mouldings have nevertheless been made commercially including chairs, horticultural sprayers and motor car parts.

With the advent of improved clarity grades in the 1990s there has been interest in replacing PVC for blow moulded containers for bottled water.

Non-oriented polypropylene film, which is glass clear, is used mainly for textile packaging but also as a confectionery wrap and for packaging 'fast-turnover' food. It also finds some acceptance in laminate production where a high heat resistance is required for the packaging of fish and meat products. Oriented film is more important because of its greater clarity, impact strength and barrier properties. Coated grades are used for bread and biscuit wrapping, for packaging potato crisps and as a capacitor dielectric. These applications are mainly at the expense of regenerated cellulose film but the latter has been more difficult to replace for cigarette wrapping.

Monoaxially oriented film tapes have been widely used for carpet backing and for sacks. In the latter case the resistance to rotting is of importance and the material has widely replaced jute. Fibrillated oriented tape has also made large inroads into the markets of another natural fibre, sisal, for twine and string purposes. Polypropylene straps have also gained rapid and widespread acceptance for packaging, combining strength, lightness and scope for attractive patterns on the strap surface.

Amongst hydrocarbon polymers polypropylene has been uniquely successful as a fibre. Its comparatively low cost and excellent wear together with resistance to staining have led to a major use in carpets as the tufting material. It has also found some use for blankets. As softer grades of fibre become available and

Table 11.8 Market breakdown for USA polypropylene Production (based on data in *Modern Plastics International*)

Market	1987		1997	
	'000 tonnes	%	'000 tonnes	%
Injection moulding	650	34	1653	41
Fibre and filaments	777	40	1508	38
Film	245	12	523	13
Blow moulding	55	3	85	2
Other extrusions	223	11	232	6

techniques are developed for dyeing, polypropylene may be expected to extend its range of fibre applications.

Polypropylene monofilaments combine low density with a high tenacity and good abrasion resistance and are finding some application in ropes and netting.

The polymer has found some small-scale outlets in other directions such as sheet, pipe and wire coating. Consumption of the polymer in these directions is, however, dependent on finding applications for which polypropylene is the most suitable material.

Although similar to polyethylene both in its structure and its properties, polypropylene has developed different patterns of usage. Estimates for the market breakdown in the United States, which are similar to those in Western Europe, are given in *Table 11.8*.

11.1.7 Atactic and Syndiotactic Polypropylene

Atactic polypropylene may be obtained either as a by-product of the manufacture of isotactic polypropylene or by specific processes designed for its direct production.

Whilst completely atactic material would be amorphous, commercial materials have a small measure of crystallinity. This is often assessed in terms of insolubility in *n*-heptane which is usually of the order of 5–10%. Viscosity average molecular weights are in the range 20 000–80 000 and specific gravities are about 0.86 g/cm³.

In appearance and on handling the material is somewhat intermediate between a wax and a rubber. It is also semi-tacky. Like isotactic polypropylene it is attacked by oxygen but unlike the isotactic material it swells extensively in aliphatic and aromatic hydrocarbons at room temperature. It is also compatible with mineral fillers, bitumens and many resins.

For many years atactic polypropylene was an unwanted by-product but today it finds use in a number of markets and is specially made for these purposes rather than being a by-product. In Europe the main use has been in conjunction with bitumen as coating compounds for roofing materials, for sealing strips where it confers improved aging properties and in road construction where it improves the stability of asphalt surfaces. Less important in Europe but more important in USA is its use for paper laminating for which low-viscosity polymers are used, often in conjunction with other resins. Limestone/atactic

polypropylene blends in ratio 70/30 are used as back coatings for self-laying carpet tiles. Here the requirements are non-slip characteristics, good dimensional stability and resistance to lateral compressive loads as well as low cost. Other uses are as sealing compounds, for adhesives and, in combination with felt or open-pore expanded plastics, for automobile vibration damping.

High molecular weight atactic polypropylene is now available (Rexene-Huntsman). This is miscible with isotactic polypropylene in any proportion to give transparent blends of interest in packaging applications.

In the early 1990s syndiotactic polypropylene became available from a number of sources (Fina, Mitsui Toastu, Sumitomo) and were joined in the late 1990s by Dow using metallocene catalyst systems. Interest in these materials is a consequence of their possessing greater toughness, clarity and heat resistance (softening point) than corresponding isotactic polypropylene. See *Table 11.6*

11.1.8 Chlorinated Polypropylene

The chlorination of polypropylene has been the subject of several fundamental studies and a variety of products is obtainable according to the tacticity of the original polymer and to the extent of chlorination.

The polymers have been offered by Sanyo Pulp of Tokyo as film-forming resins of good chemical resistance, and heat and light stability. Suggested uses include paint vehicles, printing ink binders, overprint varnishes, adhesives, additives to sealing compounds and waterproofing agents.

11.2 POLYBUT-1-ENE

Polybut-1-ene became available in the early 1960s as Vestolen BT produced by Chemische Werke Hüls in Germany. Today it is manufactured by Shell in the United States. It is produced by a Ziegler–Natta system and the commercial materials have very high molecular weights of 770 000 to 3 000 000, that is about ten times that of the normal low-density polyethylenes.

This polymer is typical of the aliphatic polyolefins in its good electrical insulation and chemical resistance. It has a melting point and stiffness intermediate between high-density and low-density polyethylene and a thermal stability intermediate between polyethylene and polypropylene.

It is less resistant to aliphatic hydrocarbons than polyethylene and polypropylene and in fact pipes may be solvent welded. At the same time the resistance to environmental stress cracking is excellent.

Polybut-1-ene is unusual in that it exhibits three crystalline forms. One form is produced on crystallisation from the melt but this is unstable and on standing for 3–10 days this is replaced by a second crystal form. A third modification may be obtained by crystallising from solution. When first cooled from the melt the polymer has a density of 0.89 g/cm^3 and a melting point of 124°C but on reversion to the second form the density rises to 0.95 g/cm^3 and the melting point to 135°C . Although ultimate tensile strength is unaffected by the change, stiffness, yield strength and hardness all increase. Freshly extruded and moulded material must be handled with care.

From the technical point of view the outstanding property of polybut-1-ene is its creep behaviour. Possibly because of its very high molecular weight the polymer has a very high resistance to creep for an aliphatic polyolefin. One

advantage of this is that the wall thicknesses of polybut-1-ene pipes may be much less than for corresponding polyethylene and polypropylene pipes; they are thus sometimes flexible enough to be coiled.

The processing behaviour of polybut-1-ene is somewhat intermediate between the behaviour of high-density polyethylene and polypropylene. Processing temperatures are in the range 160–240°C. Both die swell and cooling shrinkage are greater than for polyethylene. The crystalline material formed initially on cooling from the melt is rather weak and must be handled with care on the haul off equipment. As mentioned above the polymer must be aged for about a week in order to allow the more stable crystalline form to develop.

The main interest in polybut-1-ene is in its use as a piping material, where the ability to use a lower wall thickness for a given pressure requirement than necessary with other polyolefins, together with the low density, can lead in some cases to economic use. The principal application is for small-bore cold and hot water piping (up to 95°C) for domestic plumbing. Current world-wide sales are of the order of $16\text{--}20 \times 10^3$ tonnes per annum.

11.2.1. Atactic Polybut-1-ene

Since only a small amount of atactic material is available as a by-product from the manufacture of isotactic polybut-1-ene, atactic polybut-1-ene is normally produced directly.

Compared with atactic polypropylene it has a lower softening point (less than 100°C compared with 154°C when assessed by ball and ring methods), has better resistance to subzero temperatures and is completely soluble in aliphatic hydrocarbons. The molecular mass of atactic polybut-1-ene is about twice that of an atactic polypropylene of similar melt viscosity.

It offers technical advantages over atactic polypropylene for roof coverings, sealing strips and sealing compounds. On the other hand the longer time required for it to reach a stable hardness after processing mitigates against extensive use in carpet backings.

11.3 POLYISOBUTYLENE

In chronological terms polyisobutylene (PIB) was the first of the polyolefins. Low polymers were prepared as early as 1873 by Butlerov and Gorianov and higher molecular weight waxes in 1930 by Staudinger and Brunner. High molecular weight polymers were produced by IG Farben in the early 1930s using cationic polymerisation methods and polymers based on these methods are currently available from BASF (Oppanol) and Esso (Vistanex).

The pair of opposing methyl groups leads to a low T_g of about -73°C (c.f. -20°C for polybut-1-ene) and the lack of preference for any particular steric configuration inhibits crystallisation in the normal way although this can be induced on stretching. The methyl groups do, however, hinder rotation about the main chain bonds so the resulting material is, at sufficiently high molecular weights, a rather sluggish rubber. It has little use as a rubber in itself because of its high cold flow but copolymers containing about 2% of isoprene to introduce unsaturation for cross-linking are widely used (butyl rubber—see Section 11.9).

The homopolymer finds a variety of uses, as an adhesive component, as a base for chewing gum, in caulking compounds, as a tackifier for greases, in tank linings, as a motor oil additive to provide suitable viscosity characteristics and to improve the environmental stress-cracking resistance of polyethylene. It has been incorporated in quantities of up to 30% in high-density polyethylene to improve the impact strength of heavy duty sacks.

11.4 POLY-(4-METHYLPENT-1-ENE)

Of all the branched aliphatic polyolefins higher than the polybutenes that have been prepared in the laboratory only one has so far achieved commercial status. This predominantly isotactic polymer of 4-methylpent-1-ene was introduced as TPX by ICI in 1965, but since 1973 has been marketed by Mitsui. These materials are characterised by low density, high transparency, high melting point and excellent electrical insulation but are rather brittle, have poor aging characteristics, show a high gas permeability and are rather expensive, being at the time of writing about 3–4 times the price of low-density polyethylene.

The monomers can be prepared by isomerisation of 4-methylpent-2-ene or reaction of tri-isobutylaluminium with ethylene but commercial interest appears to centre on the dimerisation of propylene (*Figure 11.12*).

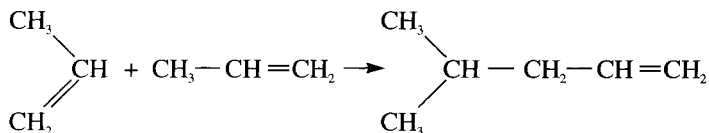


Figure 11.12

Factors affecting laboratory polymerisation of the monomer have been discussed¹¹ and these indicate that a Ziegler–Natta catalyst system of violet TiCl_3 and diethyl aluminium chloride should be used to react the monomer in a hydrocarbon diluent at atmospheric pressure and at 30–60°C. One of the aims is to get a relatively coarse slurry from which may be washed foreign material such as catalyst residues, using for example methyl alcohol. For commercial materials these washed polymers are then dried and compounded with an antioxidant and if required other additives such as pigments.

11.4.1 Structure and Properties

The commercial poly-(4-methylpent-1-ene) (P4MP1) is an essentially isotactic material which shows 65% crystallinity when annealed but under more normal conditions about 40%. For reasons given later the material is believed to be a copolymer. In the crystalline state P4MP1 molecules take up a helical disposition and in order to accommodate the side chains require seven monomer units per two turns of the helix (c.f. three monomers per turn with polypropylene and polybut-1-ene). Because of the space required for this arrangement the density of the crystalline zone is slightly less than that of the amorphous zone at room temperature.

From considerations of structure it will be recognised that as it is a paraffinic hydrocarbon the electrical insulation properties will be excellent, not unlike those of polyethylene, and that its chemical properties will also be typically paraffinic. However, like polypropylene, P4MP1 possesses tertiary carbon atoms and the material is particularly sensitive to oxygen. Inferior in this respect even to polypropylene, this property is aggravated by the high processing temperatures required for processing and by the fact that many potential end uses involve elevated temperature conditions. The use of efficient antioxidant systems therefore becomes of paramount importance. It is claimed that current commercial materials will last about one day at 200°C and one year at 125°C. Aliphatic polyolefins in general have low densities and in the case of P4MP1 the open packing of the crystalline zones leads to the very low density of 0.83 g/cm³.

Perhaps the most astounding property of this material is the high degree of transparency. This arises first because both molecules and crystals show little optical anisotropy and secondly because crystalline and amorphous zones have similar densities. They also have similar refractive indices and there is little scatter of light at the interfaces between amorphous and crystalline zones.

It has, however, been observed that mouldings made from the homopolymers often show a lack of clarity. Such mouldings appeared to contain shells of voids which formed round the edges of the spherulites. It has been suggested that these arise from the different coefficients of thermal expansion of amorphous and crystalline zones. At the melting point the crystal zone has a density about 7% greater than the amorphous zone, at 60°C the densities are equal and at room temperature the amorphous zone is slightly denser. The strains set up at the boundaries will therefore cause the amorphous polymer to tear, thus setting up voids.

Experiments were carried out¹¹ to investigate the transparency of various materials produced by copolymerising 4MP1 with other olefins such as but-1-ene, hex-1-ene and oct-1-ene.

It was found that to varying degrees the other olefin units could co-crystallise with the 4MP1 units in the main chain, being most perfect in the case of hex-1-ene, and that in many cases much better clarity was obtained. This improvement in clarity through reduction in voidage has been ascribed to the retardation of spherulite growth on cooling.

The rather 'knobbly' side groups have a stiffening effect on the chain and result in high values for T_m (245°C) and T_g (50–60°C). Copolymerisation with hex-1-ene, oct-1-ene, dec-1-ene and octadec-1-ene which may be practised to reduce voidage causes some reduction in melting point and crystallinity as indicated in *Table 11.9*.

Polymers below the glass transition temperature are usually rather brittle unless modified by fibre reinforcement or by addition of rubbery additives. In some polymers where there is a small degree of crystallisation it appears that the crystallines act as knots and toughen up the mass of material, as in the case of the polycarbonates. Where, however, there are large spherulite structures this effect is more or less offset by high strains set up at the spherulite boundaries and as in the case of P4MP1 the product is rather brittle.

Compared with most other crystalline polymers the permeability of P4MP1 is rather high. This is no doubt due to the ability of gas molecules to pass through the open crystal structure with the large molecular spacing.

Table 11.9 Copolymerisation of 4MP1 and hex-1-ene¹¹

(a) Effect on % crystallisation and melting point (T_m)		
Hex-1-ene (molar)	Crystallinity (%)	T_m (°C)
0	65	245
5	60	238
10	57	235
20	53	228

(b) Effect of adding 5% comonomer to 4MP1		
	Crystallinity (%)	T_m (°C)
Blank	65	245
Hex-1-ene	60	238
Oct-1-ene	50	234
Dec-1-ene	46	229
Octadec-1-ene	25	225

11.4.2 General Properties¹²

Some general properties of the commercial 4-methylpent-1-ene polymer (TPX) are given in *Table 11.10*.

Many properties are temperature dependent. For example up to 100°C the yield stress drops with temperature at a faster rate than does the yield stress of polypropylene; however, it retains some strength up to 160°C.

Table 11.10 Typical properties of commercial methylpentene polymer (tested according to ASTM procedures).

Property	Value	Units
Specific gravity	0.83	
Transparency	90	%
Tensile strength	4000 (27.5)	lbf/in ² (MPa)
Elongation at break	15	%
Tensile modulus	2.1×10^5 (1500)	lbf/in ² (MPa)
Water absorption, 24h	0.07	%
Crystalline melting point	240	°C
Vicat softening point	179	°C
Specific heat	2.18	Jg ⁻¹ °C ⁻¹
Mould shrinkage	0.015–0.030	cm cm ⁻¹
Thermal conductivity (by BS 874 test)	16.7×10^{-4}	J cm s ⁻¹ cm ⁻² °C ⁻¹
Permittivity 20°C, 10^2 – 10^6 Hz	2.12	
Volume resistivity	10^{18}	Ωm
Stress cracking	Yes—similar to low density polyethylene	

11.4.3 Processing

Poly-(4-methylpent-1-ene) is a highly pseudoplastic material and in the usual processing range is of low melt viscosity. There is a narrow melting range and the viscosity is highly dependent on temperature. In injection moulding this results in the use of cylinder temperatures of the order of 270–300°C, mould temperatures of about 70°C and the use of restricted nozzles to prevent 'drooling'. In extrusion, high-compression screws with a sharp transition from feed to metering zone are recommended. Melt temperatures of about 270°C are required for many operations.

11.4.4 Applications

There are a number of occasions where a transparent plastics material which can be used at temperatures of up to 150°C is required and in spite of its relatively high cost, low impact strength and poor aging properties poly-(4-methylpent-1-ene) is often the answer. Like poly(vinyl chloride) and polypropylene, P4MP1 is useless without stabilisation and as with the other two materials it may be expected that continuous improvement in stabilising antioxidant systems can be expected.

At the present time major uses are in transparent chemical plant, in electrical equipment which can withstand soldering and encapsulation processes, in transparent sterilisable medical equipment and for lamp covers. One widely publicised use has been for the cover of a car interior light. Requiring only intermittent heating the cover can be placed much nearer the light source than can competitive plastics materials because of the greater temperature resistance. This can cause a saving in the volume of material required for the moulding and also give increased design flexibility. Poly-(4-methylpent-1-ene) is not a major thermoplastic such as polyethylene but fulfils a more specialist role.

11.5 OTHER ALIPHATIC OLEFIN HOMOPOLYMERS

A number of polymers have been produced from higher olefins using catalysts of the Ziegler–Natta type.

Figure 11.13 shows the effect of increasing the length of the side chain on the melting point and glass transition temperature of a number of poly- α -olefins. As discussed previously the melting point of isotactic polypropylene is higher than that of polyethylene because the chain stiffness of the polymer has a more dominating influence than the reduction in symmetry. With an increase in side-chain length (polybut-1-ene and polypent-1-ene) molecular packing becomes more difficult and with the increased flexibility of the side chain there is a reduction in the melting point. A lower limit is reached with polyoct-1-ene and polynon-1-ene, and with polymers from higher α -olefins the melting point increases with increase in the length of the side chain. This effect has been attributed to side-chain crystallisation. It is interesting to note that a polyolefin with n carbon atoms in the side chain frequently has a similar melting point to a paraffin with $2n$ carbon atoms. Published data¹³ on glass transition temperatures show similar but less dramatic changes.

None of the polymers from unbranched olefins, other than ethylene, propylene or but-1-ene, has yet become important as a plastics material although some of them are of interest both as adhesives and release agents. One limitation of a

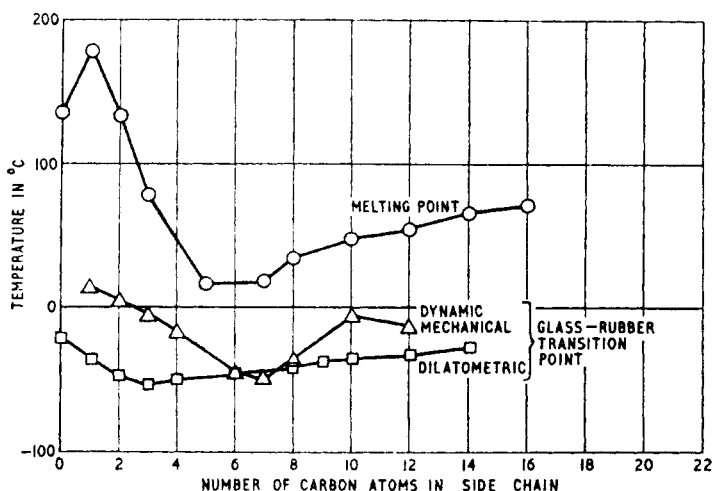
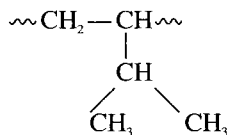


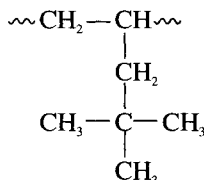
Figure 11.13. Effect of side-chain branching on the melting point and glass transition temperature of polyolefins $(-\text{CHR}-\text{CH}_2-)_n-$ (R straight chain) (Ref 13)

number of these materials is their tendency to undergo complex morphological changes on standing, with the result that fissures and planes of weakness may develop.

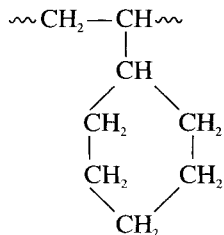
Polyolefins with branched side chains other than P4MP1 have been prepared (Figure 11.14). Because of their increased cohesive energy, ability for the molecules to pack and the effect of increasing chain stiffness some of these polymers have very high melting points. For example, poly-(3-methylbut-1-ene) melts at about 240°C and poly-(4,4-dimethylpent-1-ene) is reported to have a melting point of between 300°C and 350°C . Certain cyclic side chains can also



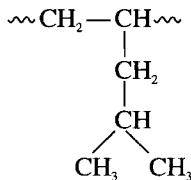
Poly-(3-methylbut-1-ene)



Poly-(4,4-dimethylpent-1-ene)



Poly-(vinylcyclohexane)



Poly-(4-methylpent-1-ene)

Figure 11.14

lead to high melting polymers; for example, poly(vinylcyclohexane) melts at 342°C^{13} .

Subsequent reviews even quoted a T_m of 385°C together with a T_g of 80°C and a crystalline specific gravity of 0.95 for poly(vinyl cyclohexane). The polymer was also reported to have good dielectric loss properties over the range -180 to $+160^{\circ}\text{C}$ but to be subject to oxidative degradation. Some 40 years or more after its original discovery Dow announced in 1998 that they were undertaking developmental work on poly(vinylcyclohexane) but using the alternative name *polycyclohexylethylene* and the abbreviation PCHE. The Dow material is said to be amorphous and is being explored for use in optical discs where its hydrocarbon nature leads to a low specific gravity (0.947 cf. 1.21 for polycarbonate), negligible water absorption (one-tenth that of polycarbonate), 91.85% light transmission (cf. 89.81% for PC) and a flexural modulus of 3400 MPa (cf. 2500 MPa for PC). Emphasis is also being put on the stress optical coefficient which determines birefringence levels across a moulded disc. Compared to an optimum value of zero PCHE is quoted at -200 brewsters and polycarbonate at 5200 brewsters. Heat distortion temperatures are said to be similar to those of polycarbonate.

In terms of processing there is no need for pre-drying PCHE granules, a standard extruder screw as used for polycarbonate may be used and discs are said to release well from the mould. Question marks remain on the oxidative stability of the polymer and on the quality of adhesion of the reflective layer but Dow claim that metallising is possible.

11.6 COPOLYMERS CONTAINING ETHYLENE

Many monomers have been copolymerised with ethylene using a variety of polymerisation systems, in some cases leading to commercial products. Copolymerisation of ethylene with other olefins leads to hydrocarbon polymers with reduced regularity and hence lower density, inferior mechanical properties, lower softening point and lower brittle point.

Two random copolymers of this type are of importance, ethylene-propylene copolymers and ethylene-but-1-ene copolymers. The use and properties of polypropylene containing a small quantity of ethylene in stereoblocks within the molecule has already been discussed. Although referred to commercially as ethylene-propylene copolymers these materials are essentially slightly modified polypropylene. The random ethylene-propylene polymers are rubbery and are discussed further in Section 11.9.

The Phillips process for the manufacture of high-density polyethylene may be adapted to produce copolymers of ethylene with small amounts of propylene or but-1-ene and copolymers of this type have been available since 1958. These soon found application in blown containers and for injection moulding. Properties of two grades of such copolymers are compared with two grades of Phillips-type homopolymer in *Table 11.11*.

From this table it will be noted that in terms of the mechanical and thermal properties quoted the copolymers are marginally inferior to the homopolymers. They do, however, show a marked improvement in resistance to environmental stress cracking. It has also been shown that the resistance to thermal stress cracking and to creep are better than with the homopolymer.¹⁵ This has led to widespread use in detergent bottles, pipes, monofilaments and cables.

Table 11.11 Comparison of major properties of ethylene-based copolymers with polyethylene¹⁴

	<i>Copolymer</i>		<i>Homopolymer</i>	
Specific gravity	0.95	0.95	0.96	0.96
Melt flow index	0.3	4.0	0.2	3.5
Tensile strength (MPa)	24.8	24.8	30.3	30.3
Elongation (%)	70	30	30	15
Vicat softening point (°C)	255	255	260	260
Environmental stress cracking (F _{50h})	400	20	60	2
Izod impact (ft lbf/in ⁻¹ notch)	4	0.8	5	1.5

The linear low-density polyethylenes discussed in the previous chapter might be considered as variations of this type of polymer.

Ethylene has also been copolymerised with a number of non-olefinic monomers and of the copolymers produced those with vinyl acetate have so far proved the most significant commercially¹⁶. The presence of vinyl acetate residues in the chain reduces the polymer regularity and hence by the vinyl acetate content the amount of crystallinity may be controlled. Copolymers based on 45% vinyl acetate are rubbery and may be vulcanised with peroxides. They are commercially available (Levapren). Copolymers with about 30% vinyl acetate residues (Elvax-Du Pont) are flexible resins soluble in toluene and benzene at room temperature and with a tensile strength of about 1000 lbf/in² (6.9 MPa) and a density of about 0.95 g/cm³. Their main uses are as wax additives and as adhesive ingredients.

Ethylene-vinyl acetate (EVA) polymers with a vinyl acetate content of 10–15 mole % are similar in flexibility to plasticised PVC and are compatible with inert fillers. Both filled and unfilled copolymers have good low-temperature flexibility and toughness and the absence of leachable plasticiser provides a clear advantage over plasticised PVC in some applications. Although slightly stiffer than normal rubber compounds they have the advantage of simpler processing, particularly as vulcanisation is unnecessary. The EVA polymers with about 11 mole % of vinyl acetate may also be used as wax additives for hot melt coatings and adhesives.

A further class of ethylene-vinyl acetate copolymer exists where the vinyl acetate content is of the order of 3 mole %. These materials are best considered as a modification of low-density polyethylene, where the low-cost comonomer introduces additional irregularity into the structure, reducing crystallinity and increasing flexibility, softness and, in the case of film, surface gloss. They have extensive clearance as non-toxic materials.

A substantial part of the market for the ethylene-vinyl acetate copolymer is for hot melt adhesives. In injection moulding the material has largely been used in place of plasticised PVC or vulcanised rubber. Amongst applications are turntable mats, base pads for small items of office equipment and power tools, buttons, car door protector strips and for other parts where a soft product of good appearance is required. Cellular cross-linked EVA is used in shoe parts.

EVA polymers have been important for film manufacture. They are not competitive with normal film because of the high surface tack and friction which make them difficult to handle on conventional processing machinery. However, because of their somewhat rubbery nature, gloss, permeability, and good impact

Table 11.12 Typical properties of three olefin-ester copolymers

Property	Ionomer	Ethylene-vinyl acetate	Ethylene-ethyl acrylate	Units
Specific gravity	0.93	0.93-0.95	0.93	
Yield strength	2.2	1.3	1.05	10 ³ lb/in ²
Tension modulus	28-40	11	6	10 ³ lb/in ²
Usual form of fracture	Tough	Tough	Tough	
Vicat softening point	71	83	64	°C
ASTM brittleness temperature	-100	-70	-100	°C
Power factor 10 ² Hz	0.0015	0.0024	0.001	
Dielectric constant 10 ³ Hz	2.5	2.8	2.8	

strength they are of interest as a stretch film for meat packaging and for cling-wrap purposes. Some EVA is used in coextrusion processes for the manufacture of laminated film.

Interest in EVA as a cable-insulating material has arisen because of the good resistance to stress cracking and because the polymer may be more easily cross-linked (see Table 11.12).

Ethylene-ethyl acrylate copolymers are very similar to the ethylene-vinyl acetate copolymers. The former materials are considered to have higher abrasion resistance and heat resistance whilst the EVA have been considered to be tougher and of greater clarity.

For many years use of this material was largely confined to America and it was seldom met in Europe because of the cheaper EVA materials available. In 1980, however, BP initiated production of such materials, whilst in the United States the material is produced by Union Carbide. The Dow company, whose product Zetafin was the most well-known grade, no longer supply the copolymer.

Ethylene-acrylic acid copolymers have been known since the 1950s but for many years found little application. About 1974 Dow introduced new grades characterised by outstanding adhesion to a variety of metallic and non-metallic substrates, outstanding toughness and with good rigidity and tensile strength. Many of the key features are a consequence of hydrogen bonding via the carboxyl groups causing an effect referred to by Dow as pseudo-crystallinity.

Current usage is almost entirely associated with the good adhesion to aluminium. Specific applications include the bonding of aluminium foil to plastics films, as the adhesive layer between aluminium foil and polyethylene in multilayer extrusion-laminated non-lead toothpaste tubes and in coated aluminium foil pouches. Grades have more recently become available for manufacture by blown film processes designed for use in skin packaging applications. Such materials are said to comply with FDA regulations.

A *terpolymer rubber* was introduced by Du Pont in 1975 (Vamac). This is based on ethylene, methyl acrylate and a third, undisclosed, monomer containing carboxylic acid groups to act as the cure site (see Section 11.9).

In September 1964 the Du Pont company announced materials that had characteristics of both thermoplastics and thermosetting materials. These materials, known as *ionomers*, are prepared by copolymerising ethylene with a small amount (1-10 % in the basic patent) of an unsaturated carboxylic acid such as acrylic acid using the high-pressure process. Such copolymers are then treated

with the derivative of a metal such as sodium methoxide or magnesium acetate with the result that the carboxylic group appears to ionise. It would seem that this leads to some form of ionic cross-link which is stable at normal ambient temperatures but which reversibly breaks down on heating. In this way it is possible to obtain materials which possess the advantages of cross-linking at ambient temperatures, for example enhanced toughness and stiffness, but which behave as linear polymers at elevated temperatures and may be processed and even reprocessed without undue difficulty. In the case of the commercial materials already available (e.g. Surlyn-Du Pont) copolymerisation has had the not unexpected effect of depressing crystallinity although not completely eliminating it, so that the materials are also transparent. Other properties claimed for the ionomers are excellent oil and grease resistance, excellent resistance to stress cracking and a higher moisture vapour permeability (due to the lower crystallinity) than polyethylene. Typical properties are given in *Table 11.12*.

The commercial grades available in the 1970s used either zinc or sodium as the cross-linking ion and ranged in melt flow index from 0.4 to 14. The main application of the ionomer resins has been for packaging film. The polymer is particularly useful in composite structures to provide an outer layer with good heat sealability. The puncture resistance of film based on ionomer film has the puncture resistance of a LDPE film of twice the gauge.

Ionomer resins today have a large portion of the golf ball cover market. They are considered superior to synthetic *trans*-polyisoprene in being virtually cut-proof in normal use and they also retain a greater resiliency over a wider temperature range. At the time of writing they are not yet preferred to the natural product, balata (see Chapter 30), for golf balls of the highest quality because the latter natural material confers better flight characteristics to the ball.

Other uses of ionomer resins are in footwear. Low-cost grades have been used for parts of shoe heels whilst grades of increased flexibility are among a wide range of polymers contesting the market for ski boots.

It is to be noted that polymers with ionic groups attached along the chain and showing the properties of both polymers and electrolytes have been known for some time. Known as polyelectrolytes, these materials show ionic dissociation in water and find use for a variety of purposes such as thickening agents. Examples are sodium polyacrylate, ammonium polymethacrylate (both anionic polyelectrolytes) and poly-(*N*-butyl-4-vinyl-pyridinium bromide), a cationic polyelectrolyte. Also somewhat related are the ion-exchange resins, cross-linked polymers containing ionic groups which may be reversibly exchanged and which are used in water softening, in chromatography and for various industrial purposes. In general, however, the polyelectrolytes and ion-exchange resins are intractable materials and not processable on conventional plastics machinery. The value of the ionomer is that the amount of ionic bonding has been limited and so yields useful and tractable plastics materials. It is also now possible to envisage a range of rubbers which vulcanise by ionic cross-linking simply as they cool on emergence from an extruder or in the mould of an injection moulding machine.

11.6.1 Ethylene-carbon Monoxide Copolymers (ECO)

Random ethylene-carbon monoxide copolymers have been known for many years and have properties somewhat similar to low density polyethylene. Alternating ECO copolymers were first produced long ago by Reppe of BASF in

the late 1940s using nickel-based catalysts but the products were not commercially attractive. However, the later development of palladium-based catalyst systems has led to commercial development. In 1996 Shell started up a plant at Carrington, UK with an annual capacity of 20 000 tonnes with a further plant at Geismar, Louisiana with an annual capacity of 25 000 tonnes scheduled to be on stream in 1999. These materials are marketed as Carilon. Additionally BP commissioned a development unit at Grangemouth, Scotland in 1996 using a palladium catalyst in a continuous slurry process to produce alternating copolymer ECOs under the trade name Ketonex.

The regular structure of the alternating copolymer with its absence of side chains enables the polymer to crystallise with close molecular packing and with interchain attraction augmented by the carbonyl groups. As a result these polymers exhibit the following characteristics:

- (i) T_m as high as 260°C.
- (ii) T_g of about 15°C.
- (iii) High tensile strength (70 MPa) for an olefin copolymer and an elongation at break in excess of 300%.
- (iv) High elasticity, resilience and impact strength.
- (v) A significantly higher density of 1.22–1.24 g/cm³ than for all-hydrocarbon polyolefins.
- (vi) A small level of water absorption (0.5% @ 23°C and 50%RH) which has a slight plasticisation effect but good resistance to hydrolysis.
- (vii) Susceptibility to UV degradation; a feature which has in the past led to some interest in the biodegradability of these polymers.
- (viii) Excellent barrier properties to gases and moisture vapour similar to ethylene-vinyl alcohol copolymers (see Section 14.5) thus leading to interest in coextruded multilayer barrier packaging applications.
- (ix) The polymers are also reported to have low coefficient of friction and good wear resistance.

Some typical properties are given in *Table 11.13* in comparison with typical properties for nylon 66 (see Chapter 18) and a polyacetal (see Chapter 19) for which it has been suggested that these materials will be competitive.

A significant modification has been the introduction of a second olefin such as propylene or a butene which substitutes randomly for the ethylene and this has

Table 11.13 Typical properties of aliphatic polyketones

<i>Property</i>	<i>Units</i>	<i>Aliphatic polyketone*</i>	<i>Acetal</i>	<i>Nylon 66 conditioned</i>
Specific gravity		1.22–1.24	1.425	
Tensile strength (at yield)	MPa	60	70	60
Strain @ yield	%	25	15	15
Strain @ break	%	300	45	>100
Flexural modulus	GPa	1.7	2.8	1
Notched Izod @23°C	J/m	140	80	110
Notched Izod @ -40°C	J/m	27	60	30
Deflection temp @0.45MPa	°C	180	172	205

* Data is for BP Developmental grade Ketonex 2202

the effect of reducing the melting point by up to 50°C. The property range may also be broadened by the use of such additives as glass-fibres and fire retardants.

Initial application development has concentrated on barrier applications (extended shelf-life food packaging, fuel tanks and fuel lines and odour-containing packaging), blends with commodity plastics such as pvc and polystyrene to give higher softening temperatures and engineering mouldings and extrudates which in particular make use of the excellent wear, low friction and high resilience properties of the polymer.

11.6.2 Ethylene-Cyclo-Olefin Copolymers

Ethylene-cyclo-olefin copolymers have been known since 1954 (DuPont USP2 721 189) but these materials only became of importance in the late 1990s with the development of copolymers of ethylene and 2-norbornene by Hoechst and Mitsui using metallocene technology developed by Hoechst. The product is marketed as Topas by Ticona. By adjustment of the monomer ratios polymers with a wide range of T_g values may be obtained including materials that are of potential interest as thermoplastic elastomers. This section considers only thermoplastic materials, cyclo-olefins of interest as elastomers are considered further in Section 11.10.

The Ticona materials are prepared by continuous polymerisation in solution using metallocene catalysts and a co-catalyst. The ethylene is dissolved in a solvent which may be the comonomer 2-norbornene itself or another hydrocarbon solvent. The comonomer ratio in the reactor is kept constant by continuous feeding of both monomers. After polymerisation the catalyst is deactivated and separated to give polymers of a low residual ash content and the filtration is followed by several degassing steps with monomers and solvents being recycled.

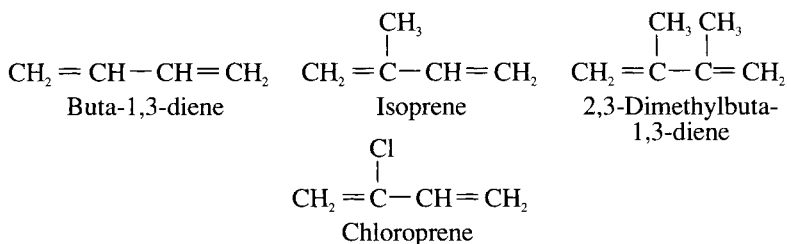
Thermoplastics grades have a norbornene content in the range 60–80% with T_g values from 60–180°C, in this range the glass transition being almost linearly related to the norbornene content. The modulus of elasticity increases with norbornene content and for commercial materials is in the range 2600–3200 MPa but density (1.02 g/cm³), tensile strength 66 MPa and water absorption (<0.01%) is little affected by the monomer ratio.

Of particular interest with these materials are their optical properties with high light transmission (92%), low chromatic aberration and low birefringence. Coupled with the low water absorption, low density and chemical properties typical of olefin polymers the materials have considerable potential for replacing optical glass parts where weight is an important factor. The materials are also of interest in electronic, particularly capacitor, applications because of their good thermal stability combined with typical polyolefin properties. Early studies also indicate suitability for pharmaceutical blister packs, syringes, bottles and vials with ability for sterilisation by γ -radiation, steam and ethylene oxide treatments.

11.7 DIENE RUBBERS

Polymerisation of conjugated dienes can frequently lead to the formation of linear polymers containing main chain double bonds. Examples of such diene

monomers are buta-1,3-diene; 2-methylbuta-1,3-diene (better known as isoprene); 2,3-dimethylbuta-1,3-diene and 2-chlorobuta-1,3-diene (better known as chloroprene). Polymerisation of these materials via the 1,4 position yields polymers with a flexible backbone. Whilst the double bond is not necessary for rubberiness it does tend to depress T_g by making adjacent bonds more flexible and, providing the polymers are not allowed to crystallise extensively, the polymers are rubbery at room temperature:



Several other elastic materials may be made by copolymerising one of the above monomers with lesser amounts of one or more monomers. Notable amongst these are SBR, a copolymer of butadiene and styrene, and nitrile rubber (NBR), a copolymer of butadiene and acrylonitrile. The natural rubber molecule is structurally a *cis*-1,4-polyisoprene so that it is convenient to consider natural rubber in this chapter. Some idea of the relative importance of these materials may be gauged from the data in *Table 11.14*.

It is interesting to note that although the market for natural rubber has grown considerably, that for the other diene rubbers has either been of slow growth or has declined. Data for approximate overall plastics production (not from IISRP data) have also been included as a comparison of the relative sizes of the rubber and plastics markets.

Table 11.14 Production of natural and synthetic rubbers 1983–1992 ('000 tonnes) (International Institute of Synthetic Rubber Producers)

	1983	1987	1992
Diene rubbers:			
Natural rubber (NR)	3057	4494	5229
Styrene–butadiene rubber (SBR)	2503	2677	2670
Butadiene rubber (BR)	903	1087	1251
Isoprene rubber (IR)	120	113	115
Chloroprene rubber (CR)	292	292	260
Nitrile rubber (NBR)	189	231	255
Olefin rubbers:			
Ethylene–propylene terpolymer (EPDM)	373	534	617
Butyl rubber (IIR)	372		
Other rubbers	92	552	606
All plastics materials (approx.)	60 000	75 000	90 000

Note:

(1) Separate data for butyl rubber not available after 1983, but it is believed to be in decline.

(2) Data for synthetic rubber production exclude production from the one-time USSR, Central Europe and Socialist Countries of Asia.

(3) Data for thermoplastic rubber (see Chapter 31) are excluded.

Polybutadiene, polyisoprene (both natural and synthetic), SBR and poly-(dimethyl butadiene) (used briefly during the First World War as methyl rubber) being hydrocarbons have limited resistance to hydrocarbon liquids dissolving in the unvulcanised state and swelling extensively when vulcanised. Being unsaturated polymers they are susceptible to attack by such agencies as oxygen, ozone, halogens and hydrohalides. The point of attack is not necessarily at the double bond but may be at the α -methylene position. The presence of the double bond is nevertheless generally crucial. In addition the activity of these agencies is affected by the nature of the groups attached to the double bond. Thus the methyl group present in the natural rubber molecule and in synthetic polyisoprene increases activity whereas the chlorine atom in polychloroprene reduces it.

In order for a rubbery polymer to realise an effectively high elastic state it is necessary to lightly cross-link the highly flexible polymer molecules to prevent them from slipping past each other on application of a stress. In the rubber industry this process is known as *vulcanisation*. Ever since the discovery of the process by Charles Goodyear in the USA about 1839 and its exploitation by Thomas Hancock in London from 1843 onwards it has been the usual practice to vulcanise diene polymers with sulphur although alternative systems are occasionally used. The reactions are very involved and appear to be initiated at the α -methylene group rather than at the double bond. Some of the structures that may be present in the vulcanised rubber are indicated schematically in *Figure 11.15* as indicated by extensive research into natural rubber vulcanisation.

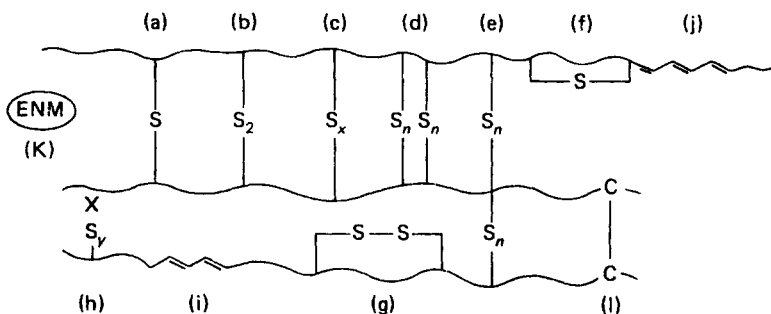


Figure 11.15. Typical chemical groupings in a sulphur-vulcanised natural rubber network. (a) Monosulphide cross-link; (b) disulphide cross-link; (c) polysulphide cross-link ($x = 3-6$); (d) parallel vicinal cross-link; ($n = 1-6$) attached to adjacent main-chain atoms and which have the same influence as a single cross-link; (e) cross-links attached to common or adjacent carbon atoms; (f) intra-chain cyclic monosulphide; (g) intra-chain cyclic disulphide; (h) pendent sulphide group terminated by moiety X derived from accelerator; (i) conjugated diene; (j) conjugated triene; (k) extra-network material; (l) carbon-carbon cross-links (probably absent)

In the case of polychloroprene the chlorine atom so deactivates both the double bond and the α -methylene group that a sulphur-based vulcanisation system is ineffective and special techniques have to be employed.

It is now common practice to use sulphur in conjunction with several other additives. First amongst them are *vulcanisation accelerators*, of which there are many types. In the absence of an accelerator about 10 parts of sulphur is required, the vulcanisation time may be a matter of hours and much of the sulphur is

consumed in intramolecular rather than cross-linking reactions. Use of about 1 part of accelerator per hundred parts of rubber (1 pts phr) enable effective vulcanisation to occur with 2–3 pts sulphur phr, not only in much shorter times (which in extreme cases may be seconds rather than minutes) but also gives much better vulcanisates. It is important that the vulcanising system should give not only a rapid and effective cross-linking system at the desired vulcanising temperatures but also that it should resist premature vulcanisation (*scorching*) at the somewhat lower temperature that may be required to mix, extruded, calender and otherwise shape the rubber before cross-linking. Hence many accelerators are of the delayed-action type exemplified by sulphenamides such as *N*-cyclohexylbenzothiazole-2-sulphenamide (CBS), *N*-*t*-butylbenzothiazole-2-sulphenamide (TBBS) and *N*-morpholinobenzothiazole (MBS). Other accelerator groups include the thiazoles such as mercaptobenzothiazole (MBT), the guanidines such as diphenylguanidine (DPG) and the very powerful dithiocarbamates, thiurams and xanthates which find particular use in latex technology where problems of scorching are less likely to arise.

Accelerated sulphur systems also require the use of an *activator* comprising a metal oxide, usually zinc oxide, and a fatty acid, commonly stearic acid. For some purposes, for example where a high degree of transparency is required, the activator may be a fatty acid salt such as zinc stearate. Thus a basic curing system has four components: sulphur vulcanising agent, accelerator (sometimes combinations of accelerators), metal oxide and fatty acid. In addition, in order to improve the resistance to scorching, a *prevulcanisation inhibitor* such as *N*-cyclohexylthiophthalimide may be incorporated without adverse effects on either cure rate or physical properties.

The level of accelerator used varies from polymer to polymer. Some typical curing systems for the diene rubbers NR, SBR and NBR and for two olefin rubbers (discussed in Section 11.9) are given in *Table 11.15*¹⁸.

In addition to the components of the vulcanising system several other additives are commonly used with diene rubbers. As a general rule rubbers, particularly the diene rubbers, are blended with many more additives than is common for most thermoplastics, with the possible exception of PVC. In addition the considerable interaction between the additives requires the rubber compounder to have an extensive and detailed knowledge concerning the additives that he employs.

Table 11.15 Conventional vulcanisation systems

Additive (per 100 pts polymer)	Polymer				
	NR	SBR	NBR	IIR	EPDM
Sulphur	2.5	2.0	1.5	2.0	1.5
Zinc oxide	5.0	5.0	5.0	3.0	5.0
Stearic acid	2.0	2.0	1.0	2.0	1.0
TBBS	0.6	1.0	—	—	—
MBTS	—	—	1.0	0.5	—
MBT	—	—	—	—	1.5
TMTD	—	—	0.1	1.0	0.5

TBBS *N*-*t*-Butylbenzothiazole-2-sulphenamide

MBTS Dibenzothiazole disulphide

MBT 2-Mercaptobenzothiazole

TMTD Tetramethylthiuram disulphide

The major additional classes of additive are:

- (1) Antioxidants.
- (2) Antiozonants.
- (3) Softeners and plasticisers.
- (4) Tackifiers and other process aids.
- (5) Blowing agents.
- (6) Pigments.
- (7) Inert particulate fillers.
- (8) Reinforcing particulate fillers.

The use of antioxidants has already been generally described in Chapter 7. The mechanism of oxidation and the effect of antioxidants are altered by the sulphide cross-links and other structures present in the vulcanisate. There are indeed grounds for arguing that a correct choice of curing system is more important than the decision whether or not to incorporate an antioxidant.

In the 1950s it became recognised that one type of antioxidant also often behaved as an *antiozonant*. These were the branched alkyl, unsubstituted aryl-*p*-phenylenediamines typified by *N*-isopropyl-*N'*-*p*-phenylenediamine (IPPD). The mechanism of their action is still not fully understood but it is to be noted that they are often improved by being used in conjunction with small amounts of hydrocarbon waxes.

The diene hydrocarbon rubbers are often blended with hydrocarbon oils. They reduce hardness, polymers viscosity and, usually, the low-temperature brittle point. They are thus closely analogous to the plasticisers used with thermoplastics but are generally known as *softeners*. Three main types are usually distinguished: aliphatic (or paraffinic), naphthenic, and aromatic. For general all-round properties the naphthenics are preferred. In the case of nitrile rubber the same materials that are used to plasticise PVC are commonly used and in this case are known as *plasticisers*. Whilst this distinction in terminology is basically historical it may be noted that with plasticisers there is usually some interaction, probably hydrogen bonding, between plasticiser and polymer whereas with the softeners this effect is very small.

Natural rubber displays the phenomenon known as *natural tack*. When two clean surfaces of masticated rubber (rubber whose molecular weight has been reduced by mechanical shearing) are brought into contact the two surfaces become strongly attached to each other. This is a consequence of interpenetration of molecular ends followed by crystallisation. Amorphous rubbers such as SBR do not exhibit such tack and it is necessary to add *tackifiers* such as rosin derivatives and polyterpenes. Several other miscellaneous materials such as factive, pine tar, coumarone-indene resins (see Chapter 17) and bitumens (see Chapter 30) are also used as *processing aids*.

The principles of use of *blowing agents*, *pigments* and *inert fillers* generally follow those described in Chapter 7. Rather peculiar to the rubber industry is the use of fine particle size reinforcing fillers, particularly carbon black. Their use improves such properties as tear and abrasion resistance and generally increases hardness and modulus. They are essential with amorphous rubbers such as SBR and polybutadiene which have little strength without them. They are less essential with strain-crystallising rubbers such as natural rubber for some applications but are important in tyre compounds.

The diene rubbers, including polychloroprene, comprise some 90% of the total rubber market. This is due to their generally low cost, the suitability of many of them as tyre rubbers and their good mechanical properties.

11.7.1 Natural Rubber

It has been estimated that some 2000 plant species yield polymers akin to that of the natural rubber molecule and that rubbers of some sort have been obtained from some 500 of them. For the past 90 years, apart from the period of World War II, only one plant has been of commercial interest, the *Hevea brasiliensis*. As its name implies, it is a native of Brazil but in 1876 and 1877 seeds were smuggled out of Brazil through the efforts of Sir Henry Wickham and planted in greenhouses in Kew Gardens, England. Seedlings that survived were sent to many equatorial countries but particular success was achieved in what were then the Dutch East Indies (now Indonesia) and Malaysia, in the latter case largely due to the efforts of H.N. Ridley who was in charge of the Botanical Gardens in Singapore. The growth of the rubber plantation industry stems entirely from the initial seedlings raised in Kew.

The *Hevea brasiliensis* may be tapped for latex by gouging the bark with a tapping knife. The composition of the *Hevea* latex varies quite widely but the following may be considered to be a typical composition:

Total solids contents	36% (including dry rubber content (DRC) of 33%)
Proteinous substances	1–1.5%
Resinous substances	1–2.5%
Ash	less than 1%
Sugar	1%
Water	0.60%

The latex may then either be concentrated to about 60% DRC, usually by centrifuging or evaporation, or alternately coagulated and dried. The two approaches lead to two quite distinct branches of rubber technology, namely latex technology and dry rubber technology.

In latex technology, concentrated latex is first blended with the different additives required. To prevent premature destabilisation the powders are added as dispersions and non-aqueous liquids are generally added as emulsions. Care must be taken to avoid destabilisation, which can be brought about in different ways¹⁹ such as

- (1) The presence of hydrogen ions.
- (2) The presence of polyvalent cations.
- (3) Heat.
- (4) Cold.
- (5) The presence of water-miscible organic solvents.
- (6) The presence of polymer-miscible organic solvents.
- (7) The presence of heat-sensitising or delayed-action coacervants.

The compounded latex is then shaped by such processes as dipping, coating, moulding and foaming and the resultant shape is set by coagulation or some related destabilising process. The major outlets of natural rubber latex are for carpet backing, adhesives, dipped goods such as gloves and contraceptives, 'latex foam' and medical tubing. Once-important applications such as latex thread and moulded toys have now been largely superseded by polyurethane spandex fibres and by plasticised PVC respectively.

A variety of coagulation methods is available to prepare the rubber for dry rubber technology processes. Since the properties of the rubber are affected by trace ingredients and by the coagulating agents used, rubbers of different properties are obtained by using the different methods. The major types of raw rubber are:

- (1) Ribbed smoked sheet (RSS) in which sheets of coagulum are obtained by vertically inserting aluminium partitions into the coagulating tanks prior to coagulation, for example by addition of acetic acid. The sheets are then passed through a series of mill rolls, the last pair of which are ribbed, giving the rubber surface a characteristic diamond pattern and increasing the surface area, thus shortening the drying time. The sheet is dried in a smokehouse at 43–60°C to give the rubber an easily recognised smell. The rubbers are dark in colour but generally age well because of the presence of natural antioxidants and can yield the toughest natural rubber vulcanisates. Non-smoked sheet is also available as air-dried sheet (ADS).
- (2) Crepes. In these cases the coagulum is washed liberally with water whilst being passed between differential speed rollers of a series of two-roll mills. For *pale crepe* high-quality latex is used and the lightest colours are obtainable by removing a coloured impurity, β -carotene, by a two-stage coagulation process, by bleaching the latex with xylyl mercaptan and by adding sodium bisulphite to inhibit an enzyme-catalysed darkening process due to polyphenol oxidase. Lower quality crepes, such as brown crepe, may be obtained from rubber which has coagulated before reaching the coagulating tanks, for example in the collecting cups, on the bark and even on the ground surrounding the tree.
- (3) Comminuted and other 'new process' rubbers. In these cases the coagulum is broken up and then dried. The rubber is then packed in flat bales similar in size to those used for the major synthetic rubbers (70–75 lb) unlike the heavier square bales used with smoked sheet and crepe rubbers.

Until 1965 rubber was graded simply by appearance using the Green Book: *International Standards of Quality and Packing of Natural Rubber Grades*. Whilst this method is still used an important, but still minority, amount of natural rubber is graded according to the Standard Malaysian Rubber (SMR) scheme. This scheme lays down standards for such characteristics as ash content, nitrogen content and plasticity retention index (a measure of rate of breakdown), and with some grades information must be provided on the curing characteristics of the batch. Whilst such grades can command a premium price they do yield more uniform polymers, a traditional deficiency of natural rubber compared with the synthetics.

A further deficiency of natural rubber, compared with the synthetics, is its very high molecular weight coupled with a variable microgel content. Whilst this is desirable in that it reduces the tendency of stacked bales of rubber to flatten out

on storage it does mean that the rubber has to be extensively *masticated* (mechanically sheared) to break down the molecules to a size that enables them to flow without undue difficulty when processing by extrusion and other shaping operations. Such processes are both time- and energy-consuming. Part of the problem appears to arise through cross-linking involving carbonyl groups prior to coagulation. It has been found that such cross-linking may be minimised by the addition of about 0.15% of hydroxylamine to the latex. The rubbers remain soft and can be processed with much lower energy requirements. Although more expensive these *constant-viscosity rubbers* find ready use, particularly by general rubber goods manufacturers.

In the United States and in Mexico there has been recent renewed interest in the *guayule* shrub as a source of natural rubber. Whilst this shrub could provide an indigenous source of supply to these countries the rubber is more difficult to obtain. At present it is necessary to pull up the bush, macerate it, extract the rubber with solvent and then to precipitate it from solvent.

Natural rubber has a number of special features distinguishing it from SBR. The most important are:

- (1) Its mastication behaviour.
- (2) Its ability to crystallise.
- (3) Its high resilience.
- (4) Its reactivity with oxygen and sulphur.

The rate of mastication, as measured by changes in plasticity or viscosity, is a complex function of temperature (*Figure 11.16*) with the rate going through a minimum at about 105°C. Below this temperature the increasing viscosity of the rubber causes increased shearing stresses at constant shearing rates and this

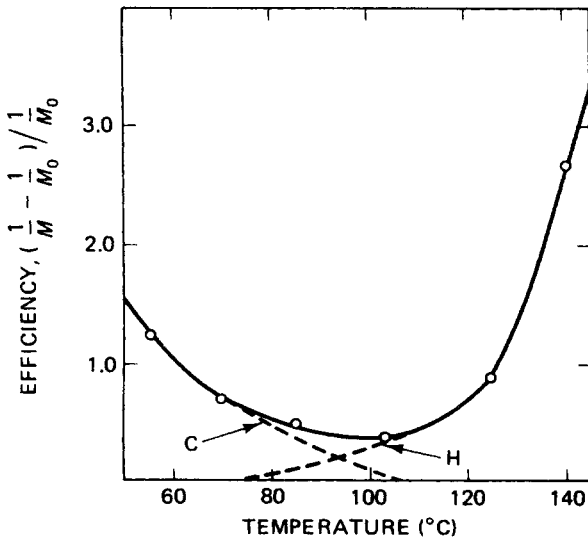


Figure 11.16. Efficiency of mastication of rubber at different temperatures. Molecular weights (M) measured after 30-minute mastication of 200 g natural rubber in a size B laboratory Banbury mixer²⁰

causes mechanical rupture of the polymer molecule. The two free radicals formed by each rupture rearrange and there is an irreversible drop in molecular mass. (Rupture may also occur with butadiene polymers and copolymers but in these cases the free-radical ends recombine with little net change in overall molecular size.) The changes at higher temperatures are ascribed to a more conventional chemical oxidation process.

Because of its highly regular structure natural rubber is capable of crystallisation. Quoted figures for T_m are in the range 15–50°C which means that for an unfilled unvulcanised material there is some level of crystallinity at room temperature. (Chemical cross-linking and the presence of fillers will impede crystallinity.) The extent of crystallisation is substantially increased by stretching of the rubber causing molecular alignment. This crystallisation has a reinforcing effect giving, in contrast to SBR, strong gum stock (i.e unfilled) vulcanisates. It also has a marked influence on many other mechanical properties. As already mentioned in the previous section, the ability of natural rubber to crystallise also has an important influence on natural tack, a property of great importance in tyre-building operations.

The proximity of the methyl group to the double bond in natural rubber results in the polymer being more reactive at both the double bond and at the α -methylenic position than polybutadiene, SBR and, particularly, polychloroprene. Consequently natural rubber is more subject to oxidation, and as in this case (c.f. polybutadiene and SBR) this leads to chain scission the rubber becomes softer and weaker. As already stated the oxidation reaction is considerably affected by the type of vulcanisation as well as by the use of antioxidants.

The effect of ozone is complicated in so far as its effect is largely at or near the surface and is of greatest consequence in lightly stressed rubbers. Cracks are formed with an axis perpendicular to the applied stress and the number of cracks increases with the extent of stress. The greatest effect occurs when there are only a few cracks which grow in size without the interference of neighbouring cracks and this may lead to catastrophic failure. Under static conditions of service the use of hydrocarbon waxes which bloom to the surface because of their crystalline nature give some protection but where dynamic conditions are encountered the saturated hydrocarbon waxes are usually used in conjunction with an antiozonant. To date the most effective of these are secondary alkyl-aryl-*p*-phenylenediamines such as *N*-isopropyl-*N*-phenyl-*p*-phenylenediamine (IPPD).

Natural rubber is generally vulcanised using accelerated sulphur systems although several alternatives have been used. At the present time there is some limited use of the cold cure process using sulphur chloride in the manufacture of rubber proofings. This process was first discovered by Alexander Parkes in 1846, which was some years before his discovery of Parkesine (see Chapter 1) and this is sometimes known as the Parkes Process. (Another Parkes Process is that of separating silver from lead!) Peroxides are also very occasionally used, particularly where freedom from staining by metals such as copper is important. Nitroso compounds and their derivatives, including the so-called urethane cross-linking systems, may also be employed. The latter in particular give a uniform state of cure to thick sections as well as an improved level of heat resistance compared to conventional sulphur-cured systems.

Because of the excellent properties of its vulcanisates under conditions not demanding high levels of heat and oil resistance, natural rubber commands a premium price over SBR, with which it vies for top place in the global tonnage

table. Besides its continuing value as a tyre rubber and in gum and other non-black compounds, natural rubber has also achieved considerable success since World War II as an engineering rubber used, for example, in bridge bearings. In some of these applications the rubber is used in thick sections or in shapes where the bulk of the rubber is more than a few millimeters from a surface exposed to air. Since it has been found that the bulk of oxidation occurs within 3 mm of an exposed surface, problems due to oxidation may often be ignored. A striking example²¹ is of a sewer gasket which was in use for more than a hundred years. Although the rubber was degraded to a depth of 2–3 mm from the surface the rubber was still quite satisfactory. Some bridge bearings have now been in use in England for more than 25 years and are still in excellent condition.

Current production of NR is about 5.2×10^6 tonnes. For some years it has enjoyed a premium price over SBR because of its desirable characteristics described above and, compared with other large tonnage polymers, a somewhat restricted supply. Clearly it is difficult to substantially increase the production of such a material in a short period of time and indeed the attractions of other crops such as palm oil as well as the desire to move away from a monoculture economy mitigate against this. The indications are that, unless there is undue intervention of political factors, the future of natural rubber as a major elastomer remains secure.

Non-elastomeric chemical derivatives of natural rubber are discussed in Chapter 30 in which chemically related naturally occurring materials such as gutta percha and balata are briefly considered.

11.7.2 Synthetic Polyisoprene (IR)

The idea of producing a synthetic equivalent of natural rubber has been long desired both as an academic challenge and for industrial use. Early attempts to make a useful material were not successful because no methods were known of producing a polymer molecule with a similar high order of structural regularity as exhibited by the natural rubber molecule. However, with the advent of the Ziegler-Natta catalysts and the alkyl lithium catalysts it was found possible in the 1950s to produce commercially useful materials. Such polymers have *cis* contents of only some 92–96% and as a consequence these rubbers differ from natural rubber in a number of ways. The main reason for this is that due to the lower *cis* content the amount of crystallinity that can develop either on cooling or on stretching the rubber is somewhat less; in general, the lower the *cis* content the more the rubber differs from natural rubber. In particular the synthetic polyisoprenes have a lower green strength (lower strength in the unvulcanised state), and show inferior fatigue, cut-growth and flexing characteristics, inferior tread wear resistance, and inferior retention of properties at higher temperatures. In addition, because the polymer has a low viscosity there are certain problems with compounding. Somewhat lower shearing stresses are set up in the mixing equipment and it is more difficult to thoroughly disperse fillers and other powdery additives. As a consequence, special techniques have to be adopted in order to overcome these problems. A further disadvantage of these rubbers is that they have to be produced from a somewhat expensive monomer and this has to some extent limited the development of these materials. On the other hand, they do impart useful properties to blends, are easy to injection mould, and may be used as a processing aid. Continuing developments with these materials are now helping to overcome some of the disadvantages mentioned earlier.

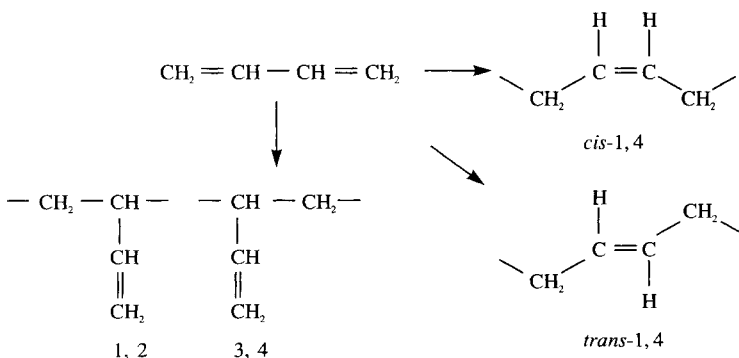
However, in spite of these developments the market for the synthetic polymer has proved disappointing and many plants in the Western world have been 'mothballed'. The greatest use appears to be in the one-time Soviet Union, where it was developed to avoid dependence on the natural material.

One important, if low tonnage, application for synthetic polyisoprene rubber is for the manufacture of negative photoresists used in the preparation of semiconductors. In this process the rubber is first *cyclised*, which gives a harder product with ring structures in the chain. (This process is described further for natural rubber in Chapter 30.) The polymer is then blended with cross-linking agents such as bis-azido compounds and then spin-coated onto the base of the semiconductor. After masking off appropriate parts, the polymer is then exposed to ultra violet light to cross-link the polymer and the unexposed portion is removed by a developing process. The substrate or base thus exposed is then subjected to an etching process, and at the end of this process the cyclised rubber is stripped off, having fulfilled its role. Even in this application polyisoprene rubber is being replaced by positive photoresists, largely based on novolak resins.

11.7.3 Polybutadiene

Polybutadiene was first prepared in the early years of the 20th century by such methods as sodium-catalysed polymerisation of butadiene. However, the polymers produced by these methods and also by the later free-radical emulsion polymerisation techniques did not possess the properties which made them desirable rubbers. With the development of the Ziegler-Natta catalyst systems in the 1950s, it was possible to produce polymers with a controlled stereo regularity, some of which had useful properties as elastomers.

Polymers containing 90–98% of a *cis*-1,4-structure can be produced using Ziegler-Natta catalyst systems based on titanium, cobalt or nickel compounds in conjunction with reducing agents such as aluminium alkyls or alkyl halides. Useful rubbers may also be obtained by using lithium alkyl catalysts but in which the *cis* content is as low as 44%.



The structure of *cis*-1,4-polybutadiene is very similar to that of the natural rubber molecule. Both materials are unsaturated hydrocarbons but, whereas with the natural rubber molecule, the double bond is activated by the presence of a methyl

group, the polybutadiene molecule, which contains no such group, is generally somewhat less reactive. Furthermore, since the methyl side group tends to stiffen the polymer chain, the glass transition temperature of polybutadiene is consequently less than that of natural rubber molecules.

This lower T_g has a number of ramifications on the properties of polybutadiene. For example, at room temperature polybutadiene compounds generally have a higher resilience than similar natural rubber compounds. In turn this means that the polybutadiene rubbers have a lower heat build-up and this is important in tyre applications. On the other hand, these rubbers have poor tear resistance, poor tack and poor tensile strength. For this reason, the polybutadiene rubbers are seldom used on their own but more commonly in conjunction with other materials. For example, they are blended with natural rubber in the manufacture of truck tyres and, widely, with SBR in the manufacture of passenger car tyres. The rubbers are also widely used in the manufacture of high-impact polystyrene.

Perhaps the main reason for the widespread acceptance of polybutadiene rubbers arose when it was found that they gave a vastly reduced tendency for the circumferential cracking at the base of tyre tread grooves with crossply tyres when used in blends with SBR. With crossply tyres now replaced by radial tyres, this factor is no longer of great importance but the rubbers continue to be used because of the improved tread wear and good low-temperature behaviour imparted by their use.

In the mid-1970s there was a short period during which styrene was in very short supply. This led to the development of what were known as *high-vinyl polybutadienes* which contained pendent vinyl groups as a result of 1,2-polymerisation mechanisms. These rubbers had properties similar to those of SBR and could replace the latter should it become economically desirable.

11.7.4 Styrene-Butadiene Rubber (SBR)

In the 1970s there was no argument that, in tonnage terms, SBR was the world's most important rubber. At that time about half of the total global consumption of rubber of about 8×10^6 tonnes per annum was accounted for by SBR. Today natural rubber has about half the market, which has now grown to about 11×10^6 tonnes, and the share of SBR has fallen to about 24%. Nevertheless SBR remains a material of great importance.

In many respects it is not a particularly good rubber, but it has achieved a high market penetration on account of three factors:

- (1) Its low cost.
- (2) Its suitability for passenger car tyres, particularly because of its good abrasion resistance.
- (3) A higher level of product uniformity than can be achieved with natural rubber.

Although first prepared about 1930 by scientists at the German chemical company of IG Farben the early products showed no properties meriting production on technical grounds. However, towards the end of the 1930s commercial production of the copolymer commenced in Germany as Buna S. (The term Buna arose from the fact that the early polymers of butadiene were made by sodium (Na) catalysed

polymerisation of butadiene (Bu). In fact Buna S was made by a free-radical process.) Somewhat earlier than this start of commercial production IG Farben, as a result of an information exchange agreement, had disclosed to Standard Oil details of manufacture of the copolymer so that when in World War II, Malaysia and the then Dutch East Indies were overrun by the Japanese a crash programme for the manufacture of the polymer was initiated by the United States and Canadian governments. By 1945 production of the copolymer, then known as GR-S (Government Rubber-Styrene) was of the order of 10^6 tonnes per annum, but so inferior was the product at that time at the end of World War II in 1945 production slumped dramatically. The wartime materials had been produced with, as is still common, a styrene content of about 23.5% by free-radical emulsion polymerisation of about 50°C. About 1950 there appeared new rubbers produced using more powerful 'redox' free-radical initiators which had been polymerised at about 5°C. These rubbers had a more linear molecular structure and gave vulcanisates of much improved properties. The outbreak of the Korean War in 1952 led many countries, and in particular the United States, to take steps to become less dependent for rubber supplies on south-east Asia and this led to an expansion in SBR production. Because of the low polymerisation temperatures the new rubbers were referred to as *cold rubbers* in distinction from the earlier materials which became known as *hot rubbers*.

Since the early 1950s there have been a number of further important technical developments. These include:

- (1) The development of oil-extended SBR in which a rubbery polymer of very high molecular weight is blended with substantial amounts of hydrocarbon oil. This provides a lower cost alternative to a polymer of more conventional average molecular weight.
- (2) The development of rubbers with a more closely controlled molecular structure. Such materials are made using anionic or Ziegler-Natta catalysts and are polymerised in solution (solution SBRs).
- (3) The development of thermoplastic SBRs (see Section 11.8).

The properties of SBRs may be divided into two groups:

- (1) Those properties in which they are similar to natural rubber.
- (2) Those properties in which they are distinct from natural rubber.

Like NR, SBR is an unsaturated hydrocarbon polymer. Hence unvulcanised compounds will dissolve in most hydrocarbon solvents and other liquids of similar solubility parameter, whilst vulcanised stocks will swell extensively. Both materials will also undergo many olefinic-type reactions such as oxidation, ozone attack, halogenation, hydrohalogenation and so on, although the activity and detailed reactions differ because of the presence of the adjacent methyl group to the double bond in the natural rubber molecule. Both rubbers may be reinforced by carbon black and neither can be classed as heat-resisting rubbers.

The differences between the rubbers can be subdivided into three categories:

- (1) In the materials supplied.
- (2) In processing behaviour.
- (3) In the properties of the vulcanisate.

Compared with the natural material, raw SBR is more uniform in a variety of ways. Not only is it more uniform in quality so that compounds are more consistent in both processing and product properties but it is also more uniform in the sense that it usually contains fewer undesired contaminants. In addition, over a period of years it has been generally less subject to large price variations. These differences in uniformity have, however, tended to lessen with the advent of improved grades of natural rubber such as Standard Malaysian Rubber which have appeared in recent years.

A major difference between SBR and natural rubber is that the former does not break down to any great extent on mastication. The synthetic material is supplied at a viscosity considered to provide the best balance of good filler dispersability (requiring a high viscosity) and easy flow in extrusion, calendaring and moulding. This provides savings in both energy consumption and time, and hence on costs. Since the viscosity changes little with working it is much easier to work re-worked stock into a compound. In many other respects the processing behaviour of SBR is not as good as natural rubber. Mill mixing is generally more difficult, and the synthetic material has lower green strength (i.e. inferior mechanical properties in the unvulcanised state) and does not exhibit the characteristic of natural tack which is so useful in plying together or otherwise assembling pieces of unvulcanised rubber.

Whereas natural rubber is crystalline with a T_m of about 50°C, SBR with its irregular molecular structure is amorphous. Although the crystallinity in natural rubber is reduced by the presence of cross-links and by fillers and other additives it still crystallises on extension and normal ambient temperatures to give a good tensile strength even with gum (i.e. unfilled) stocks. Gum vulcanisates of SBR on the other hand are weak and it is essential to use reinforcing fillers such as fine carbon blacks to obtain products of high strength. Black-reinforced SBR compounds do, however, exhibit a very good abrasion resistance and are commonly superior to corresponding black-reinforced NR vulcanisates at temperatures above 14°C. Against this the SBR vulcanisates have lower resilience and resistance to tearing and cut growth. It is largely the deficiency in these properties together with the lack of green strength and natural tack which has led to the natural material recovering some of the market for tyre rubbers, particularly since the change over from crossply to radial tyres.

SBR also differs from NR in its aging behaviour. Whereas oxidation causes chain scission of the NR molecule and a softening of the rubber in bulk, SBR molecules tend to cross-link, this leading eventually to hardening and embrittlement.

As might be expected from the above comments SBR is invariably used reinforced with carbon black. Besides its very wide use as a tyre rubber it is also extensively used where its low cost coupled with adequate physical properties lead to its preference over more expensive materials, particularly natural rubber. It has also been widely used in the manufacture of high-impact polystyrene (q.v.) although in recent years it has largely been replaced by polybutadiene for this application. In the late 1970s production capacity of SBR became much higher than consumption and this situation has continued over the subsequent decade. Not only has this depressed the price of the polymer but it has also slowed down the replacement of free-radical emulsion polymerisation plant with that for making the solution polymers, which are regarded as having generally superior properties.

11.7.4.1 'High-styrene resins'

Butadiene and styrene may be polymerised in any proportion. The T_g 's of the copolymers vary in an almost linear manner with the proportion of styrene present. Whereas SBR has a styrene content of about 23.5% and is rubbery, copolymers containing about 50% styrene are leatherlike whilst with 70% styrene the materials are more like rigid thermoplastics but with low softening points. Both of these copolymers are known in the rubber industry as high-styrene resins and are usually used blended with a hydrocarbon rubber such as NR or SBR. Such blends have found use in shoe soles, car wash brushes and other mouldings but in recent times have suffered increasing competition from conventional thermoplastics and to a less extent the thermoplastic rubbers.

11.7.5 Nitrile Rubber (NBR)

The butadiene-acrylonitrile rubbers were first prepared about 1930 about five years after the initial development of free-radical-initiated emulsion polymerisation. Commercial production commenced in Germany in 1937, with the product being known as Buna N. By the late 1980s there were about 350 grades marketed by some 20 producers and by the early 1990s world production was of the order of 250 000 tonnes per annum, thus classifying it as a major special purpose rubber.

The acrylonitrile content of the commercial rubbers ranges from 25 to 50%, with 34% being a common and typical value. This non-hydrocarbon monomer imparts very good hydrocarbon oil and petrol resistance to the binary copolymer. As a general rule raising the acrylonitrile level also increases the compatibility with polar plastics such as PVC, slightly increases tensile strength, hardness and abrasion resistance and also makes for easier processing. This is at some detriment to low-temperature flexibility and resilience.

The rubbers may be vulcanised by conventional accelerated sulphur systems and also by peroxides. The vulcanisates are widely used in petrol hose and seal applications. Two limiting factors of the materials as rubbers are the tendency to harden in the presence of sulphur-bearing oils, particularly at elevated temperatures (presumably due to a form of vulcanisation), and the rather limited heat resistance. The latter may be improved somewhat by judicious compounding to give vulcanisates that may be used up to 150°C. When for the above reasons nitrile rubbers are unsatisfactory it may be necessary to consider acrylic rubbers (Chapter 15), epichlorohydrin rubbers (Chapter 19) and in more extreme conditions fluororubbers (Chapter 13).

Nitrile rubbers are sometimes used in conjunction with plastics. Blends with PVC provide an early example of polyblends. (In fact this word has been used by one company as a trade description for such blends for over 25 years.)

Low molecular weight liquid nitrile rubbers with vinyl, carboxyl or mercaptan reactive end groups have been used with acrylic adhesives, epoxide resins and polyesters. Japanese workers have produced interesting butadiene-acrylonitrile alternating copolymers using Ziegler-Natta-type catalysts that are capable of some degree of crystallisation.

Hydrogenated nitrile rubbers were introduced in the mid-1980s as Therban by Bayer. The initial grade had an acrylonitrile content of only 17% instead of approx. 34% in conventional NBR. Whilst non-sulphur-curing systems such as the use of peroxides with triallyl cyanurate or isocyanurate are necessary, the saturated rubber has a number of advantages over NBR. These include improved

heat resistance, because of the absence of double bonds, excellent wear resistance, low brittle temperature and hot tear resistance, properties associated with the low T_g . Other useful properties are very good weathering and ozone resistance and resistance to many oil additives as well as H_2S and amines present in crude oil. The rubber is of interest and competitive with fluororubbers (see Chapter 13) in oil drilling, nuclear power plant and automotive applications. In 1987 Bayer announced further grades, one of which was only partially hydrogenated and which could be sulphur-cured, and another with an acrylonitrile content of 44%. Other companies have also shown interest in making this rubber.

11.7.6 Chloroprene Rubbers (CR)

The polychloroprenes have been commercially available for half a century, being first marketed by Du Pont in 1931. Today these materials are amongst the leading special purpose rubbers (which in the language of the rubber technologist effectively means non-tyre rubbers) and are well known under such commercial names as Baypren (Bayer), Butachlor (Distagul) and Neoprene (Du Pont).

The monomer, 2-chlorobuta-1,3-diene, better known as chloroprene, is polymerised by free-radical emulsion methods to give a polymer which is predominantly (~85%) *trans*-1,4-polychloroprene but which also contains about 10% *cis*-1,4- 1.5%, 1,2- and 1% of 3,4-structures (Figure 11.17). The commercial polymers have a T_g of about $-43^\circ C$ and a T_m of about $45^\circ C$ so that at usual ambient temperatures the rubber exhibits a measure of crystallinity.

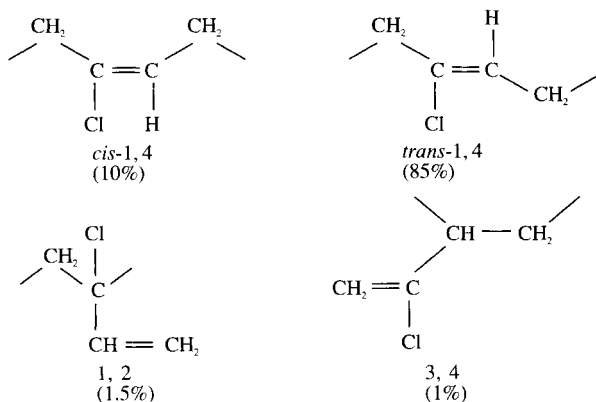


Figure 11.17

The close structural similarities between polychloroprene and the natural rubber molecule will be noted. However, whilst the methyl group activates the double bond in the polyisoprene molecule the chlorine atom has the opposite effect in polychloroprene. Thus the polymer is less liable to oxygen and ozone attack. At the same time the α -methylene groups are also deactivated so that accelerated sulphur vulcanisation is not a feasible proposition and alternative curing systems, often involving the pendant vinyl groups arising from 1,2-polymerisation modes, are necessary.

The chlorine atom has two further useful influences on the properties of the polymer. Firstly the polymer shows improved resistance to oil compared with all-hydrocarbon rubbers. The rubbers also have a measure of resistance to burning which may be further improved by use of fire retardants. These features together with a somewhat better heat resistance than the diene hydrocarbon rubbers have resulted in the extensive use of these rubbers over many years.

The polychloroprene suppliers have, however, faced several difficulties in recent times. These include:

- (1) The price of these rubbers has become such that for many applications they have been replaced by less expensive alternatives. These include the use of EPDM rubbers for automotive parts not requiring oil resistance and plasticised PVC for applications where flexibility rather than high elasticity is required.
- (2) Higher specifications, particularly by the automobile industries, have led to their replacement by rubbers of higher performance in terms of heat and oil resistance.
- (3) Health hazards now associated with what was one of the most common vulcanising agents for the rubber (ethylenethiourea) have caused problems because of the difficulties of finding an acceptable alternative.
- (4) There have been some questions raised concerning possible carcinogenic hazards of residual monomer.
- (5) The announcement by Goodyear in 1980 of new copolymers based on cyclic monomers (see Section 11.10.3).

In spite of these problems the rubber continues to be widely used in mechanical goods, wire covering, auto applications and adhesives.

11.7.7 Butadiene–Pentadiene Rubbers

In 1978 research workers of the Italian company Snamprogetti described a rubbery copolymer of butadiene and penta-1,3-diene (also known as piperylene). This rubber was found to crystallise rapidly on stretching, a feature that is generally considered desirable, particularly in that it contributes to a high green strength. At the same time crystallisation rates have a low temperature sensitivity, which is also considered a good feature. In addition to a good green strength the rubber showed a good tack. It was also found that T_g increased linearly with the piperylene content (about 0.3°C per mole %).

11.8 THERMOPLASTIC DIENE RUBBERS

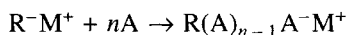
Traditional rubbers are shaped in a manner akin to that of common thermoplastics. Subsequent to the shaping operations chemical reactions are brought about that lead to the formation of a polymeric network structure. Whilst the polymer molecular segments between the network junction points are mobile and can thus deform considerably, on application of a stress irreversible flow is prevented by the network structure and on release of the stress the molecules return to a random coiled configuration with no net change in the mean position of the junction points. The polymer is thus rubbery. With all the major rubbers the

network comprises atoms that are held together by bonds that are predominantly covalent. As a consequence the material cannot dissolve or melt unless the network structure is irreversibly destroyed. For this reason vulcanised rubbers cannot be reprocessed like thermoplastics. It is partly because of this that many products at one time made from rubbers are now made from thermoplastics. It is thus reasonable to suppose that if a polymer could be prepared which showed the desirable properties of a rubber at normal service temperatures but could be repeatedly processed like a thermoplastics material it would be of great interest.

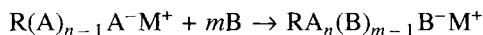
During the past three decades polymer chemists have produced at least four groups of materials that could be considered as being in this category. They are:

- (1) Styrene–diene triblock copolymers.
- (2) Thermoplastic polyolefin elastomers (see Section 11.9.1).
- (3) Thermoplastic polyester elastomers (see Chapter 25).
- (4) Thermoplastic polyurethane elastomers (see Chapter 27).

The styrene–diene triblocks, the main subject of this section, are made by sequential anionic polymerisation (see Chapter 2). In a typical system *sec*-butyllithium is used to initiate styrene polymerisation in a solvent such as cyclohexane. This is a specific reaction of the type



Since all of the chains are initiated at about the same time and because growth continues until all of the styrene has been consumed, the chains will have similar lengths, i.e. there will be a narrow molecular weight distribution. In addition the chains will still have reactive ends. If, subsequently, additional monomer is fed to the reactor the chain growth will be renewed. If the additional monomer is of a different species to the styrene, e.g. butadiene, a binary diblock copolymer will be formed.



In turn binary triblock copolymer may be obtained by adding styrene monomer when all of the second monomer has been consumed. In this way two important triblock copolymers have been produced, the styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS) materials developed by Shell. The Shell commercial rubbers, Cariflex TR, are obtained, however, by joining styrene–butadiene or styrene–isoprene diblocks at the active ends using a difunctional coupling agent. Molecules in the shape of a T, X or star have been produced (e.g. Solprene-Phillips) by using coupling agents of higher functionality.

The outstanding morphological feature of these rubbers arises from the natural tendency of two polymer species to separate one from another, even when they have similar solubility parameters. In this case, however, this is restrained because the blocks are covalently linked to each other. In a typical commercial triblock the styrene content is about 30% of the total, giving relative block sizes of 14:72:14. At this level the styrene end blocks tend to congregate into spherical or rod-like glassy domains embedded in an amorphous rubbery matrix. These domains have diameters of about 30 nm.

Table 11.16

<i>Rubber</i>	<i>Tensile strength (MPa)</i>
Uncompounded polybutadiene	0.3–0.5
Polybutadiene (S vulcanised)	3–5
Polybutadiene + carbon black (S vulcanised)	15–20
SBS (unvulcanised)	30–35

Such domains appear to fulfil two roles:

- (1) By linking the chain ends of different molecules they form a type of network structure as long as the domains remain glassy. As the polymer is heated above the T_g of the domain polymer block the domain molecules become mobile and on application of a stress the material flows like a thermoplastic. On cooling, new domains will be formed, thus regenerating the elastic state.
- (2) By acting like a reinforcing particulate filler.

It is an apparent consequence of the second role that SBS polymers with a molecular mass of about 80 000 behave like carbon-black-reinforced elastomers as illustrated in *Table 11.16* in respect of tensile strength.

Whilst, chemically, SBS triblocks are similar to SBR, for example they do not show measurable breakdown on mastication, they are seriously deficient in one respect, they show a high level of creep. This would indicate that the concept of all the styrene blocks being embedded in the domains with all of the polybutadiene blocks being in the amorphous matrix is rather too simplistic. It has also resulted in these materials not being used extensively in traditional rubber applications. One exception from this is in footwear, where blends of SBS and polystyrene have been used with noted success for 'crepe' soles.

Another major area of use is in the field of adhesives. The main attractions of the material are the absence of a need for mastication, easy solvation of the polymer, which is supplied in a crumb form, the production of low-viscosity solutions and high joint strength. In conjunction with aromatic resins they are used for contact adhesives whilst with aliphatic resin additives they are used for permanently tacky pressure-sensitive adhesives. In addition to being applied from solution they may be applied as a hot melt.

Other uses include bitumen additives (to reduce brittleness), and as modifiers for thermoplastics.

Hydrogenated SBS triblock polymers have become increasingly important (Kraton G by Shell). With the original polybutadiene block comprised of 65% 1,4- and 35% 1,2-structures the elastomeric central block is equivalent to that of a high-ethylene ethylene-butene rubber.

The hydrogenated materials have a higher maximum service temperature than the conventional SBS materials and, because of the absence of double bonds in the chain, better weathering properties. Known as SEBs these materials now find use in adhesives, sealants and roofing membrane compounds. These also find use in highly filled automotive acoustic barriers and in medical, sports and leisure applications.

Somewhat less well known are the *styrene-isoprene-styrene* (SIS) triblocks. The commercial grade (Cariflex TR-1107) is stated to have a styrene-isoprene

ratio of 14:86. The product is much softer, has a lower tensile strength and modulus and is more extensible with an elongation at break of about 1300%. On the other hand it exhibits extensive creep and breaks down, like other polyisoprenes, on mastication. It is also more susceptible to oxidative breakdown. An important application is in the manufacture of hot melt pressure-sensitive adhesives showing a high level of tack.

In addition to the somewhat sophisticated triblock thermoplastic elastomers described above, mention should be made of another group of thermoplastic diene rubbers. These are physical blends of polypropylene with a diene rubber such as natural rubber. These may be considered as being an extension to the concept of thermoplastic polyolefin rubbers discussed in Section 11.9.1 and although extensive experimental work has been carried out with these materials they do not yet appear to have established themselves commercially.

11.9 ALIPHATIC OLEFIN RUBBERS

In spite of possessing a flexible backbone and low interchain attraction polyethylene is not a rubber. This is because its chain regularity enables a measure of crystallinity which does not disappear until temperatures of the order of 100°C are reached. It therefore follows that if crystallinity can be substantially reduced it should be possible to obtain an ethylene-based polymer which is rubbery. The means by which this objective has been achieved on a commercial scale may be classified into three categories:

- (1) Copolymerisation with other hydrocarbon monomers.
- (2) Copolymerisation with non-hydrocarbon monomers.
- (3) Chemical modification of polyethylene.

In addition there is the possibility that other olefins may generate polymers with low T_g 's which show little or no crystallinity at room temperature and are therefore potentially elastomeric. One commercial example is butyl rubber (designated IIR), a copolymer of isobutene with a small amount of isoprene.

The first of the above approaches was successfully achieved in the early 1950s with the advent of the Ziegler-Natta catalysts. Whilst attempts to produce ethylene-propylene copolymers using heterogeneous catalysts, so successful with polyethylene, led to blocky copolymers with poor elastomeric properties, the use of homogeneous systems gave more random copolymers. Typical catalysts included blends of an alkyl aluminium halide (e.g. $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$) with a hydrocarbon-soluble vanadium compound (e.g. VOCl_3), with at least one component requiring a halogen in the molecular structure.

Because of their saturated structure the raw polymers could not be vulcanised using accelerated sulphur systems and the less convenient peroxide curing systems were required. Binary copolymers of this type are designated as EPM rubbers. Such ethylene-propylene rubbers were accepted reluctantly by the rubber industry. Such reluctance was largely due to the real risks of mixing EPM stocks with those of diene rubbers and thus causing considerable problems because of the different curing systems. In addition peroxide curing systems are much more liable to premature vulcanisation (scorch) than accelerated sulphur systems and this can lead to high scrap rates.

In consequence ethylene-propylene rubbers were introduced with a small amount (3–8%) of a third, diene, monomer which provided a cross-link site for accelerated sulphur vulcanisation. Such ethylene-propylene-diene monomer ternary copolymers are designated as EPDM rubbers.

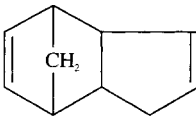
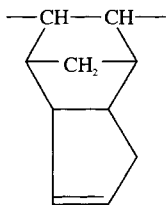
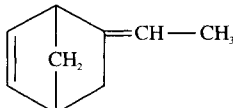
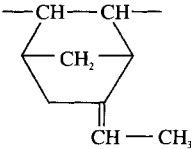
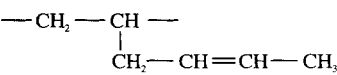
The EPDM rubbers, whilst hydrocarbon, differ significantly from the diene hydrocarbon rubbers considered in Section 11.7 in two principal ways:

- (1) The level of unsaturation is much lower, giving rubbers of much better heat, oxygen and ozone resistance.
- (2) The dienes used are such that the double bonds in the polymer are either on a side chain or as part of a ring in the main chain. Hence should the double bond become broken the main chain will remain substantially intact. Dienes commonly used include dicyclopentadiene, ethylidene-norbornene and hexa-1,4-diene (*Table 11.17*).

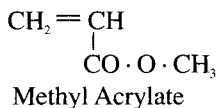
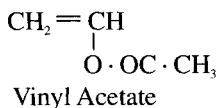
At one time it was widely expected that EPDM rubbers would become of significance in the tyre sector. For a variety of reasons but primarily because of the high cost of the diene monomers this expectation has not been realised. On the other hand these rubbers have become widely accepted as moderately heat-resisting materials with good weathering, oxygen and ozone resistance and they find extensive use in cars, domestic and industrial equipment.

These rubbers are now also being blended on a large scale with polyolefin plastics, particularly polypropylene, to produce a range of materials which at one extreme are tough plastics and at the other the so-called thermoplastic polyolefin rubbers (TPORs) (see Section 11.9.1).

Table 11.17 Principal diene monomers used in manufacture

<i>Monomer</i>	<i>Predominant structure present in terpolymer</i>
(1) Dicyclopentadiene 	
(2) 4-Ethylidenenorborn-2-ene 	
(3) Hexa-1, 4-diene $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_3$	

As already mentioned in previous sections ethylene may also be copolymerised with several non-hydrocarbon polymers. Some of these copolymers are elastomeric and they also have a measure of oil resistance. Two monomers used commercially are vinyl acetate and, the structurally very similar, methyl acrylate:



Ethylene-vinyl acetate copolymers have been available for several years from Bayer (Levapren 450) and these contain about 45% of vinyl acetate units. As with EPM these rubbers cannot be cured with accelerated sulphur systems but by peroxides.

More recently, in 1975, Du Pont introduced a terpolymer (Vamac) based on ethylene, methyl acrylate and a third monomer of undisclosed composition which contained a carboxylic acid group to provide a cure site for use with peroxides or amines. Both types of rubber exhibit good heat, oxygen and ozone resistance.

The Du Pont material also has good aliphatic hydrocarbon oil resistance and usage has been roughly evenly split between cables and automotive uses. In the former case it has become of particular interest for ignition wire sheathing and for medium-voltage cables, with its high temperature rating and zero halogen content which helps it to meet low toxicity and smoke-generating levels, particularly important in ships, submarines and underground applications.

Interestingly, later grades of Vamac to become available did not employ the cure site monomer, using instead a peroxide-curing system. Some of these copolymers also contained higher levels of methyl acrylate (up to 69%) to enhance the oil resistance.

Broadly similar effects may be brought about by chemical modification of polyethylene. If polyethylene is subjected to a chlorination process the initial effect is that the chlorination reduces the regularity and lowers the softening point of the polymer. Eventually this is reduced to such a level that the material becomes rubbery. At the same time the chlorination increases the interchain attraction, and once there is sufficient bound chlorine to give an amorphous product, further chlorination causes the softening point to rise. The *chlorinated polyethylenes* are usually rubbery in the 25–40% range, this depending on whether high- or low-density polyethylene is used. Chlorinated polyethylene rubbers have become commercially available but because of difficulties in processing and, particularly, vulcanisation, the rubbers have only recently become of any significance.

More successful have been the chlorinated polyethylenes which additionally contain sulphonyl chloride groups. These were introduced by Du Pont in 1952 as Hypalon. Today both linear and branched polyethylenes are used and the polymers contain 29–43% of chlorine and 1–1.5% sulphur. The materials are designated as CSM rubbers and are generally known as *chlorosulphonated polyethylenes*. CSM rubbers have very good heat, ozone and weathering resistance together with a good resistance to oils and a wide range of chemicals. About one-third of the output is used for fabric coating and film sheeting

applications. Whilst these are usually vulcanised, unvulcanised high green strength rubbers have been used in the construction industry and for pit liner systems. In such applications they act more like plastics than rubbers.

High elasticity is also not utilised in the main application of chlorosulphonated polyethylenes, in wire and cable coating, which consume about 40% of output. The combination of heat and oil resistance has led to widespread use as sheathing for nuclear power cables, offshore oil rig cables and in diesel electric locomotives. Other uses include chemical plant hose, spark plug boots and as a base for flexible magnetic strips.

A modified form of chlorosulphonated polyethylene has more recently been introduced by Du Pont under the trade mark Acsium and given the designation ACSM. In addition to chlorine and sulphonyl chloride side groups, this rubber also has alkane side groups, which makes the material more rubbery in terms of dynamic properties. The polymer has good heat resistance, including heat aging, and also retains its rubberiness at low temperatures (down to -40°C).

Whilst polyisobutene is a non-rubbery polymer exhibiting high cold flow (see Section 11.3), the copolymer containing about 2% isoprene can be vulcanised with a powerful accelerated sulphur system to give moderately rubbery polymers. The copolymers were first developed in 1940 by Esso and are known as *butyl rubbers* and designated as IIR. As they are almost saturated they have many properties broadly similar to the EPDM terpolymers. They do, however, have two properties that should be particularly noted:

- (1) A very low air permeability for a rubber (although not particularly low for polymers in general) which has led to extensive use in tyre inner tubes and liners.
- (2) A very low resilience at normal ambient temperatures but which increases steeply with increase of temperature.

The low unsaturation requires powerful curing systems whilst the hydrocarbon nature of the polymer causes bonding problems. To overcome these problems *chlorinated* and *brominated butyl rubbers* (CIIR and BIIR) have been introduced and have found use in the tyre industry.

11.9.1 Thermoplastic Polyolefin Rubbers

In the 1970s many companies supplying either polypropylene or ethylene-propylene rubber began to market blends of these two polymers. Such blends became available in a very wide range of ratios so that at one extreme were materials very much like polypropylene but with some added toughness and low temperature resistance and at the other extreme much more rubber-like materials. Although the latter materials were not vulcanised they did show good recoverable high elasticity and it is believed that this may be due to short propylene blocks in the ethylene-propylene rubber co-crystallising with segments of the polypropylene molecules so that the crystal domains act like cross-linking agents.

Subsequently, much improved thermoplastic polyolefin rubbers were obtained by invoking a technique known as *dynamic vulcanisation*. This process has been defined (Coran, 1987) 'as the process of vulcanizing elastomer during its intimate melt-mixing with a non-vulcanizing thermoplastic polymer. Small elastomer droplets are vulcanized to give a particulate

vulcanized elastomer phase of stable domain morphology during melt processing and subsequently.'

In the early developments the vulcanisation was brought about by the use of peroxides. Better results can be obtained if an EPDM terpolymer is used in conjunction with polyethylene and/or, preferably, polypropylene with vulcanisation of the elastomer using a sulphur-based curing system. In practice the elastomeric polymer and the polypropylene are melt-mixed in an internal mixer or an extruder mixer. After the desired degree of melt mixing has been achieved, the curing system (vulcanisation ingredients) is added and vulcanisation occurs whilst the mixing continues. The more rapid the vulcanisation, the faster the mixing rate to ensure good processability. Although commercial blends usually have a polypropylene content of less than 50%, this thermoplastic material usually forms the continuous phase, so that the material is thermoplastic overall. For optimum rubbery properties a low particle size (e.g. 1.5 μm) is required. It is common practice to use a mineral oil as a plasticiser which lowers the melt viscosity of the thermoplastic phase during processing, but on partial crystallisation of the polypropylene on cooling the plasticiser is driven into the elastomeric polymer and at this stage acts more as a softener.

Although the elastomer phase is essentially in particulate form, the tensile strength of the blend can be increased five-fold by increasing the cross-link density from zero to that conventionally used in vulcanisation processes, whilst tension set may be reduced by over two-thirds. Since the thermoplastic polyolefin phase may be completely extracted by boiling decalin or xylene, there is apparently no covalent chemical bonding of elastomer and thermoplastic phases.

Such rubbery and thermoplastic polymers may be blended in any proportion, so that on one hand the product may be considered as a thermoplastic elastomer, and on the other as an elastomer-modified thermoplastic. There is, furthermore, a spectrum of intermediate materials, including those which might be considered as leather-like. In this area the distinction between rubber and plastics material becomes very blurred.

It is somewhat difficult conceptually to explain the recoverable high elasticity of these materials in terms of flexible polymer chains cross-linked into an open network structure as commonly envisaged for conventionally vulcanised rubbers. It is probably better to consider the deformation behaviour on a macro, rather than molecular, scale. One such model would envisage a three-dimensional mesh of polypropylene with elastomeric domains embedded within. On application of a stress both the open network of the 'hard phase' and the elastomeric domains will be capable of deformation. On release of the stress, the cross-linked rubbery domains will try to recover their original shape and hence result in recovery from deformation of the blended object.

The rubbers are particularly attractive because of their reasonable price structure, good weathering properties, apparently negligible toxicity hazards and easy processability and re-processability. They have received rapid acceptance in the automotive industry for such uses as radiator grilles, headlight surrounds, bumper covers, fascia panels, door gaskets and other car parts. They have also found use in cable insulation. In common with blends in general the blending technique has an influence both on absolute properties and on product consistency.

Interesting blends have been prepared by Exxon using *sulphonated EPDM*. In one experiment a terpolymer of composition 55% ethylene units, 40% propylene

units and 5% ethyridenenorbornene units had its backbone sulphonated to a level of about 1 mol% and which was then neutralised to produce a zinc salt.

This rubber has a very high melt viscosity and this was reduced by using a polar flow promoter such as zinc stearate at levels of 9.5 and 19%. This not only reduced the viscosity at low shear rates but also increased the level of pseudoplasticity so that at the high shear rates used in injection moulding flow was even more enhanced.

When compared with straight EPDM–PP blends at equal ratios the sulphonated materials exhibited markedly higher tensile strength, tear strength and modulus. Since optical studies showed no great differences in morphology it appears that the effect is due to the stiffer rubber phase being able to have a greater load-bearing function when the blend is stressed.

A somewhat different approach to the production of thermoplastic polyolefin rubbers has been adopted by Allied Chemical with their ET polymers. With these materials butyl rubber is grafted on to polyethylene chains using a phenolic material such as brominated hydroxymethyl phenol. The initial grades of these polymers, which were introduced commercially towards the end of the 1970s, had polyethylene : butyl rubber ratios of 50 : 50 and 75 : 25. Both low-density and high-density polyethylene-based varieties were produced.

11.10 RUBBERY CYCLO-OLEFIN (CYCLO-ALKENE) POLYMERS

The use of supported transition metal oxide and Ziegler–Natta-type catalysts for polymerising aliphatic olefins (alkenes) was extended in the 1960s and 1970s to the ring-opening polymerisation of cyclo-olefins.

It is convenient to classify the polymerisable cyclo-olefins into the following groups:

- (1) Unsubstituted monocyclic mono-olefins, e.g. cyclopentene and cyclo-octene, which yield poly-pentenamers and poly-octenamers respectively.
- (2) Unsubstituted monocyclic di- or multi-olefins, e.g. cyclo-octa-1,5-diene.
- (3) Substituted derivatives of groups (1) and (2) above, e.g. 3-methylcyclo-butene and 1-methylcyclo-octa-1,5-diene.
- (4) Substituted and unsubstituted bi- or multi-cyclic mono-, di- or multi-olefins, i.e. containing condensed rings at least one of which contains a double bond. Norbornene is homopolymerised commercially whilst, as previously mentioned, ethyridenenorbornene and dicyclopentadiene are used as the cure site monomer in EPDM rubbers.

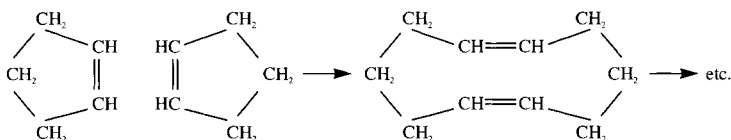
Of these various groups there was extensive interest for some years in polyalkenamers such as *trans*-poly-pentenamer which has now abated whilst interest in polynorbornene is steadily increasing. Since the chemistry and technology of the two types is somewhat different each type will be dealt with separately. A third group comprises the chlorine-containing polymers announced by Goodyear in 1980.

11.10.1 Aliphatic Polyalkenamers

The polyalkenamers are usually prepared by means of a Ziegler–Natta catalyst system. For example *trans*-poly-pentenamer may be obtained from cyclopentene

using a three-part system based on tungsten hexachloride (WCl_6), a peroxide such as cyclopentene hydroperoxide and tri-isobutyl aluminium. The reaction mechanism is not fully understood but one hypothesis is that the cyclopentene rings are joined to form a decadiene ring which in turn reacts to form larger and, eventually, macrocyclic rings:

Because of side reactions which break the ring the ultimate polymers are more likely to be linear.



As a class the aliphatic polyalkenamers have low T_g values due to a combination of low chain stiffness and low interchain attraction. The presence of double bonds has the effect of increasing the flexibility of adjacent single bonds (see Chapter 4) and overall this leads to a reduction in T_g . Thus in the sequence from polydecenamer down to polypentenamer an increase in the double bond concentration leads to a lowering of T_g . On the other hand the T_g of polybutenamer, i.e. polybutadiene, is somewhat higher than that of polypentenamer, presumably because the proportion of stiff links, i.e. double bonds, becomes sufficiently high to override the flexibilising effect on adjacent chains. Consequently the polypentenamers have the lowest T_g values known for hydrocarbon polymers (*cis*- -114°C , *trans*- -97°C).

Such low T_g values are indicative of a very rubbery polymer. Furthermore, careful control of the polymerisation enables highly stereoregular polymers to be produced, i.e. polymers that are essentially *cis* or essentially *trans*. This gives the possibility that the rubber may crystallise and thus show that great virtue of natural rubber—self-reinforcement, brought about by crystallisation on extension. In practice the T_m of the *cis*-polymer at -41°C is too low to be of any consequence at room temperature but the *trans*-polymer with a T_m of $+15^\circ\text{C}$ is closer to that of natural rubber and the polymer exhibits high green strength, good building tack, and generally good processability. The polymer may be vulcanised using conventional accelerated sulphur systems to give vulcanisates with good strength and abrasion resistance.

As a consequence considerable interest was shown in the *trans*-polypentenamer by Bayer as a potential general purpose rubber and particularly as a tyre rubber. In the event this hope did not materialise, apparently due to the following reasons:

- (1) The uncompetitive costs of production.
- (2) Low skid resistance.
- (3) The low road-holding characteristics of tyres made from them.

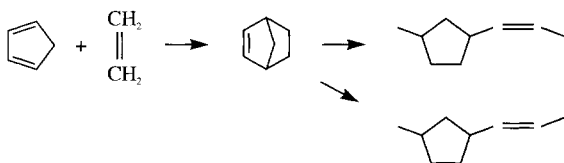
Rather more success has been achieved by *trans*-polyoctenamer, which was introduced by Hüls in 1980 under the name Vestenamer. The two initial grades had *trans*-contents of approx. 80 and approx. 62%. The polymers have a low molecular weight, and above the T_m , which increases with increasing *trans*-content once the latter exceeds 30% and is about 60°C with the high *trans*-grades, the polymer on its own has a very low melt viscosity. Below the melting

point, however, the polymers, and particularly the high *trans*-grades, are highly crystalline. They are not used on their own but are useful in blends with other diene rubbers where they aid flow during shaping but impart useful stiffness and form stability to green stocks (unvulcanised compounds). They can co-cure with diene rubbers using conventional accelerated sulphur systems, and the vulcanised blends may show improved dynamic behaviour, resilience, modulus and hardness compared to more conventional SBR compounds. The polymers are of particular interest in blends for tyre manufacture, but also have potential in non-tyre applications.

11.10.2 Polynorbornene

Commercial manufacture of this polymer was first announced by CdF Chimie in 1975 following about 10 years of study on the Diels–Alder reactions of alkenes with cyclopentadiene. In 1976 a plant with a capacity of 5000 tonnes per annum was put on stream and product marketed as Norsorex. Manufacturing under licence is now being extended to American Cyanamid whilst CdF Chimie has also signed a marketing agreement with Nippon Zeon.

The monomer, norbornene (or bicyclo[2.2.1]hept-2-ene), is produced by the Diels–Alder addition of ethylene to cyclopentadiene. The monomer is polymerised by a ring-opening mechanism to give a linear polymer with a repeat unit containing both an in-chain five-membered ring and a double bond. Both *cis*- and *trans*- structures are obtainable according to the choice of catalyst used:



Because of the in-chain ring the T_g is as high as $+35^\circ\text{C}$ and the polymer is therefore not rubbery at usual ambient temperatures. If, however, the polymer is blended with an aromatic oil or certain ester plasticisers a rubbery material is obtained. Because of the ability of the polymer to take up large quantities of oil the T_g of a polymer-oil blend can be as low as -60°C . Such polymer-oil blends can also incorporate very large amounts of filler.

Blending of polymer, plasticiser and filler may be carried out using two-roll mills or internal mixers as commonly used in the rubber industry. Alternatively, since the raw polymer is supplied as a free-flowing powder a dry blending process similar to that now widely used with PVC (see Chapter 12) is also used.

Whilst the blend has a good green strength it is usual to vulcanise the rubber by an accelerated sulphur system using a higher than usual accelerator sulphur ratio.

Interest in the vulcanisates arises largely from two characteristics:

- (1) The ability to produce very soft solid rubbers but which still retain a good tensile strength. (For example, a vulcanisate with a hardness as low as 18 Shore A is claimed to have a tensile strength as high as 10 MPa).
- (2) The rubber shows interesting damping and anti-vibration characteristics.

The low hardness has led to uses in printers' rollers and stereos. It is, however, to be noted that when the material has been used to replace cellular rubbers or flexible polyurethane foams in sealing applications, problems have arisen where it has not been appreciated that although the rubber is very soft it is for practical purposes incompressible.

Polynorbornene is also of interest to the plastics processor since by using a dry blending process for mixing and a modified injection moulding process for fabricating, the use of conventional rubber-processing equipment may be avoided.

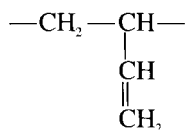
Ethylene-norbornene copolymers of interest as thermoplastics were discussed in Section 11.6.2. It is however to be noted that copolymers with a norbornene content of about 30 wt% have a glass transition temperature of about 0°C and that copolymers with norbornene contents up to this amount are being evaluated as thermoplastic elastomers

11.10.3 Chlorine-containing Copolymers

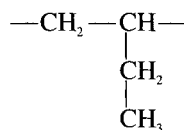
In 1980 the Goodyear company announced copolymers of cyclopentadiene, cyclo-octene or cyclo-octa-1,5-diene with the Diels–Alder addition product of hexachlorocyclopentadiene and cyclo-octa-1,5-diene. This material has been proposed as an alternative to the polychloroprenes, with lower T_g (–45°C), and superior ozone resistance.

11.11 1,2-POLYBUTADIENE

Whilst *cis*-1,4-polybutadiene is a rubber, 1,2-polybutadiene is thermoplastic. Such a material is very similar in structure to polybut-1-ene except that the hydrocarbon side chain is unsaturated:



1,2-Polybutadiene



Polybut-1-ene

As with polybut-1-ene and many other vinyl monomers that contain an asymmetric carbon, isotactic, syndiotactic and atactic structures may be drawn. Using co-ordination catalysts such as mixtures of cobalt chlorides, aluminium alkyls, pyridine and water high-1,2 (high vinyl) polymers may be obtained. One product marketed by the Japan Synthetic Rubber Company (JSR 1,2 PBD) is 91% 1,2, and 51–66% of the 1,2 units are in the syndiotactic state. The molecular mass is said to be 'several hundred thousand' and the ratio M_w/M_n is in the range 1.7–2.6.

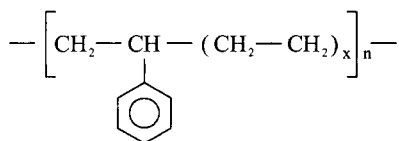
Since the polymer is far from completely stereoregular the level of crystallinity is fairly modest, with a typical value of 25%. The crystalline melting point is about 90°C and the T_g is –23°C. Such materials are rheologically similar to LDPE. Bottles and films are transparent. The particular features of the polymer

in film form are its high permeability (useful for the packing of fresh fruit, vegetables and fish), the very high tear resistance and resistance to puncturing and its photo/biodegradability.

11.12 ETHYLENE-STYRENE COPOLYMERS

Attempts to produce copolymers of ethylene and styrene by free radical and by conventional Ziegler–Natta catalysts systems have, over the years, not proved successful. However, in 1998 Dow announced novel polymers using a metallocene process with the intention of commercial polymerisation using a 23 000 t.p.a. capacity plant starting in 1999.

The products have been described as pseudo-random copolymers. The reason for this is that successive head-to-tail styrene-styrene insertions do not occur. The structure may thus be formally represented as



Where $x=1$ or more

It follows directly from this that the theoretical maximum amount of styrene units in the polymer is 50 mole%, i.e. 77% by weight and Dow claim that it can produce copolymers (which it tends to refer to as interpolymers, or more specifically as ethylene-styrene interpolymers, ESIs) from this figure down to 17 wt%. As experienced with ethylene-propylene copolymers the copolymers with high ethylene contents show a measure of crystallinity and indeed crystallinity can be traced in polymers up to 50 wt% styrene (*Figure 11.18*). Data on glass transition temperatures indicate that the polymers are rubbery below normal indoor ambient temperatures with up to about 70 wt% of styrene. (It is of interest here that the data here is in line with the author's suggestion for the T_g of polyethylene given in Section 10.4.)

It thus follows that three types of ESI may be distinguished:

- (i) Semi-crystalline elastomers (referred to by Dow as Semicrystalline thermoplastics plastomer elastomer).
- (ii) Amorphous elastomers (amorphous rubbers).
- (iii) Glassy (amorphous) thermoplastics (Glasstomer) (in practice as previously mentioned there is a limit of 77 wt% possible for the styrene content; unless it is a 100% homopolymer).

It is interesting to compare the effect of inserting the compact 6-membered benzene ring onto the chain with the insert of an aliphatic chain of a similar length, e.g. by using octene-1 instead of styrene. As might be expected the glass transition temperatures are reported to be somewhat higher (25°C or more) for the ESIs than their ethylene-octene copolymer counterparts.

As saturated hydrocarbon copolymers the ESIs will have many of the characteristics of such materials including good electrical insulation properties,

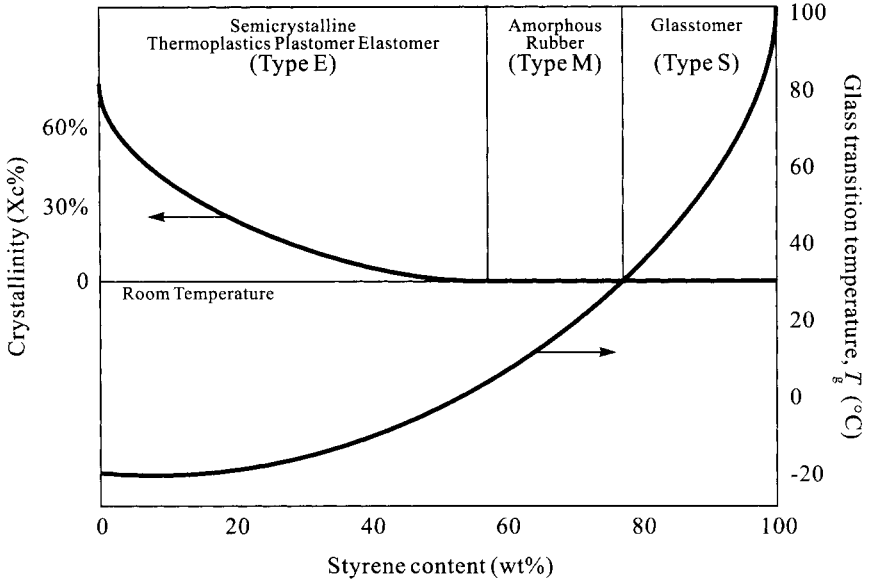


Figure 11.18 Influence of styrene content on properties of ethylene-styrene copolymers (based on Dow literature)

solubility in hydrocarbons but resistance to polar chemicals and ability to burn. With the commercial grades possessing transition temperatures (both T_m and T_g) close to normal ambient temperatures the mechanical properties of ESIs will, like plasticised pvc, be very temperature sensitive. It is therefore not surprising that initial suggestions for applications have been for 'pvc-type' applications such as flooring and extruded profiles particularly where a halogen-free polymer is specified. It remains to be seen to what extent useful blends of ESIs with other polymers can be produced and indeed what commercial success these materials will achieve.

11.13 OTHER ELASTOMERS

In this chapter brief consideration has been given to the major tonnage rubbers. Derivatives of natural rubber such as ebonite are discussed in Chapter 30 and thermoplastic rubbers are reviewed in Chapter 31. Other important speciality rubbers (with their ASTM designations) include:

- Ethylene-vinyl acetate rubbers (EAM)—this chapter
- Ethylene-acrylate rubbers (AEM)—this chapter
- Fluororubbers (FKM, CFM, FFKM, FZ, AFMU etc.)—Chapter 13
- Silicone and fluorosilicone rubbers (MQ, VMQ, PMQ, PVMQ and FVMQ)—Chapter 29
- Polysulphide rubbers—Chapter 19
- Epichlorhydrin rubbers (CO, ECO and AECO)—Chapter 19
- Propylene oxide rubber (GPO)—Chapter 19

Chlorinated (CM) and chlorosulphonated polyethylenes (CSM and ACSM)—
this chapter

Polynorbornene (PNR), polyoctenamer and hydrogenated nitrile rubber
(HNBR)—this chapter

References

1. CRESPI, D. and RANALLI, F., *Trans. Plastics Inst.*, **27**, 55 (1959)
2. VAN DER WEGT, A. K., *Trans. Plastics Inst.*, **32**, 165 (1964)
3. CHARLEY, R. V., *Brit. Plastics*, **34**, 476 (1961)
4. *Technical trade literature*, ICI Ltd., Welwyn Garden City
5. KRESSER, T. O. J., *Polypropylene*, Reinhold, New York (1960)
6. PRITCHARD, R., *Soc. Plastic Eng. J.*, **4**, 66 (1964)
7. TURNER, L. W. and YARSLEY, V. E., *Brit. Plastics.*, **5**, 32 (1962)
8. LEYLAND, B. N. and WATTS, J. T., Chapter in *Developments with Natural Rubber* (Ed. BRYDSON, J. A.), Maclaren, London (1967)
9. O'DONNELL, J. F. and SELLDORF, J. J., *Mod. Packaging*, **33**, 133 (1961)
10. D. J. GRAY, *Plast. Rubb. Process.*, 60 (1977)
11. CLARK, K. J. and PALMER, R. P., *S.C.I. Monogr. No. 20*
12. DAY, M. R., *Plast. Polym.*, **36**, 101 (1968)
13. RAINE, H. C., *Trans. Plastics Inst.*, **28**, 153 (1960)
14. PRITCHARD, J. E., MCGLAMERY, R. M. and BOEKE, P. J., *Mod. Plastics*, **37**, (2) 132 (1959)
15. HAYES, R. and WEBSTER, W., *Trans. Plastic Inst.*, **32**, 219 (1964)
16. STREIB, H., PUMP, W. and RIESS, R., *Kunststoffe*, **67**, 118 (1977)
17. *IISRP Worldwide Rubber Statistics 1993*
18. RODGER, E. R., Chapter 3 in *Developments in Rubber Technology—I* (Eds. A. WHELAN and K. S. LEE), Applied Science, London (1979)
19. BLACKLEY, D.C., *High Polymer Latices*, Vol 1, Applied Science, London (1966)
20. PIKE, M. and WATSON, W. F., *J. Polymer Sci.*, **9**, 229, (1952)
21. SMEE, A. R., *Rubber Developments*, **16**, 115 (1963)

Bibliography

- BHOWMICK, A. K. and STEPHENS, H. L. (Eds.) *Handbook of Elastomers—New Developments and Technology*, Marcel Dekker, New York and Basel (1985)
- BLOW, C. M. and HEPBURN, C. (Eds.), *Rubber Technology and Manufacture* (2nd edn), Butterworths, London (1982)
- BRYDSON, J. A., *Rubber Chemistry*, Applied Science, London (1978)
- BRYDSON, J. A., *Rubbery Materials and their Compounds*, Applied Science, London (1988)
- KRESSER, T. O. J., *Polypropylene*, Reinhold, New York (1960)
- RITCHIE, P. D. (Ed.), *Vinyl and Allied Polymers*, Vol. 1—*Aliphatic Polyolefins and Polydienes: Fluoro-olefin Polymers*, Iliffe, London (1968)
- BOENIG, H. V., *Polyolefins: Structure and Properties*, Elsevier (1966)
- FRANK, H. P., *Polypropylene*, Macdonald, London (1966)
- LEGGE, N. R. HOLDEN, G. and SCHROEDER, H. E (Eds.) *Thermoplastic Elastomers*, Hanser, München, Vienna, New York (1987)
- RAFF, R. A. V. and DOAK, K. W. (Eds.), *Crystalline Olefin Polymers*, Interscience, New York (1964)
- RUBIN, I. D., *Poly-1-butene: its Preparation and Properties*, Macdonald, London (1969)
- WHELAN, A. and LEE, K. S., *Developments in Rubber Technology I* (1979); *II* (1981); *III* (1982), *IV* (1987), Applied Science, London

Review

- BEER, G., *Kunststoffe*, **86**, 1460–1463 (1986)
- BRYDSON, J. A., *Speciality Rubbers*. RAPRA Review Report 74 (1994)
- BRYDSON, J. A., *Thermoplastic Elastomers*. RAPRA Review Report 81 (1995)

12

Vinyl Chloride Polymers

12.1 INTRODUCTION

It is an interesting paradox that one of the least stable of commercially available polymers should also be, in terms of tonnage consumption at least, one of the two most important plastics materials available today. Yet this is the unusual position held by poly(vinyl chloride) (PVC),* a material whose commercial success has been to a large extent due to the discovery of suitable stabilisers and other additives which has enabled useful thermoplastic compounds to be produced.

The preparation of the monomer was first reported by Regnault¹ in 1835 although it may have been prepared earlier by Liebig. The method used was to treat ethylene dichloride with an alcoholic solution of potassium hydroxide. Vinyl bromide was also obtained by a similar method using ethylene dibromide. It is reported that in 1872 vinyl bromide was also prepared by reacting acetylene and hydrogen bromide.² The analogous reaction with hydrogen chloride, discovered by F. Klatte³ in 1912, subsequently became one of the two major routes for vinyl chloride production.

The polymerisation in sealed tubes of vinyl chloride and vinyl bromide, when exposed to sunlight, was reported in 1872 by Baumann.⁴ Further work on these polymerisations was carried out by Ostromislensky in Moscow and this was duly reported in 1912.⁵

Commercial interest in poly(vinyl chloride) was revealed in a number of patents independently filed in 1928 by the Carbide and Carbon Chemical Corporation, Du Pont and IG Farben. In each case the patents dealt with vinyl chloride–vinyl acetate copolymers. This was because the homopolymer could only be processed in the melt state at temperatures where high decomposition rates occurred. In comparison the copolymers, which could be processed at much lower temperatures, were less affected by processing operations.

An alternative approach, which in due course became of great commercial significance, was made by W. L. Semon.⁶ He found that if poly(vinyl chloride)

* The IUPAC systematic name is poly(-1-chloroethylene). The term *vinyl* is commonly, if misleadingly and unscientifically, used to describe compounds and products based on PVC.

was heated at 150°C with tritolyl phosphate, then rubber-like masses which remained homogeneous at room temperature could be obtained. The blending of PVC with this and other similar non-volatile liquids to give *plasticised PVC* is now of great importance in the plastics industry.

During the next few years PVC was steadily developed in the United States and in Germany. Both countries were producing the material commercially before World War II. In Great Britain, ICI in 1942 and the Distillers Company in 1943 also commenced pilot-plant production of PVC, a material then in demand as a rubber substitute for cable insulation. Paste-forming grades suitable for the production of leathercloth also became available soon afterwards.

After the war developments in Britain and the United States were concerned largely with plasticised PVC, handled mainly by extrusion, calendering and paste techniques. However, on the continent of Europe, particularly in Germany, development work was also proceeding with unplasticised PVC, a rigid material which only achieved significance in Britain in the 1960s. The use of copolymers has not grown in the same way as the homopolymer in spite of their early importance. Instead the former have become useful special purpose materials for the flooring, gramophone record and surface coating industries. Perhaps the greatest developments over the past few years have not been concerned with the molecular structure of the polymers but rather with the particles formed during polymerisation. Such factors as particle shape, size, size distribution and porosity vitally affect the processing characteristics of the polymer and a more complete knowledge of their influence has led to many useful new grades of polymer.

By the early 1970s PVC was being manufactured in a large number of countries and was contending with polyethylene for the title of the world's number one plastics material in terms of tonnage consumption. In 1971, however, some evidence was presented which showed that the vascular disturbance known as acro-osteolysis, Reynauds syndrome and scleroderma were all associated with exposure to vinyl chloride monomer. These diseases were characterised by symptoms such as increased sensitivity to cold, changes in skin colour and thickness, changes in bone formation and the shape of the digits. Further studies then indicated that animals exposed to monomer levels in the atmosphere as low as 250 ppm had a higher than normal incidence to the rare cancer form, angiosarcoma of the liver, and in 1974 it was found that this cancer had occurred at above-normal incidence among workers in some PVC polymerisation plants and by 1976 a total of 55 deaths due to angiosarcoma of the liver had been recorded amongst those who had worked with vinyl chloride.

These findings led to rapid and important changes in the details of PVC manufacture in the mid-1970s. As a result monomer concentration levels around polymerisation plants were reduced from 300–400 ppm in the late 1960s to about 2–5 ppm by late 1976. Not surprisingly the effort expended in this direction as well as the adverse public image retarded the expected growth patterns for PVC and also led to its withdrawal from certain applications. However, with the containment of the hazards associated with the monomer, the natural growth patterns for PVC were resumed within a few years. This growth has occurred in spite of continuing questions on health and safety aspects such as the toxicity of plasticisers such as phthalates and of stabilisers, and the nature of products produced during processing, thermal decomposition and composting of a halogen-containing polymer.

12.2 PREPARATION OF VINYL CHLORIDE

There are three general methods of interest for the preparation of vinyl chloride, one for laboratory synthesis and the other two for commercial production.⁷

Vinyl chloride (a gas boiling at -14°C) is most conveniently prepared in the laboratory by the addition of ethylene dichloride (1,2-dichloroethane) in drops on to a warm 10% solution of sodium hydroxide or potassium hydroxide in a 1:1 ethyl alcohol–water mixture (Figure 12.1). At one time this method was of commercial interest. It does, however, suffer from the disadvantage that half the chlorine of the ethylene dichloride is consumed in the manufacture of common salt.

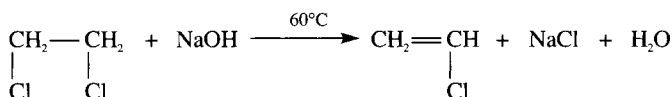


Figure 12.1

The major method for preparing the monomer commercially since the early 1960s has been the so-called *balanced process* from ethylene. In the first stage of the reaction, 1,2-dichloroethane is prepared by reacting ethylene with chlorine in either the vapour or the liquid phase (Figure 12.2). In a typical liquid phase



Figure 12.2

process, reaction would be in the range $30\text{--}50^{\circ}\text{C}$ in the presence of an iron chloride catalyst. The crude 1,2-dichloroethane is washed with sodium hydroxide solution and then purified and dried by distillation. The dry 1,2-dichloroethane is then cracked to give vinyl chloride (Figure 12.3). This is achieved by vaporising

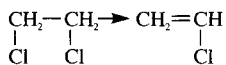


Figure 12.3

the 1,2-dichloroethane and feeding through a series of tubes sited in a furnace. By adjustment of the temperature (in the range $300\text{--}600^{\circ}\text{C}$ and typically about 530°C) and the residence time (approx. 20 s) a 40–65% conversion may be obtained. The reaction product is then quenched and the monomer isolated by fractional distillation. The particular feature of the balanced process is that the hydrogen chloride formed during the dehydrochlorination stage and recovered during the purification is then used to generate more 1,2-dichloroethane by an *oxychlorination reaction*. In this process ethylene and hydrogen chloride gases are passed, with air, over a finely divided bed of copper(II) chloride supported on alumina. The reaction may be represented by the equation in Figure 12.4.

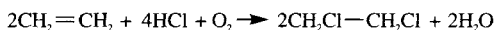
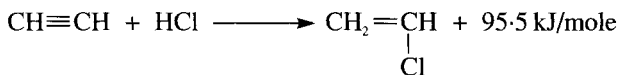
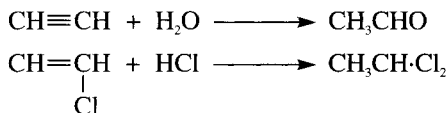


Figure 12.4

For many years a major route to the production of vinyl chloride was the addition of hydrochloric acid to acetylene (*Figure 12.5*). The acetylene is usually prepared by addition of water to calcium carbide, which itself is prepared by heating together coke and lime. To remove impurities such as water, arsine and phosphine the acetylene may be compressed to 15 lbf/in² (approx. 100 kPa), passed through a scrubbing tower and chilled to -10°C to remove some of the water present and then scrubbed with concentrated sulphuric acid.

*Figure 12.5*

Hydrochloric acid may conveniently be prepared by combustion of hydrogen with chlorine. In a typical process dry hydrogen chloride is passed into a vapour blender to be mixed with an equimolar proportion of dry acetylene. The presence of chlorine may cause an explosion and thus a device is used to detect any sudden rise in temperature. In such circumstances the hydrogen chloride is automatically diverted to the atmosphere. The mixture of gases is then led to a multi-tubular reactor, each tube of which is packed with a mercuric chloride catalyst on an activated carbon support. The reaction is initiated by heat but once it has started cooling has to be applied to control the highly exothermic reaction at about 90–100°C. In addition to the main reaction the side reactions shown in *Figure 12.6* may occur.

*Figure 12.6*

The gases from the reactor are then cooled and subjected to a caustic wash to remove unreacted hydrogen chloride. This is then followed by a methanol wash to remove water introduced during the caustic wash. A final purification to remove aldehydes and ethylidene dichloride, formed during side reactions, is then carried out by low-temperature fractionation. The resulting pure vinyl chloride is then stored under nitrogen in a stainless steel tank.

In one process the ethylene and acetylene routes have been combined. A mixed feedstock of acetylene and ethylene together with diluents such as carbon monoxide, hydrogen and methane, all obtained by pyrolysis of a naphtha fraction, is employed. The only pyrolysis products that need to be removed are higher unsaturated hydrocarbons. The mixed stream is first sent to a hydrochlorination reactor where the acetylene present reacts to give vinyl chloride. The vinyl chloride is washed out of the stream and the remainder of the feed gas, consisting of ethylene and inert diluents, is passed to a dichloroethane reactor. The chlorine-ethylene reaction is carried out in the vapour phase over a fixed-bed catalyst. The resulting dichloroethane (ethylene dichloride) is then cracked to give vinyl chloride and hydrochloric acid, these being individually isolated by distillation processes.

Potential advantages of this route are the ability to use a mixed feedstock and the fact that hydrochloric acid formed in one part of the process may be used in the other part.

12.3 POLYMERISATION

In commercial practice vinyl chloride is polymerised by free radical mechanisms in bulk, in emulsion and in suspension, the latter process dominating with about 85% of the market. Today emulsion polymers are mainly used for paste applications and the bulk polymerised material for UPVC applications. The general kinetics are influenced by a significant chain transfer to monomer reaction (see Chapter 2), which increases more rapidly with temperature than the chain propagation reaction. In consequence the molecular weight of the resultant PVC is determined by the polymerisation temperature and little affected by the initiator concentration. In practice, polymerisations are usually carried out in the temperature range 50–75°C although this range may be extended upwards by the use of chain transfer agents.

Bulk polymerisation processes have been known for many years but until the mid-1960s the only commercial process was one operated by Pechiney-St Gobain in France. This process was a one-stage process and according to one patent example⁸ vinyl chloride was polymerised with 0.8% of its own weight of benzoyl peroxide in a rotating cylinder containing steel balls for 17 hours at 58°C.

Bulk polymerisation is heterogeneous since the polymer is insoluble in the monomer. The reaction is autocatalysed by the presence of solid polymer whilst the concentration of initiator has little effect on the molecular weight. This is believed to be due to the overriding effect of monomer transfer reactions on the chain length. As in all vinyl chloride polymerisation oxygen has a profound inhibiting effect.

One function of the steel balls was to facilitate the removal of heat but difficulties in control, particularly of particle size of the polymer which was ground by the tumbling of the balls, limited the attraction of the process. This solution changed quite considerably with the development by Pechiney-St Gobain (now Rhône-Poulenc) of a two-stage process. The first stage is carried out as a liquid with up to about 15% conversion whilst the second stage carried out as a powder takes the conversion to 80–85%. The presence of two stages allows considerable flexibility for the process, particle characteristics usually being determined by the operation of the first stage and average molecular weight by the second stage. By early 1970s at least 20 companies throughout the world had taken out licences to operate this process.

Suspension polymerisations are generally easier to control and there is little, if any, loss in clarity or electrical insulation properties. Particle shape, size and size distribution may be controlled by varying the dispersing systems and the rate of stirring. A typical polymerisation vessel for suspension polymerisation is shown in *Figure 12.7*. It should, however, be noted that many more modern reactors are fitted with shorter bottom-entry agitators. Autoclave sizes of 40–80m³ (1400–2800 ft³) are used by most manufacturers although autoclaves as large as 200m³ are in commercial use.

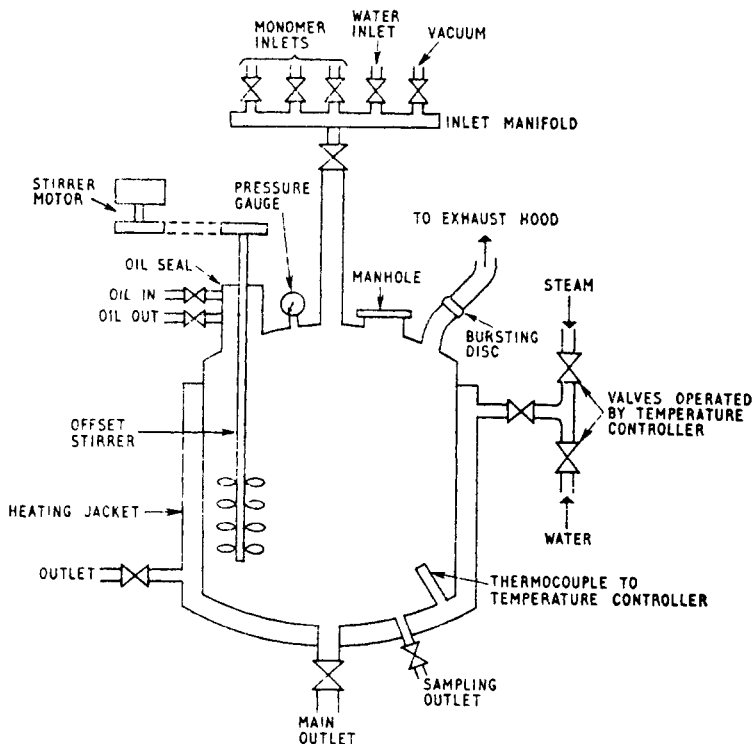


Figure 12.7. Typical polymerisation vessel suitable for suspension or emulsion polymerisation of vinyl chloride

A typical charge would be:

Monomer	Vinyl chloride	30–50 parts
Dispersing agent	Gelatine	0.001 parts
Modifier	Trichlorethylene	0.1 parts
Initiator	Caproyl peroxide	0.001 parts
	Demineralised water	90 parts

In addition, buffer salts such as disodium hydrogen phosphate may be used to prevent the pH of the aqueous phase falling during polymerisation. Small amounts of an anti-foam agent may be employed to reduce frothing when discharging from the vessel at the end of the polymerisation process.

The trichlorethylene is a solvent transfer agent used to control molecular weight.

Over the past years considerable attention has been paid to the dispersing system since this controls the porosity of the particle. This is important both to ensure quick removal of vinyl chloride monomer after polymerisation and also to achieve easy processing and dry blendable polymers. Amongst materials quoted as protective colloids are vinyl acetate–maleic anhydride copolymers, fatty acid esters of glycerol, ethylene glycol and pentaerythritol, and, more recently, mixed cellulose ethers and partially hydrolysed poly(vinyl acetate). Much recent emphasis has been on mixed systems.

There has also been a trend in recent years to the use of free-radical initiators that decompose more rapidly than the traditional initiators such as caproyl and lauryl peroxides. Currently used initiators include peroxydicarbonates, t-butylperpivalate, azobis-(2,4-dimethylvaleronitrile) and acetyl cyclohexylsulphonyl peroxide.

Using the above recipe the dispersing agent is first dissolved in a known weight of water, and added to the kettle. The rest of the water, the peroxide and the modifier are then added to the kettle which is sealed down and evacuated to 28 inHg. The vinyl chloride is then drawn in from the weighing vessel. In some cases pressurised oxygen-free nitrogen may be used to force all the monomer into the vessel. This is then closed and heated to about 50°C. Through the rise in temperature a pressure of about 100 lbf/in² (0.7 MPa) will be developed in the reactor. As reaction proceeds the temperature is maintained until the pressure starts to fall, due to consumption of the monomer. When the pressure has dropped to 10–20 lbf/in² (0.07–0.13 MPa) excess monomer is removed, either in the autoclave, for example by a steam stripping process, or outside the autoclave in a column in which the slurry of polymer particles in water passes through a counter current of steam. The technology of this stage of the process has been subject to considerable development since the discovery of the toxicity hazards associated with vinyl chloride monomer in the early 1970s. The slurry is then de-watered, dried, packed and stored. The product is checked for particle size by sieve analysis, for colour, contamination and for viscosity in a dilute solution. Other tests may be carried out on electrical insulation and paste grades.

Because of its low water solubility (0.09% at 20°C) vinyl chloride may be polymerised in emulsion. Using secondary alkyl sulphonates or alkali salts of alkyl sulphates as emulsifiers rapid polymerisation can occur in oxygen-free environments. The use of 'redox' initiating systems has made possible rapid reaction at temperatures as low as 20°C whilst in recent laboratory work sub-zero temperatures have been used. As explained in Chapter 2 water-soluble initiators are employed. Ammonium persulphate, potassium persulphate and hydrogen peroxide are typical initiators whilst bisulphites and ferrous salts are useful reducing agents. Modifiers are often employed to control the molecular weight. Reaction times are commonly of the order of 1–2 hours. After polymerisation the particles are normally spray dried. There will thus be residual emulsifier which will adversely affect clarity and electrical insulation properties. Some improvement is, however, obtained using special washing operations.

Vinyl chloride is occasionally copolymerised with monomers, notably with vinylidene chloride, vinyl acetate and propylene. Where vinylidene chloride is used as comonomer there is a reduction in the overall polymerisation rate. In addition, since vinylidene chloride radicals add preferentially to a vinylidene chloride molecule during chain growth a heterogenous product is formed. This can be overcome by drip feeding the vinylidene chloride through the reaction at such a rate as to give a constant monomer composition. In the case of vinyl chloride–vinyl acetate copolymerisations the vinyl chloride is consumed preferentially and this will, without special steps being taken, also lead to some heterogeneity.

12.4 STRUCTURE OF POLY(VINYL CHLORIDE)

It is useful to compare the structures of PVC and polyethylene (*Figure 12.8*) since this enables predictions of the properties of the former to be made. Both materials are linear polymers and substantially thermoplastic. The presence of the

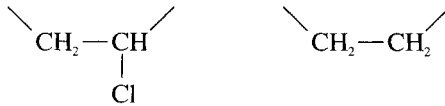


Figure 12.8

chlorine atom causes an increase in the inter chain attraction and hence an increase in the hardness and stiffness of the polymer. PVC is also more polar than polyethylene because of the C—Cl dipole. Thus PVC has a higher dielectric constant and power factor than polyethylene, although at temperatures below the glass transition temperature (+80°C) the power factor is still comparatively low (0.01–0.05 at 60Hz) because of the immobility of the dipole.

The solubility parameter of PVC is about $19.4 \text{ MPa}^{1/2}$ and the polymer is thus resistant to non-polar solvents which have a lower solubility parameter. In fact it has very limited solubility, the only solvents that are effective being those which appear to be capable of some form of interaction with the polymer. It is suggested⁹ that PVC is capable of acting as a weak proton donor and thus effective solvents are weak proton acceptors. These include cyclohexanone ($\delta = 20.2 \text{ MPa}^{1/2}$) and tetrahydrofuran ($\delta = 19.4 \text{ MPa}^{1/2}$). There are many materials that are suitable plasticisers for PVC. They have similar solubility parameters to PVC and are also weak proton acceptors. These are of too high a molecular weight and too large a molecular size to dissolve the polymer at room temperature but they may be incorporated by mixing at elevated temperatures to give mixtures stable at room temperature. The presence of chlorine in large quantities in the polymer renders it flame retarding. The presence of plasticisers, however, reduces the resistance to burning.

Much work has been carried out in order to elucidate the molecular structure of poly(vinyl chloride). In 1939, Marvel, Sample and Roy¹⁰ dechlorinated PVC with zinc dust to give linked cyclic structures (Figure 12.9).

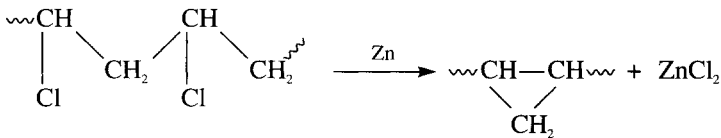


Figure 12.9

By noting the amount of chlorine that could be removed in this way they were able to determine whether the polymer was formed by head-to-tail linkage (Figure 12.10(a)) or head-head and tail-tail linkage (Figure 12.10(b)).

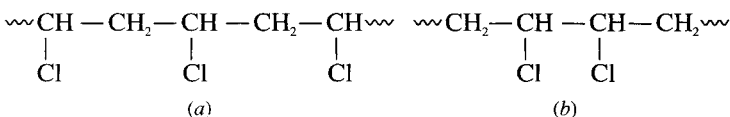


Figure 12.10

It would be expected that if linkage was by the latter mechanism complete dechlorination would occur, the adjacent chlorine atoms being removed together. In the case of head-tail polymerisation it would be expected that because the reaction does not occur in steps along the chain, but at random, a number of unreacted chlorine atoms would become isolated and thus complete dechlorination could not occur (Figure 12.11).

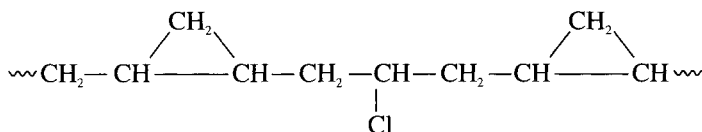


Figure 12.11

It was found that the amount of chlorine that could be removed (84–87%) was in close agreement to that predicted by Flory¹¹ on statistical grounds for structure Figure 12.10(a). It is of interest to note that similar statistical calculations are of relevance in the cyclisation of natural rubber and in the formation of the poly(vinyl acetals) and ketals from poly(vinyl alcohol). Since the classical work of Marvel it has been shown by diverse techniques that head-to-tail structures are almost invariably formed in addition polymerisations.

X-ray studies indicate that the vinyl chloride polymer as normally prepared in commercial processes is substantially amorphous although some small amount of crystallinity (about 5% as measured by X-ray diffraction methods) is present. It has been reported by Fuller¹² in 1940 and Natta and Carradini¹³ in 1956 that examination of the crystalline zones indicates a repeat distance of 5.1 Å which is consistent with a syndiotactic (i.e. alternating) structure. Later studies using NMR techniques indicate that conventional PVC is about 55% syndiotactic and the rest largely atactic in structure.

Over the years there has been considerable controversy over the nature and extent of branching in poly(vinyl chloride). At one time it was believed that in normal commercial PVC there might be up to 16 long chain branches per molecule. Recent studies, however, suggest that the existence of more than one long branch per molecule is not very probable. There may, however, be a few (usually <10) short branches per molecule arising from a back-biting mechanism analogous to that described with low-density polyethylene in Chapter 10.

It is of interest to note that free-radical polymerisation at lower temperatures, e.g. at -40°C using γ -radiation or by the use of highly active initiators such as the alkylboranes, increasingly favours the formation of syndiotactic structures. These more regular polymers also show freedom from branching. The greater regularity and absence of branching result in crystalline polymers with decreased solubility in cyclohexanone. The polymers also have, as would be expected, greater density and a high softening point. Such polymers, however, are more difficult to process and the products generally more brittle. It has, however, been claimed that through careful control of molecular weight and crystallinity useful materials can be obtained.

PVC has a rather limited thermal stability. This is rather surprising since it is known that low molecular weight materials containing similar structures are far more stable. It would thus appear that this instability is due to imperfections or weak points in the structure at which degradation can commence. The

mechanism of degradation is far from being well understood and since the various theories do not as yet contribute to the technology of PVC they will not be dealt with here. The technological aspects of degradation are, however, considered in Section 12.5.1, dealing with stabilisers, and also in the processing sections.

12.4.1 Characterisation of Commercial Polymers

As indicated in the previous section, commercial PVC polymers are largely amorphous, slightly branched molecules with the monomer residues arranged in a head-to-tail sequence. Individual grades of materials do, however, differ in average molecular weight, molecular weight distribution, particle shape, size and size distribution, and the presence of impurities. Some grades may also contain small quantities of comonomer residues.

The molecular weights for the bulk of commercial polymers are in the range $\bar{M}_w = 100\,000\text{--}200\,000$, $\bar{M}_n = 45\,000\text{--}64\,000$, although values may be as low as 40 000 and as high as 480 000 for the weight average molecular weight. The ratio \bar{M}_w/\bar{M}_n is usually about 2 for the bulk of commercial material although it may increase with the higher molecular weight grades.

For commercial purposes the molecular weight is usually characterised from measurements of the viscosity of dilute solutions. It has been shown that, for dilute solutions, the relation between the viscosity and the molecular weight (in this case the 'viscosity average' molecular weight) may be given by the relationship

$$[\eta] = KM^a$$

Where K and a are constants

M is the molecular weight

$[\eta]$ is the intrinsic viscosity or limiting viscosity number

This is obtained by plotting $(\eta - \eta_0)/\eta_0 c$ against concentration c and noting its extrapolated value at infinite dilution. In this case η is the viscosity of the polymer solution and η_0 the viscosity of the pure solvent. By correlating with results obtained by direct techniques (e.g. by osmosis) it is possible to give values for K for a given polymer and hence subsequently use the relationship to obtain the molecular weight. In practice it has been common to characterise the molecular weight of a PVC polymer by its Fikentscher K -value rather than to quote an actual figure for molecular weight. This is *not* the same K as given in the above equation but is obtained from the following relationship and is a measure of the molecular weight, the lower the K -value the lower the molecular weight.

$$\log_{10} \eta_{\text{rel}} = \left[\left(\frac{75 K^2 \times 10^{-6}}{1 + 1.5 Kc \times 10^{-3}} \right) + (K \times 10^{-3}) \right] c$$

where $\eta_{\text{rel}} = \text{relative viscosity} = \eta/\eta_0$, $K = K\text{-value}$ and $c = \text{concentration in g/100 ml}$.

The K -value is, however, rather dependent on the method of measurement and in the past different suppliers have used different solvents and different polymer concentrations. For this reason it is now becoming more common to quote the

ISO viscosity number. Table 12.1 compares typical correlations between number and weight average molecular weights with ISO numbers, *K*-values and ASTM viscosity measurements.

Most general purpose polymers for use in plasticised PVC compounds have ISO numbers of about 125 although polymers with values as high as 185 have been produced. Paste-making polymers tend once again to have ISO values of about 125 or perhaps a little higher. Because of processing problems the polymers for unplasticised PVC compounds have lower molecular weights, typical ISO numbers being 105 for pipe, 85–95 for rigid sheet and as low as 70 for injection moulding compounds. In general it may be said that in the above molecular weight range an increase in molecular weight leads to a small but nevertheless important improvement in mechanical properties such as tensile strength but also to a very large increase in melt viscosity. There is in fact some evidence that in certain circumstances melt viscosity is more dependent on \bar{M}_w than by the usual 3.4–3.5 exponent mentioned in Chapter 8.

The properties of PVC may also be expected to depend on the molecular weight distribution. Most commercial polymers, however, appear to have similar values for \bar{M}_w/\bar{M}_n and in any case there is little published information on effects of altering the parameter. It is perhaps rather surprising that there appears to be little work reported on the effect of blends of polymers of differing molecular weight on mechanical and rheological properties.

With commercial polymers the major differences are, perhaps, not differences in molecular structure but in the characteristics of the particle, i.e. its shape, size distribution and porosity. Such differences will considerably affect the processing behaviour of a polymer.

In the early days of the commercial development of PVC, emulsion polymers were preferred for general purpose applications. This was because these materials exist in the form of the fine primary particles of diameter of the order of 0.1–1.0 μm , which in the case of some commercial grades aggregate into hollow secondary particles or cenospheres with diameters of 30–100 μm . These emulsion polymer particles have a high surface/volume ratio and fluxing and gelation with plasticisers is rapid. The use of such polymers was, however, restricted because of the presence of large quantities of soaps and other additives necessary to emulsion polymerisation which adversely affect clarity and electrical insulation properties.

Table 12.1 Molecular weight characterisation of PVC¹⁴

Average molecular weight		ISO/R174–1961(E): viscosity number	<i>K</i> -value			ASTM D1243–58T	
Weight	Number		0.5% in ethylene dichloride	1% in cyclohexanone	0.4% in nitrobenzene	Method A: inherent viscosity	Method B: specific viscosity
54 000	26 000	57	45	47	52	0.49	0.19
70 000	36 000	70	50	54	57.5	0.62	0.24
100 000	45 500	87	55	60	62.5	0.75	0.3
140 000	55 000	105	60	65	68	0.88	0.36
200 000	64 000	125	65	70	70.5	1.01	0.41
260 000	73 000	145	70	74	78	1.13	0.47
340 000	82 000	165	75			1.26	0.54

Early suspension polymers, although less contaminated, were supplied as more or less spherical particles with a diameter in the range 50–100 μm . Such materials had a much lower surface/volume ratio than the emulsion polymers and, being of low porosity, the materials were much slower in their gelation with plasticisers. The obvious requirement was to produce more porous particles and these became available about 1950 as easy-processing resins.

Considerable effort has been expended in order to control porosity, surface area and diffusivity of PVC particles and this has led to great improvements over the years in the processability of PVC.

Later work has thrown further light on particle development during polymerisation. It appears that with both mass and suspension polymers, small particles (approx. 10 nm dia.) are formed at less than 0.1% conversion and by about 3% conversion they grow into microgranules of about 1 μm diameter. These in turn aggregate to particles of 200–300 μm diameter. Mass polymer aggregates seem to be more open and sponge-like than typical suspension polymer particles, which also show a characteristic 'skin'. It is also stated that the particle sizes of mass polymers are more narrowly distributed and give higher bulk density for a given porosity, which is a generally desirable processing feature.

If PVC polymer particles are mixed, at room temperature, with plasticisers the immediate product may take one of two forms. If there is insufficient plasticiser to fill all the gaps between the particle a 'mush' will be produced. If all the voids are filled then the particles will become suspended in the plasticiser and a paste will be formed. In the case of conventional granular polymer, or with emulsion polymer cenospheres, the particles are too large to remain in suspension and will settle out. Therefore compounds used in 'paste-processes' must use polymers with a small particle size. On the other hand there is a lower limit to this, since small particles will have a very high surface/volume ratio and measurable plasticiser absorption will occur at room temperature to give a paste whose viscosity will increase unduly with time. As a consequence paste polymers have an average particle size of about 0.2–1.5 μm .

It is found that the viscosity of a paste made from a fixed polymer/plasticiser ratio depends to a great extent on the particle size and size distribution. In essence, in order to obtain a low-viscosity paste, the less the amount of plasticiser required to fill the voids between particles the better. Any additional plasticiser present is then available to act as a lubricant for the particles, facilitating their general mobility in suspension. Thus in general a paste polymer in which the pastes have a wide particle size distribution (but within the limit set by problems of plasticiser absorption and settling out, so that particles pack efficiently, will

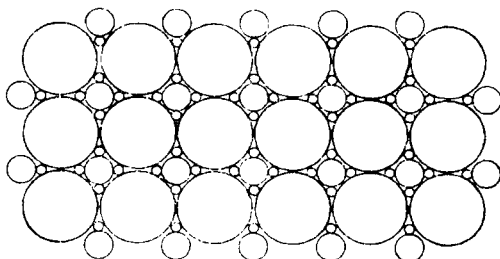


Figure 12.12. PVC paste polymer particles with distribution of size-efficient packing

give lower viscosity pastes than those of constant particle size. The polymer particles shown in *Figure 12.12* pack more closely and with less voids than those in *Figure 12.13* and hence give a lower viscosity polymer.

The success of 'filler' polymers used in increasing quantities in PVC technology paste can be considered as an extension of this principle. These filler polymers are made by suspension (granular, dispersion) polymerisation and by

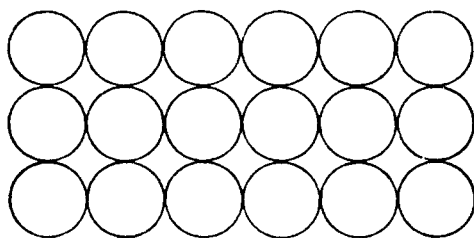


Figure 12.13. PVC paste polymer with homogeneous particle size-less efficient packing

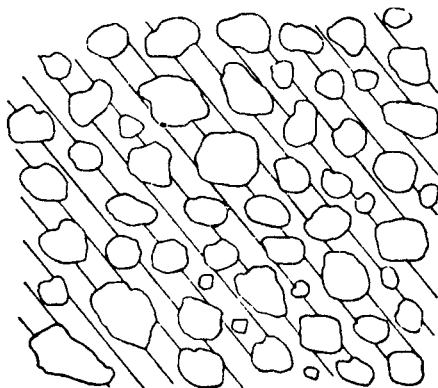


Figure 12.14. Paste polymer suspended in plasticiser

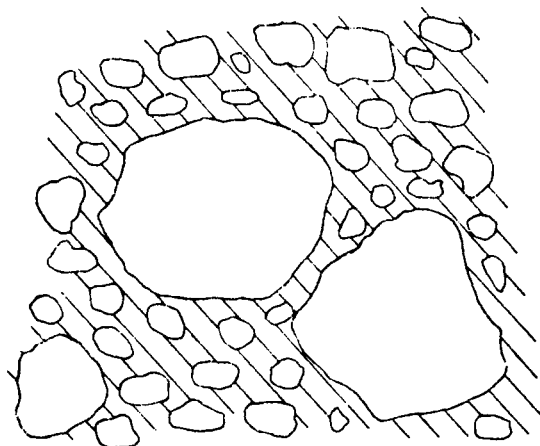


Figure 12.15. PVC containing filler polymer. Less plasticiser required to fill voids in unit volume

themselves the particles are too large to make stable pastes. However, in the presence of paste-polymer particles they remain in stable suspension. Being very much larger than paste-polymer particles they take up comparatively large volumes in which no plasticiser is required whatsoever. This is shown in *Figures 12.14 and 12.15* where it is seen that the replacement in space of a mixture of paste-polymer particles and plasticiser by a large granular polymer particle releases plasticiser for use as lubricant, i.e. a viscosity depressant.

There is a further complication with paste polymers in that paste behaviour is non-Newtonian. The viscosities of paste are dependent on the shear rate and on the time of shear. The main possibilities are shown in *Figures 12.16 and 12.17*. Thus a paste viscosity may increase with shear rate (dilatancy) or decrease (shear thinning or pseudoplasticity). Some pastes may show dilatant tendencies over one range of shear rates but be shear thinning over another range. Such behaviour has a profound effect on such processes as spreading. The viscosities may also decrease with time of stirring (thixotropy) or increase with it (rheopexy). Thus particular care must be taken in measuring rheological properties.

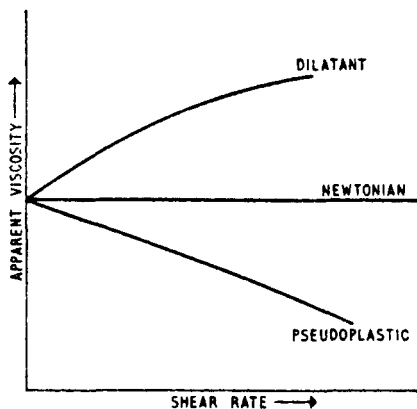


Figure 12.16. Classification of liquids according to dependence of apparent viscosity on shear rate

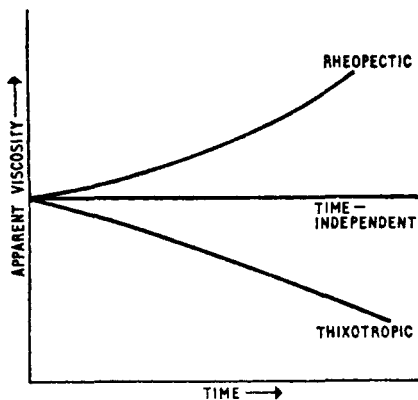


Figure 12.17. Classification of liquids according to dependence of apparent viscosity on time (constant shear rate)

A certain amount of correlation between shear rate dependence and particle characteristics is now possible. It has been observed that spherical particles giving a high degree of packing are closest to Newtonian liquids in their behaviour. Very coarse lumpy uneven granules do not slide past each other easily in pastes and tend to become more entangled as shear rate increases. Such pastes commonly show dilatant behaviour. It has also been found that spherical particles of homogeneous size shear thinning pastes. This may be due to the fact that these particles tend to aggregate (an observed fact) at rest whilst shearing causes disaggregation and hence easier movement of particles.

In addition to homopolymers of varying molecular and particle structure, copolymers are also available commercially in which vinyl chloride is the principal monomer. Comonomers used commercially include vinyl acetate, vinylidene chloride, propylene, acrylonitrile, vinyl isobutyl ether, and maleic, fumaric and acrylic esters. Of these the first three only are of importance to the plastics industry. The main function of introducing comonomer is to reduce the regularity of the polymer structure and thus lower the interchain forces. The polymers may therefore be processed at much lower temperatures and are useful in the manufacture of gramophone records and flooring compositions.

12.5 COMPOUNDING INGREDIENTS

In the massive form poly(vinyl chloride) is a colourless rigid material with limited heat stability and with a tendency to adhere to metallic surfaces when heated. For these, and other, reasons it is necessary to compound the polymer with other ingredients to make useful plastics materials. By such means it is possible to produce a wide range of products, including rigid piping and soft elastic cellular materials.

A PVC compound may contain the following ingredients:

- | | |
|-------------------|--------------------------------|
| (1) Polymer. | (6) Fillers. |
| (2) Stabilisers. | (7) Pigments. |
| (3) Plasticisers. | (8) Polymeric processing aids. |
| (4) Extenders. | (9) Impact modifiers. |
| (5) Lubricants. | |

Other miscellaneous materials also used occasionally include fire retardants, optical bleaches and blowing agents.

12.5.1 Stabilisers

It is an observed fact that heating PVC at temperatures above 70°C has a number of adverse effects on the properties of the polymer. At processing temperatures used in practice (150–200°C) sufficient degradation may take place during standard processing operations to render the product useless. It has been found that incorporation of certain materials known as stabilisers retards or moderates the degradation reaction so that useful processed materials may be obtained.

There is a great deal of uncertainty as to the mechanism of PVC degradation but certain facts have emerged. Firstly dehydrochlorination occurs at an early stage in the degradation process. There is some infrared evidence that as hydrogen chloride is removed polyene structures are formed (*Figure 12.18*).

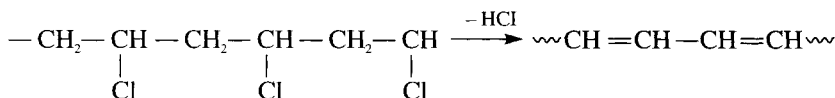


Figure 12.18

There has been much argument for many years as to whether the liberated hydrogen chloride accelerated further decomposition. This theory of auto-catalysis has now swung back into favour. A second fact that has emerged is that oxygen has an effect on the reaction. It is believed that oxygen can cause both scission and cross-linking reactions whilst it has also been observed that the presence of oxygen accelerates colour formation.

The first physical manifestation of degradation, used in the widest sense, is a change in the colour of PVC. Initially water-white, on heating it will turn, in sequence, pale yellow, orange, brown and black. Further degradation causes adverse changes in mechanical and electrical properties. For most commercial purposes, the 'end-point' is in fact the formation of colour. With some applications some colour change can be acceptable; in other cases little or no change may be tolerated. Thus in practice changes in colour on heating provide a simple and readily obtainable criterion of degradation.

Many attempts have been made to correlate rate of colour formation with rate of hydrogen chloride evolution in polymer and compounded products but such attempts have not been successful. Thus for practical purposes a stabiliser is most conveniently defined as material that retards the formation of colour in unpigmented PVC compounds. Beyond this the situation becomes complex. Some stabilisers increase the rate of dehydrochlorination, while some decrease it. With some stabilisers the development of colour occurs slowly and steadily whilst with others formation of deep colours may take place quite suddenly after a prolonged induction time. Some stabilisers are synergistic. That is x parts of one stabiliser with y parts of a second stabiliser are often much more effective than $x+y$ parts of either used on its own. Some stabilisers are more effective in the presence of oxygen, and some are less effective. Some systems are highly effective in one grade of PVC polymer but only moderate in another. The presence of other additives such as plasticisers and fillers can also strongly influence the efficiency of a stabiliser. Thus phosphates and chlorinated extenders frequently reduce the stability of a compound.

The choice of a stabiliser thus becomes an empirical yet systematic process. The following factors are the most important which must be considered:

- (1) The grade of polymer used.
- (2) The nature of other ingredients present.
- (3) The cost of stabiliser required to give adequate stabilisation for the processing and anticipated service life of the compound.
- (4) The clarity required of the compound.
- (5) Toxicity.
- (6) The effect on lubrication, printing, heat sealing and plate-out.

Many tests have been devised for assessing the effect of a stabiliser in a given compound. That most successfully employed is to prepare a moulded sheet of a compound under strictly controlled conditions and to heat samples in a ventilated oven for various periods of time at various elevated temperatures. Small pieces

of the samples are then bound on to cards giving data on the processing and heating conditions. These are then available for visual comparison of colour forming. For technical reports it is common to give the colour a numerical rating. Thus water-white samples can be given a number 0, a pale yellow 1, an orange 2, a brown 3 and a black sample 4 and these numbers can be tabulated in the report. It is, however, common experience that such a technique is far less effective in imparting information than the use of well-displayed samples.

In some laboratories samples are heated for prolonged periods in a press at a suitably elevated temperature. Such results may frequently fail to correlate with oven-heated samples since oxygen is largely excluded from the samples.

As already indicated, the measurement of dehydrochlorination rates is not a practical way of assessing the effect of a stabiliser. Thus the congo red test sometimes specified in standards, in which a piece of congo red paper is held in a test tube above a quantity of heated PVC and the time taken for the paper to turn blue due to the evolution of a certain amount of hydrogen chloride, cannot be considered as being of much value.

Many stabilisers are also useful in improving the resistance of PVC to weathering, particularly against degradation by ultraviolet radiation. This is an important consideration in building applications and other uses which involve outdoor exposure. The efficiency of stabilisers in improving resistance of PVC compounds to degradation is best measured by lengthy outdoor weathering tests. Accelerated weathering tests using xenon lamps or carbon arcs have not proved to be reliable even for purposes of comparison.

The most important class of stabilisers are the lead compounds which form lead chloride on reaction with hydrogen chloride evolved during decomposition. As a class the lead compounds give rise to products of varying opacity, are toxic and turn black in the presence of certain sulphur-containing compounds but are good heat stabilisers.

Of these materials *basic lead carbonate (white lead)* has been, and probably still is, the most important stabiliser for PVC. It may be considered as typical of the lead compounds and has a low weight cost. It is appreciated that weight cost is not, however, the best criterion to be considered in assessing the economics of a stabiliser. Far more relevant is the cost required to stabilise the material to an acceptable level for the processing and service conditions involved. One additional disadvantage of the lead carbonate is that it may decompose with the evolution of carbon dioxide at the higher range of processing conditions, thus leading to a porous product.

For this reason *tribasic lead sulphate*, a good heat stabiliser which gives polymer compounds with better electrical insulation properties than lead carbonate, has increased in popularity in recent years at the expense of white lead. Its weight cost is somewhat higher than that of lead carbonate but less than most other stabilisers. This material is used widely in rigid compounds, in electrical insulation compounds and in general purpose formulations.

Other lead stabilisers are of much specific applications. *Dibasic lead phosphite* gives compounds of good light stability but because of its higher cost compared with the sulphate and the carbonate its use is now restricted. In spite of its even greater weight cost *dibasic lead phthalate* finds a variety of specialised applications. Because it is an excellent heat stabiliser it is used in heat-resistant insulation compounds (for example in 105°C wire). It is also used in high-fidelity gramophone records, in PVC coatings for steel which contain polymerisable plasticisers and in expanded PVC formulations which use azodicarbonamide as

a blowing agent. In this latter application the phthalate stabiliser also acts as a 'kicker' to accelerate the decomposition of the blowing agent.

Normal and dibasic lead stearate have a stabilising effect but their main uses are as lubricants (see section 12.5.4). *Lead silicate* is sometimes used in leathercloth formulations but is today of little importance. Other lead compounds now of negligible importance are coprecipitated *lead orthosilicates* and *lead salicylate*.

The use of lead compounds as stabilisers has been subject to regulation and legislation arising from their toxicity. Whilst legislation varies from country to country, lead stabilisers are not generally allowed in food packaging compounds but in most countries are allowed for use, under certain conditions, in pipes for conveying drinking water. Where lead stabilisers continue to be used there has commonly been a reduction in the level of use in a particular compound. The resulting lower level of protection may cause problems in the use of scrap and in general polymer re-work operations.

Whilst lead compounds have been, and still are, the most important class of stabiliser for PVC the metallic soaps or salts have steadily increased in their importance and they are now widely used. At one time a wide range of *metal stearates*, *ricinoleates*, *palmitates* and *octoates* were offered as possible stabilisers and the efficiency of many of them has been examined. Today only the compounds of *cadmium*, *barium*, *calcium* and *zinc* are prominent as PVC stabilisers.

The most important of these are *cadmium-barium* systems. These first became significant when it was discovered that stabilisers often behaved synergistically. Of the many stabilising systems investigated, cadmium-barium systems gave considerable promise. The first of these systems to be used successfully were based on cadmium octoate in conjunction with barium ricinoleate. Alone the cadmium salt gave good initial colour but turned black after a relatively short heating period. The use of the barium soap in conjunction with the cadmium salt extended this period. The addition of antioxidants such as *trisnonyl phenyl phosphite* was found to greatly increase the heat stability whilst the further addition of *epoxidised oils* gave even better results. It was, however, found that on exposure to light an interaction took place between the ricinoleate and the epoxidised oil, with the formation of products incompatible with the PVC. These products exuded and caused tackiness of the compound and problems in calendaring. Replacement of the octoate and ricinoleate with *laurates* avoided the undesirable interaction but instead led to plate-out, difficulties in heat sealing and printing and compounds yellowish in colour and lacking in clarity. However, the laurates continue to find some limited use in PVC compounding.

Somewhat better results have been obtained with *octoates* and *benzoates* but these still lead to some plate-out. The use of liquid *cadmium-barium phenates* has today largely resolved the problem of plate-out whilst the addition of a trace of a zinc salt helps to improve the colour. Greater clarity may often be obtained by the addition of a trace of stearic acid or stearyl alcohol. Thus a modern so-called cadmium-barium stabilising system may contain a large number of components. A typical 'packaged' stabiliser could have the following composition:

Cadmium-barium phenate	2-3 parts
Epoxidised oils	3-5 parts
Stearic acid	0.5-1 part
Trisnonyl phenyl phosphite	1 part
Zinc octoate	0.5 parts

It appears that the zinc salt functions by preferentially reacting with sulphur to form white zinc sulphide rather than coloured cadmium sulphide and thus helps to reduce colour in the compound.

The use of cadmium stabilisers, as with the lead compounds, gives rise to some concern because of possible toxicity and environmental problems. This has led to large efforts to produce non-toxic systems. Mixtures of calcium and zinc soaps, sometimes in conjunction with epoxidised oils, have been used for many years but these soap-based materials are both less powerful than the Cd–Ba complexes and also fail to give glass-clear products. Calcium/zinc non-soap liquid compounds, and to some extent, strontium/zinc compounds have found increasing use in recent years in efforts to cope with this problem. For flooring compositions, magnesium–barium, calcium–barium and copper–barium compounds are sometimes used in conjunction with pentaerythritol. The latter material has the function of chelating iron present in the asbestos and thus reducing colour formation.

Another group of stabilisers are the *organo-tin compounds*. These materials found early applications because of their resistance to sulphur and because they can yield crystal-clear compounds. The older organo-tin compounds such as *dibutyltin dilaurate*, however, give only limited heat stability and problems may arise with high processing temperatures. *Dibutyltin maleate* imparts somewhat greater heat resistance. The availability of a number of sulphur-containing organo-tin compounds, such as *dibutyltin di-iso-octylthioglycollate*, which impart excellent heat resistance and clarity, has to some extent increased the scope of organo-tin compounds. They are, however, more expensive in terms of weight cost. It should be noted that the sulphur-containing organo-tin compounds should not be used where lead derivatives are present in the PVC compound since cross-staining will occur to form black lead sulphide. Such lead compounds could be present as added stabiliser or even because the polymer on manufacture was washed with water fed through lead pipes.

The butyltins generally show a level of toxicity that prevents them being used in application in contact with foodstuffs. On the other hand the octyltin materials such as dioctyltin dilaurate and dioctyltin octylthioglycollate are much better in this respect and many of them meet stringent requirements for use in contact with foodstuffs. The low toxicity, excellent stabilising performance and improving relative price situation has led to considerable growth in the organo-tin market during the 1970s and their status has changed from special purpose to that of general purpose stabilisers. Furthermore, additions to this class of material have been made, including the ester tins, characterised by low odour, volatility and toxicity, and the methyl tins which, with their high metal content, may be used in lower amounts than the more common organo-tins to achieve comparable efficiency.

Mention has already been made of *epoxide stabilisers*. They are of two classes and are rarely used alone. The first class are the epoxidised oils, which are commonly employed in conjunction with the cadmium–barium systems. The second class are the conventional bis-phenol A epoxide resins (see Chapter 22). Although rarely employed alone, used in conjunction with a trace of zinc octoate (2 parts resin, 0.1 part octoate) compounds may be produced with very good heat stability.

There has been a revival of interest in recent years in antimony mercaptides as alternatives to the organo-tin stabilisers. This stems from the low level of toxicity and the strong synergism with calcium stearate. However, compared to the

organo-tins they have lower resistance to sulphur staining and to ultraviolet radiation, particularly with transparent sheet.

A further class of stabilisers are the amines, such as *diphenylurea* and *2-phenylindole*. These materials are effective with certain emulsion polymers but rather ineffective with many other polymers.

There is somewhat more interest in the *aminocrotonates* of the general formula

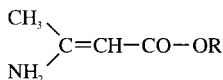


Figure 12.19

many of which are approved for food packaging applications in Western Europe. They are used mainly in UPVC compounds for packaging film and blow moulded containers.

In addition to stabilisers, antioxidants and ultra-violet absorbers may also be added to PVC compounds. Amongst antioxidants, trisnonyl phenyl phosphite, mentioned previously, is interesting in that it appears to have additional functions such as a solubiliser or chelator for PVC insoluble metal chlorides formed by reaction of PVC degradation products with metal stabilisers. Since oxidation is both a degradation reaction in its own right and may also accelerate the rate of dehydrochlorination, the use of antioxidants can be beneficial. In addition to the phenyl phosphites, hindered phenols such as octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate and 2,4,6-tris (2,5-di-*tert*-butyl-4-hydroxybenzyl)-1,3,5-trimethylbenzene may be used.

Low levels of ultraviolet absorbers (typically 0.2–0.8 pphr [parts per hundred resin]) can also be useful in preventing initiation of degradation mechanisms. Modified benzophenones and benzotriazoles are in widest commercial use.

12.5.2 Plasticisers

The tonnage of plasticisers consumed each year exceeds the annual tonnage consumption of most plastics materials. Only PVC, the polyolefins, the styrene polymers, the aminoplastics and, possibly, the phenolics are used in large quantity.

As explained in Chapter 5, these materials are essentially non-volatile solvents for PVC. Because of their molecular size they have a very low rate of diffusion into PVC at room temperature but at temperatures of about 150°C molecular mixing can occur in a short period to give products of flexibility varying according to the type and amount of plasticiser added.

All PVC plasticisers have a solubility parameter similar to that of PVC. It appears that differences between liquids in their plasticising behaviour is due to differences in the degree of interaction between polymer and plasticiser. Thus such phosphates as tritolyl phosphate, which have a high degree of interaction, gel rapidly with polymer, are more difficult to extract with solvents and give compounds with the highest brittle point. Liquids such as dioctyl adipate, with the lowest interaction with polymer, have the converse effect whilst the phthalates, which are intermediate in their degree of interaction, are the best all-round materials.

Phthalates prepared from alcohols with about eight carbon atoms are by far the most important class and probably constitute about 75% of plasticisers used. There are a number of materials which are very similar in their effect on PVC compounds but for economic reasons *di-iso-octyl phthalate* (DIOP), *di-2-ethylhexyl phthalate* (DEHP or DOP) and the phthalate ester of the C7–C9 oxo-alcohol, often known unofficially as *dialphanyl phthalate* (DAP), are most commonly used. (The term dialphanyl arises from the ICI trade name for the C7–C9 alcohols—Alphanol 79.) As mentioned in the previous paragraph these materials give the best all-round plasticising properties. DIOP has somewhat less odour whilst DAP has the greatest heat stability. Because of its slightly lower plasticising efficiency, an economically desirable feature when the volume cost of a plasticiser is less than that of polymer, *dinonyl phthalate* (DNP) may also be an economic proposition. Its gelation rate with PVC is marginally less than with DIOP, DAP and DEHP.

In spite of their high volatility and water extractability, *dibutyl phthalate* and *di-isobutyl phthalate* continue to be used in PVC. They are efficient plasticisers and their limitations are of greatest significance in thin sheet.

Until comparatively recently the bulk of general purpose phthalate plasticisers have been based on the branched alcohols because of low cost of such raw material. Suitable linear alcohols at comparative prices have become available from petroleum refineries and good all-round plasticisers are produced with the additional advantage of conferring good low-temperature flexibility and high room temperature resistance to plasticised PVC compounds. A typical material (Pliabrac 810) is prepared from a blend of straight chain octyl and decyl alcohols.

Certain higher phthalates are also available. For example, *ditridecyl phthalate* and *di-isodecyl phthalate* are used in high-temperature cable insulation, the former having the better high-temperature properties. Because of its greater hydrocarbon nature than DIOP, *di-isodecyl phthalate* has lower water extractability and is used, for example, with epoxidised oils in baby-pants.

Developments in the USA have led to the availability of terephthalate plasticisers, for example dioctyl terephthalate (DOTP). Whilst these materials are very similar to the corresponding *o*-phthalate esters they are generally less volatile and are best compared with *o*-phthalates with one or more carbon atom in the alkyl chain. As with the linear dialkyl phthalates the terephthalates show good fogging resistance. This is a phenomenon in which new cars on storage fields awaiting delivery develop misting on the windows due, apparently, to the volatility of additives in PVC compounds used with the car.

In the 1950s phosphate plasticisers had an importance comparable with the phthalates. However, during the 1960s the development of the petrochemicals industry resulted in the phthalate plasticisers becoming available at much lower prices than obtained for the phosphates such as *tritoyl phosphate* (TTP) for which the cresols were obtained from coal tar. During this period *trixyllyl phosphate* (TXP) tended to replace TTP because of its lower price structure. Because of their high price phosphates tend to be limited to products where good flame resistance is required, such as in insulation and mine belting. Other advantages of these materials are their high compatibility with PVC and good solvent resistance. On the debit side they are toxic and give products with a high cold flex temperature.

The development of natural gas as a fuel source in the UK has led to reductions in tar acid supplies and this has prompted the petrochemicals industry to make

Table 12.2 Comparison of the principal plasticisers for PVC

Plasticiser	Properties of plasticiser		Properties of plasticised PVC sheet ³					Volume resistivity at 20°C (Ω m)
	Specific gravity at 25°C	Refractive index n_D^{20}	Efficiency proportions ^b	Cold flex temp.(°C)	Volatility (%) ^c	Water extraction (%) ^d	Iso-octane extraction (%) ^e	
Di-n-butyl phthalate	1.045	1.49	54	-18	7.20	0.50	1.85	1×10^{15}
Diethylhexyl phthalate	0.985	1.49	63	-26	0.35	0.10	20.3	1.5×10^{15}
Di-iso-octyl phthalate	0.984	1.49	64	-25	0.40	0.05	20.2	1×10^{15}
Di-C ₇ -C ₉ phthalate	0.995	1.49	58.7	-26	0.35	0.10	20.1	2×10^{15}
Dinonyl phthalate	0.970	1.48	69.5	-20	0.35	0.05	28.9	2×10^{15}
Tritoyl phosphate	1.165	1.56	71	-7	0.30	0.10	0.6	2×10^{15}
Trixylyl phosphate	1.137	1.55	75	-5	0.25	0.10	0.7	3×10^{15}
Di-iso-octyl adipate	0.927	1.45	52.7	-42	0.55	0.10	23.9	5×10^{13}
Iso-octyl ester of saturated C ₄ -C ₆ dibasic acid	0.930	1.45	55	-42	1.70	0.20	22.7	2.5×10^{13}
Epoxidised soya bean oil	0.993	1.47	66.5	-20	0.20	0.10	1.30	6×10^{14}
Polypropylene sebacate	1.060	1.47	—	—	very low	—	very low	—

(a) All properties are measured on sheets of modulus of 1100 lbf/in² at 100% elongation.

(b) The efficiency proportion is the number of parts of plasticisers required per 100 parts of polymer to give a modulus of 1100 lbf/in² at 100% elongation.

(c) Weight loss of test-pieces 3 in \times 2 in \times 0.05 in in 24 hours in air circulated over at 85°C.

(d) 240 hours at 23°C.

(e) 24 hours at 23°C.

available synthetic alkylated phenols such as the isopropyl phenols. *Triisopropylphenol phosphates* are more price stable than the older phosphates, but have otherwise similar properties. Some problems are, however, said to arise with PVC pastes based on these materials because of their high pseudoplasticity and thixotropy leading to draining difficulties in dipping operations.

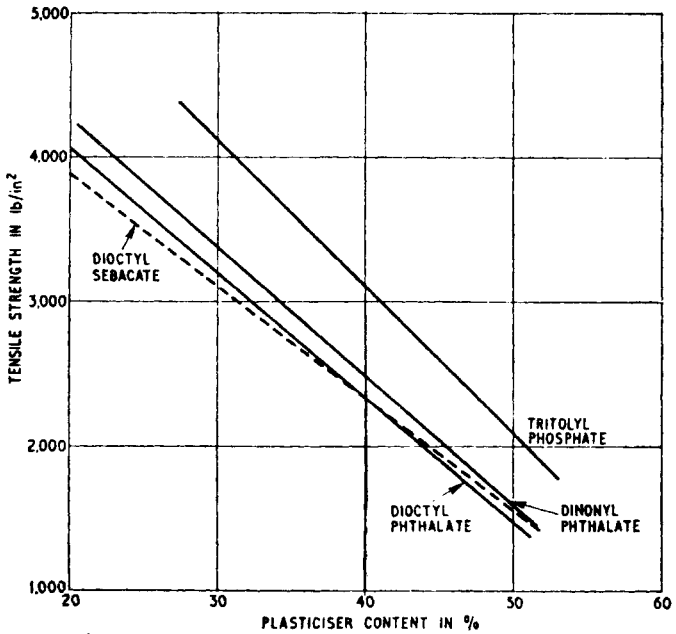
For some applications it is important to have a compound with good low-temperature resistance, i.e. with a low cold flex temperature. For these purposes aliphatic esters are of great value. They have a lower interaction with PVC and thus are incorporated with greater difficulty and extracted with greater facility. For many years the sebacates such as *dibutyl sebacate* (DBS) and *dioctyl sebacate* (DOS) were used where good low-temperature properties are required. Today they have been largely replaced by cheaper esters of similar effect in PVC derived from mixed acids produced by the petrochemical industry. The most important of these mixed acids are the AGS acids (a mixture of adipic, glutaric and succinic acids). These are esterified with octyl, nonyl and decyl alcohols to give plasticisers now generally referred to as nylonates but occasionally as sugludates. The sebacate, adipate and sugludate-type plasticisers can also be used to give compounds of high resilience.

Esters based on trimellitic anhydride, the *trimellitates*, have become very popular primary plasticisers for use at high temperatures or where a high level of resistance to aqueous extraction is required. Because of their frequency of use at elevated temperatures, they are usually supplied commercially containing an antioxidant.

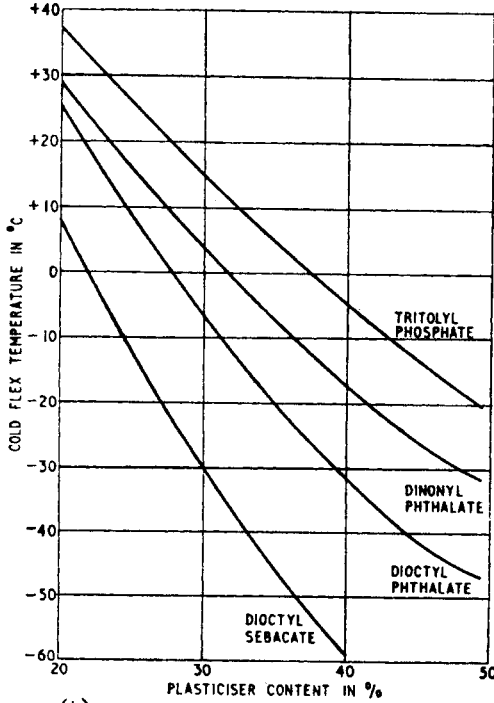
A number of other special purpose plasticisers are also available. The *epoxidised oils* and related materials are good plasticisers and very good light stabilisers and are often used in small quantities in PVC compounds. Polymeric plasticisers such as *polypropylene adipate*, *polypropylene sebacate* and similar products capped with lauric acid end groups are used where non-volatility and good hydrocarbon resistance is important. They are, however, rather expensive and are rather difficult to flux with PVC. Solid ethylene-vinyl acetate modified polymers have also recently been offered as polymeric plasticisers (e.g. Elvaloy by Du Pont). These are claimed to be true plasticisers and are non-volatile, non-migratory and, unlike most PVC plasticisers, have a high resistance to biodegradation. Certain esters of citric acid, such as *acetyl tributyl citrate*, find an outlet where minimum toxicity is of importance.

The development of PVC as a metal-finishing material has led to the need for a good PVC-metal adhesive. For some purposes it is found convenient to incorporate the adhesive component into the PVC compound. Esters based on allyl alcohol, such as *diallyl phthalate* and various polyunsaturated acrylates, have provided useful in improving the adhesion and may be considered as polymerisable plasticisers. In PVC pastes they can be made to cross-link by the action of peroxides or perbenzoates simultaneously with the fluxing of the PVC. When the paste is spread on to metal the 'cured' coating can have a high degree of adhesion. The high adhesion of these rather complex compounds has led to their development as metal-to-metal adhesives used, for example, in car manufacture. Metal coatings may also be produced from plasticised powders containing polymerisable plasticisers by means of fluidised bed or electrostatic spraying techniques.

Many other liquids have been found to be effective plasticisers for PVC but are of limited commercial value, at least in Britain. The effect of plasticisers on the properties of PVC is illustrated in *Figure 12.20* (a-e).



(a)



(b)

Figure 12.20. See page 336 for key

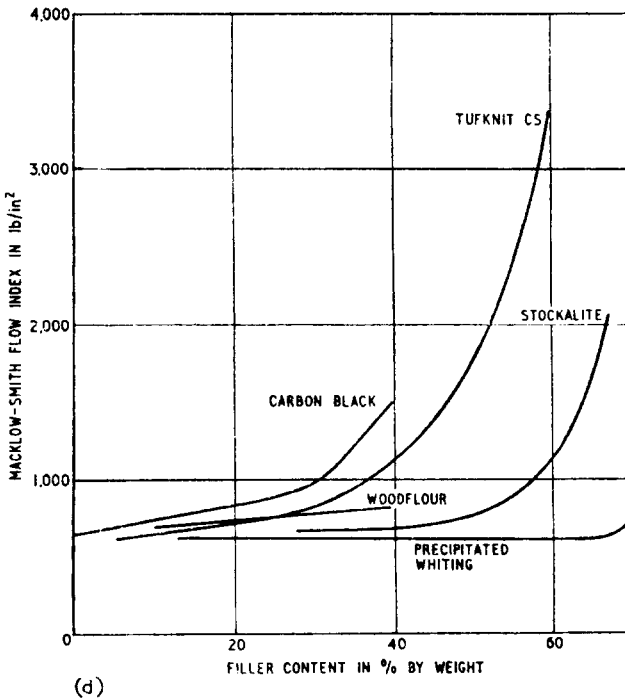
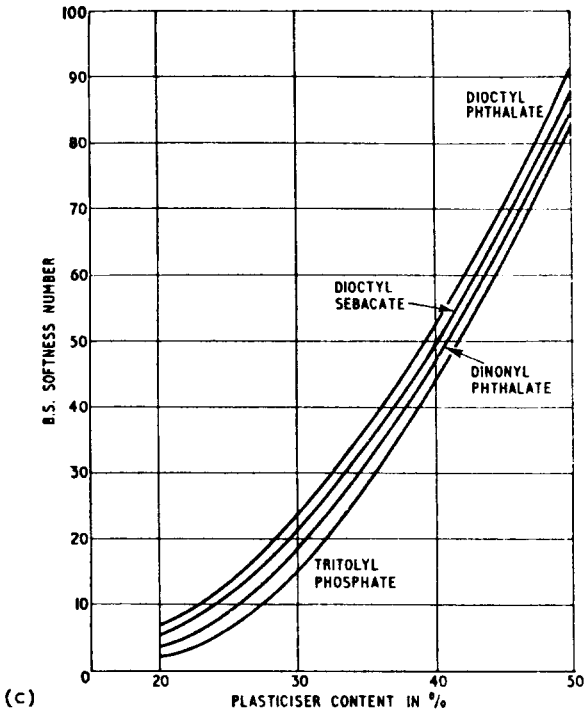


Figure 12.20. See page 336 for key

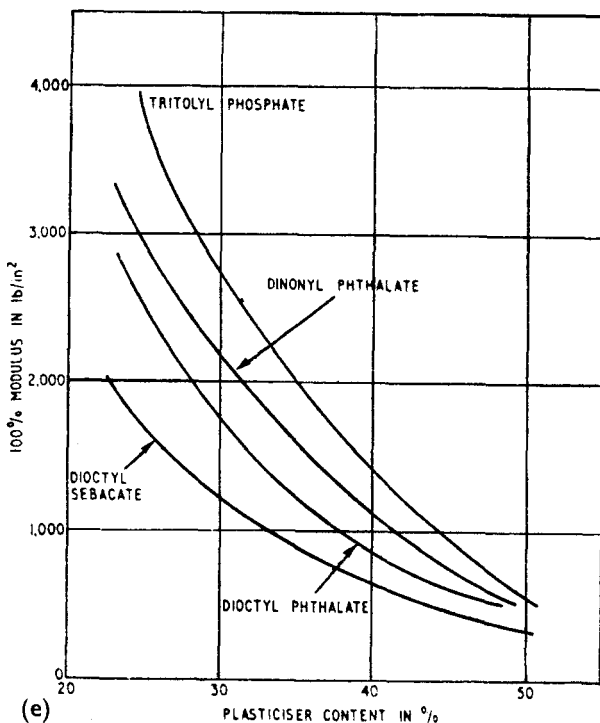


Figure 12.20. Effect of change of plasticiser on the properties of polyvinyl chloride compounds.¹⁵ (a) Tensile strength. (b) Cold flex temperature. (c) BS softness number. (d) Elongation at break. (e) 100% modulus. (The Distillers Company Ltd.)

12.5.3 Extenders

A number of materials exist which are not in themselves plasticisers for PVC because of their very limited compatibility with the polymer, but in conjunction with a true plasticiser a mixture is achieved which has a reasonable compatibility. Commercial *extenders*, as these materials are called, are cheaper than plasticisers and can often be used to replace up to a third of the plasticiser without serious adverse effects on the properties of the compound.

Three commonly employed types of extender are:

- (1) Chlorinated paraffin waxes.
- (2) Chlorinated liquid paraffinic fractions.
- (3) Oil extracts.

The solubility parameters of these extenders are generally somewhat lower than that of PVC. They are thus tolerated in only small amounts when conventional plasticisers of low solubility parameter, e.g. the sebacates, are used but in greater amounts when phosphates such as tritolyl phosphate are employed.

12.5.4 Lubricants

In plasticised PVC the main function of a lubricant is to prevent sticking of the compound to processing equipment. This is brought about by selecting a material

of limited compatibility which will thus sweat out during processing to form a film between the bulk of the compound and the metal surfaces of the processing equipment. When used for such a purpose the additives are known as *external lubricants*.

In Britain *calcium stearate* has been most commonly used with non-transparent products and *stearic acid* with transparent compounds. In the United States *normal lead stearate*, which melts during processing and lubricates like wax, is commonly employed. *Dibasic lead stearate*, which does not melt, lubricates like graphite and improves flow properties, is also used.

The quantity of an external lubricant to be used has to be chosen with care. If too little is used sticking problems occur; if too much the compound may develop haze and greasiness, printing and heat sealing may be difficult and gelation and fusion of the compound may be slowed down. In addition, too much slip of compound against machinery walls will prevent the development of the shear forces which are required to ensure a smooth and even flow. In an extruder the extent of lubricant may be used to control the gelation of powder blends. If this occurs too early then undue working of the polymer, causing some degradation, may occur before the material emerges from the die. On the other hand there should be sufficient time for proper gelation and homogenisation to take place before the die is reached. A further problem that may arise with lubricants (and those stabilisers which can also act as lubricants) is that because of their low compatibility they may deposit on to calender and mill rolls and on to extruder dies, carrying with them particles of pigments, fillers and other additives. Such a phenomenon, which is often more severe at high shear rates, is commonly known as *plate-out*.

In unplasticised PVC it is common practice to incorporate at least one other lubricant. Such materials are primarily intended to improve the flow of the melt, i.e. they lower the apparent melt viscosity. Known as *internal lubricants*, such materials are reasonably compatible with the polymer and are rather like plasticisers in their behaviour at processing temperatures, although at room temperature this effect is negligible. Such materials do not retard gelation, cause haze or cause greasiness. It should be pointed out that whereas the above classification of lubricants into internal and external types appears clear cut, in reality the situation is more complex and some materials seem to have a more or less dual function. Amongst materials which are usually classified as internal lubricants are wax derivatives, particularly from montan wax, glyceryl esters, particularly glyceryl monostearate, and long chain esters such as cetyl palmitate.

It has been pointed out¹⁶ that for rigid PVC extrusion compositions best results are obtained with a lubricant, or mixture of lubricants, which melt in the range 100–120°C, since these generally give a lubricating film of the correct viscosity at the processing temperature of about 165°C. For calendaring operations it is suggested that lubricants should be chosen with higher melting points, i.e. in the range 140–160°C. *Aluminium and magnesium stearate* fall within this melting point range.

12.5.5 Fillers

Fillers are commonly employed in opaque PVC compounds in order to reduce cost. They may also be employed for technical reasons such as to increase the hardness of a flooring compound, to reduce tackiness of highly plasticised

compounds, to improve electrical insulation properties and to improve the hot deformation resistance of cables.

In evaluating the economics of a filler it is important to consider the volume of filler that can be added bringing the processing and service properties below that which can be tolerated. Thus in some cases it may be more economical to use a filler with a higher volume cost because more can be incorporated. To judge the economics of a filler simply on its price per unit weight is of little merit.

For electrical insulation *china clay* is commonly employed whilst various *calcium carbonates* (whiting, ground limestone, precipitated calcium carbonate, and coated calcium carbonate) are used for general purpose work. Also occasionally employed are *talc*, *light magnesium carbonate*, *barytes* (barium sulphate) and the *silicas* and *silicates*. For flooring applications *asbestos* has been an important filler. The effect of fillers on some properties of plasticised PVC are shown in *Figure 12.21* (a–d).

12.5.6 Pigments

A large number of pigments are now commercially available which are recommended for use with PVC. Before selecting a pigment the following questions should be asked:

- (1) Will the pigment withstand processing conditions anticipated, i.e. will it decompose, fade or plate-out?
- (2) Will the pigment adversely affect the functioning of stabiliser and lubricant?
- (3) Will the pigment be stable to conditions of service, i.e. will it fade, be leached out or will it bleed?
- (4) Will the pigment adversely affect properties that are relevant to the end-usage? (NB many pigments will reduce the volume resistivity of a compound.)

When there remains a choice of pigments which fulfil the above requirements then economic factors have to be taken into account. The cost function relevant is again not the weight cost or volume cost but the cost of adding the amount of pigment required to give the right colour in the compound. Thus a pigment with a high covering power may be more economic to use than a pigment of lower cost per pound but with a lower covering power.

12.5.7 Polymeric Impact Modifiers and Processing Aids

Unplasticised PVC has a high melt viscosity leading to some difficulties in processing. The finished product is also too brittle for some applications. In order to overcome these problems it has become common practice to add certain polymeric additives to the PVC. The *impact modifiers* generally are semi-compatible and often somewhat rubbery in nature. Whilst the mechanism of toughening is not fully understood it appears to be on the lines suggested in Chapter 3. In practice it seems that the greatest improvement in impact strength occurs with polymer additives having a solubility parameter about $0.4\text{--}0.8\text{ MPa}^{1/2}$ different from that of PVC ($\delta = 19.4\text{ MPa}^{1/2}$). Data by Bramfitt and Heaps¹⁷ are largely in accord with this supposition (*Table 12.3*).

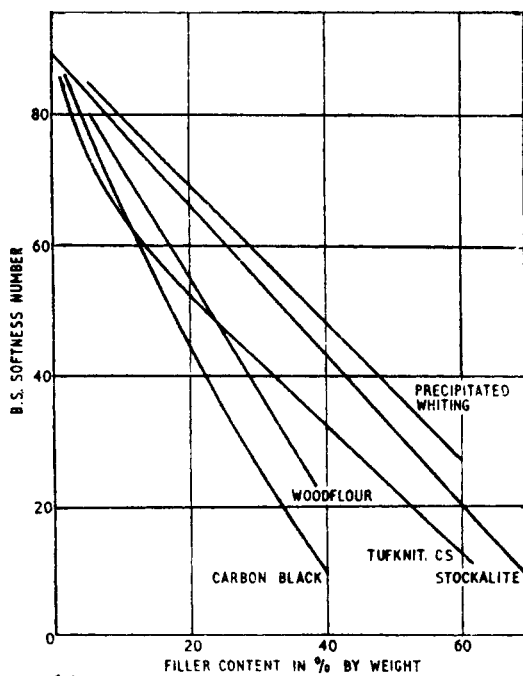
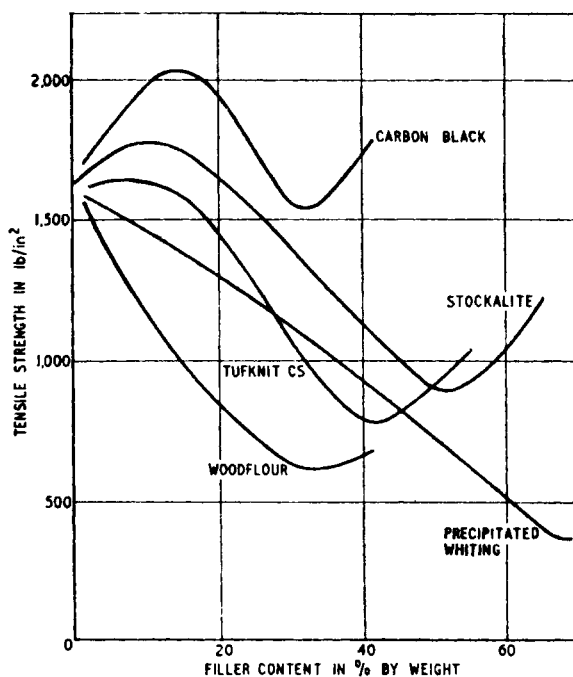
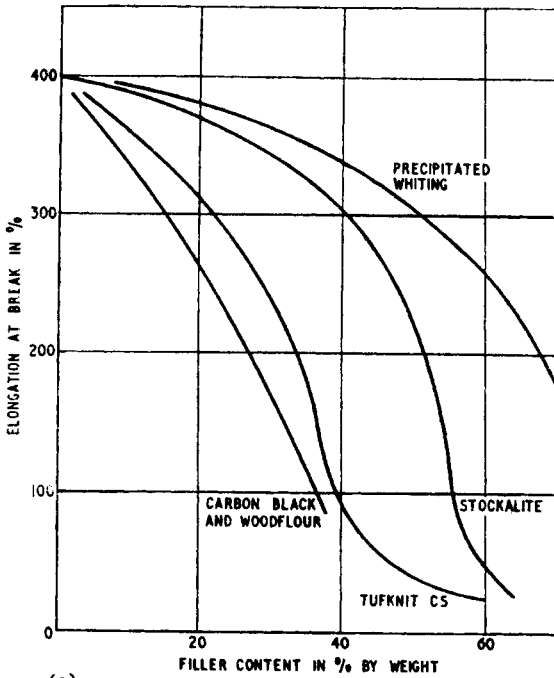
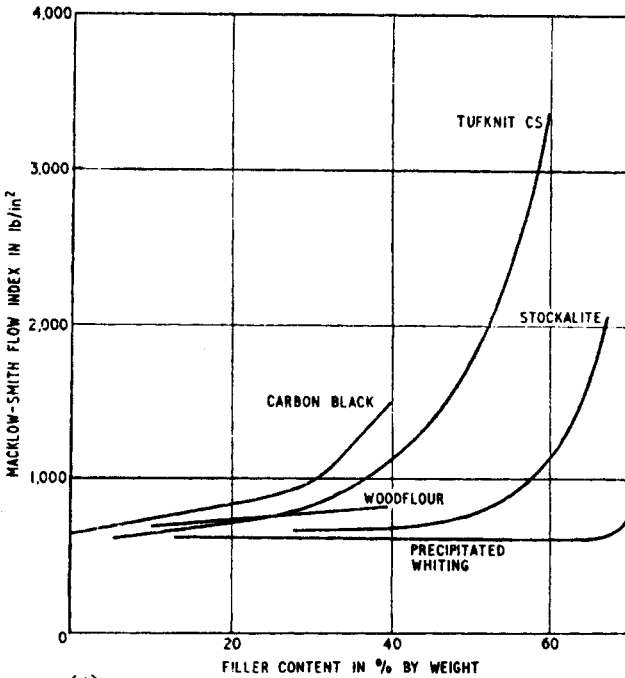


Figure 12.21. Effect of filler content on the properties of plasticised PVC compounds.¹⁵ (a) Tensile strength. (b) BS softness number.



(c)



(d)

Figure 12.21. (c) Elongation at break. (d) Macklow-Smith flow index. (The Distillers Company Ltd.)

Table 12.3 Effect of solubility parameter of rubber on its effect on the impact strength of a PVC-rubber blend (5 parts rubber per 100 parts PVC)¹⁷

<i>Rubber</i>	<i>Solubility parameter (MPa^{1/2})</i>	<i>Izod impact strength (ft lbf/in of notch)</i>
Butadiene-2-vinylpyridine (30:70)	19.3	3
Chlorinated polyethylene (44% chlorine)	19.2	4.4
Butadiene-styrene-acrylonitrile (67:17:16)	18.7	17.4
Butadiene-2-vinylpyridine (40:60)	18.7	10.0
Butadiene-methyl methacrylate (35:65)	18.2	2.8
Butadiene-methyl acrylate	17.9	3.3
Butadiene-methyl isopropenyl ketone	17.4	15.9
Butadiene-diethyl fumarate	17.2	15.0

The anomalous effect of the last two rubbers in the table with their low solubility parameters is possibly explained by specific interaction of PVC with carbonyl and carboxyl groups present respectively in the ketone- and fumarate-containing rubbers to give a more than expected measure of compatibility. It is important to note that variation of the monomer ratios in the copolymers and terpolymers by causing changes in the solubility parameter and compatibility will result in variation in their effect on impact strength.

At one time butadiene-acrylonitrile copolymers (nitrile rubbers) were the most important impact modifiers. Today they have been largely replaced by acrylonitrile-butadiene-styrene (ABS) graft terpolymers, methacrylate-butadiene-styrene (MBS) terpolymers, chlorinated polyethylene, EVA-PVC graft polymers and some polyacrylates.

ABS materials are widely used as impact modifiers but cause opacity and have only moderate aging characteristics. Many grades show severe stress-whitening, generally a disadvantage, but a phenomenon positively employed in labelling tapes such as Dymotape.

There are a number of applications such as bottle and film where tough materials of high clarity are desired. The advent of MBS material has been a significant advance to meet the requirements. It has been found possible here to produce an additive with sufficiently different solubility parameters from the PVC for it to exist in the disperse phase but with a very similar refractive index to the PVC so that light scattering at the interface between the two phases is at a minimum. However, owing to differences in the formulation of PVC compounds, a particular MBS modifier may not have exactly the same refractive index as the PVC compound.

When the disperse phase has a slightly higher refractive index the compound tends to be blue; when it is lower than that of the PVC the compound tends to be yellow and hazy. In order to overcome this a carefully determined quantity of a second MBS additive, with an appropriate refractive index and which is compatible with the PVC compound and hence forms a continuous phase with it, may be added to match the refractive indices. Such a matching operation should be evaluated at the proposed service temperature range of the product since the temperature coefficients of the two phases are usually different and a film which is blue at processing temperature may become yellow at 20°C.

MBS materials vary considerably in their tendency to cause stress-whitening in PVC and in their effect on impact strength. They are generally considered to lead to better aging than ABS additives but are marginally more expensive.

Chlorinated polyethylene has also been widely used as an impact modifier, particularly where good aging properties are required. Such good aging behaviour arises from the absence of butadiene and hence double bonds in such materials. Such materials tend, however, to give lower softening points and higher processing die swell to the PVC compounds.

In addition to acting as impact modifiers a number of polymeric additives may be considered as *processing aids*. These have similar chemical constitutions to the impact modifiers and include ABS, MBS, chlorinated polyethylene, acrylate-methacrylate copolymers and EVA-PVC grafts. Such materials are more compatible with the PVC and are primarily included to ensure more uniform flow and hence improve surface finish. They may also increase gelation rates. In the case of the compatible MBS polymers they have the special function already mentioned of balancing the refractive indices of the continuous and disperse phases of impact-modified compound.

12.5.8 Miscellaneous Additives

A number of ingredients may be used from time to time in PVC formulations. For example, blowing agents such as azodicarbonamide and azodi-isobutyronitrile are frequently used in the manufacture of cellular PVC.

Antimony oxide¹⁸ is useful in improving the fire retardance of PVC compounds. This is sometimes necessary since, although PVC itself has good flame retardance, phthalate plasticisers will burn.

For some applications it is necessary that static charge should not accumulate on the product. This is important in such diverse applications as mine belting and gramophone records. The use of antistatic agents such as quaternary ammonium compounds has been of some limited value in solving this problem.

The viscosity of PVC pastes may be reduced in many instances by the presence of certain polyethylene glycol derivatives and related materials. Because of their tendency to exude, the use of these viscosity depressants should be restricted to levels of less than 1% of the total mix.

12.5.9 Formulations

It is obvious that the range of possible formulations based on poly(vinyl chloride) and related copolymers is very wide indeed. For each end-use the requirements must be carefully considered and a formulation devised that will give a compound of adequate properties at the lowest cost. In assessing cost it is not only important to consider the cost of the compound but also comparative processing costs, the possible cost of storing additional materials and many other cost factors.

The few formulations given below are intended as a general guide. They should not be taken as recommendations for a specific application where many factors, not considered in the brief discussion here, would need to be taken into account. Formula 1 gives a typical general purpose insulation compound.

Formula 1

Suspension polymer (ISO No. 125)	100
DIOP	40
Trixylyl phosphate	20
China clay	20
Tribasic lead sulphate	7
Stearic acid	0.5
Pigment	2

Suspension polymer is chosen because its relative freedom from emulsifier and other surface active material gives polymers of better electrical insulation characteristics than emulsion polymers. Di-isooctyl phthalate is a low-cost good all-round plasticiser whilst some trixylyl phosphate is added to improve the fire-retarding properties. China clay is a cheap filler with good insulation properties, whilst lead sulphate gives compounds of high heat stability, long-term aging stability and good insulation characteristics. Formula 2 is a transparent calendering compound

Formula 2

Suspension polymer (ISO No. 125)	100
DIOP	40
Ba–Cd phenate	3
Trisnonyl phenyl phosphite	1
Epoxidised oil	5
Stearic acid	0.4

Each of the ingredients is chosen with a view to obtaining high clarity at a moderate cost. In Formula 3 the stabilising system has been replaced by a less powerful, but also less toxic, stabiliser.

Formula 3

Suspension polymer (ISO No. 125)	100
DIOP	40
Epoxidised oils	5
Ca–Zn stabiliser	2.5

The requirements for garden hose are somewhat less critical and both filler and extender may be incorporated to reduce cost (Formula 4).

Formula 4

Suspension polymer (ISO No. 125)	100
DAP	50
Extender	25
Whiting	30
Tribasic lead sulphate	6
Calcium stearate	1
Pigment	3

The main requirements for a flooring composition are that it should be hard, durable and competitive in price with other materials. This calls for highly filled

materials which are consequently harder to process than unfilled materials. The problem is alleviated by use of copolymers with their easier processing characteristics. Formula 5 is an example of a flooring recipe.

Formula 5

Vinyl chloride–vinyl acetate copolymer (ISO No. 55–80)	100
DAP	30
Extender	15
Whiting	150
Asbestos	150
Ba–Zn complex	3
Calcium stearate	1
Pigment	as required

Copolymers were also used in gramophone record formulations (Formula 6). No filler can be tolerated and stabilisers and lubricants are chosen that give records of minimum surface noise. Antistatic agents may also be incorporated into the compound.

Formula 6

Vinyl chloride–acetate copolymer (ISO No. 60)	100
Diabasic lead stearate	0.75
Dibasic lead phthalate	0.75
Lamp black	2

Formula 7 is a leathercloth formulation for use in spreading techniques. There are many possible formulations and that given is for a product with a soft dry feel.

Formula 7

Paste-making polymer (ISO No. 125–140)	100
DIOP	50
Extender	20
Ba–Cd system	2
Epoxidised oil	3
Pigment	as required

In the case of unplasticised polymer the main concern is with control of gelation and ensuring processability and adequate stabilisation. The formulation selected thus depends almost as much on the actual processing equipment used as on the end-product. Formula 8 gives a typical rigid opaque formulation suitable for pipes and Formula 9 a transparent calendering compound.

Formula 8

Suspension polymer (ISO No. 85–100)	100
Tribasic lead sulphate	6
Lead stearate	1
Glyceryl monostearate	0.4
Acrylic process aid	2

Formula 9

Mass polymer (ISO No. 80)	100
Octyltin stabiliser	1.5
MBS impact modifier	10
Acrylic process aid	3.0
Montan wax	2.0
Glyceryl monostearate	0.5

12.6 PROPERTIES OF PVC COMPOUNDS

Because of the wide range of possible formulations it is difficult to make generalisations about the properties of PVC compounds. This problem is illustrated in *Table 12.4*, which shows some differences between three distinct types of compound.

Table 12.4 Properties of three types of PVC compound

	<i>Unplasticised PVC</i>	<i>Vinyl chloride– vinyl acetate copolymer (sheet)</i>	<i>PVC + 50 p.h.r. DIOP</i>
Specific gravity	1.4	1.35	1.31
Tensile strength lbf/in ² (MPa)	8500(58)	7000(48)	2700(19)
Elongation at break %	5	5	300
BS softness No.	—	—	35
Vicat softening point (°C)	80	70	flexible at room temperature

Mechanical properties are considerably affected by the type and amount of plasticiser. This was clearly shown in *Figure 12.20*. To a lesser extent fillers will affect the physical properties, as indicated in *Figure 12.21*.

Unplasticised PVC is a rigid material whilst the plasticised material is flexible and even rubbery at high plasticiser loadings. It is of interest to note that the incorporation of small amounts of plasticiser, i.e. less than 20%, does not give compounds of impact strength higher than that of unplasticised grades, in fact the impact strength appears to go through a minimum at about 10% plasticiser concentration. As a result of this behaviour, lightly plasticised grades are used only when ease of processing is more important than in achieving a compound with a good impact strength.

Poly(vinyl chloride) has a good resistance to hydrocarbons but some plasticisers, particularly the less polar ones such as dibutyl sebacate, are extracted by materials such as iso-octane. The polymer is also resistant to most aqueous solutions, including those of alkalis and dilute mineral acids. Below the second order transition temperature, poly(vinyl chloride) compounds are reasonably good electrical insulators over a wide range of frequencies but above the second order transition temperature their value as an insulator is limited to low-frequency applications. The more plasticiser present, the lower the volume resistivity.

Vinyl chloride–vinyl acetate copolymers have lower softening points than the homopolymers and compounds and may be processed at lower temperatures than

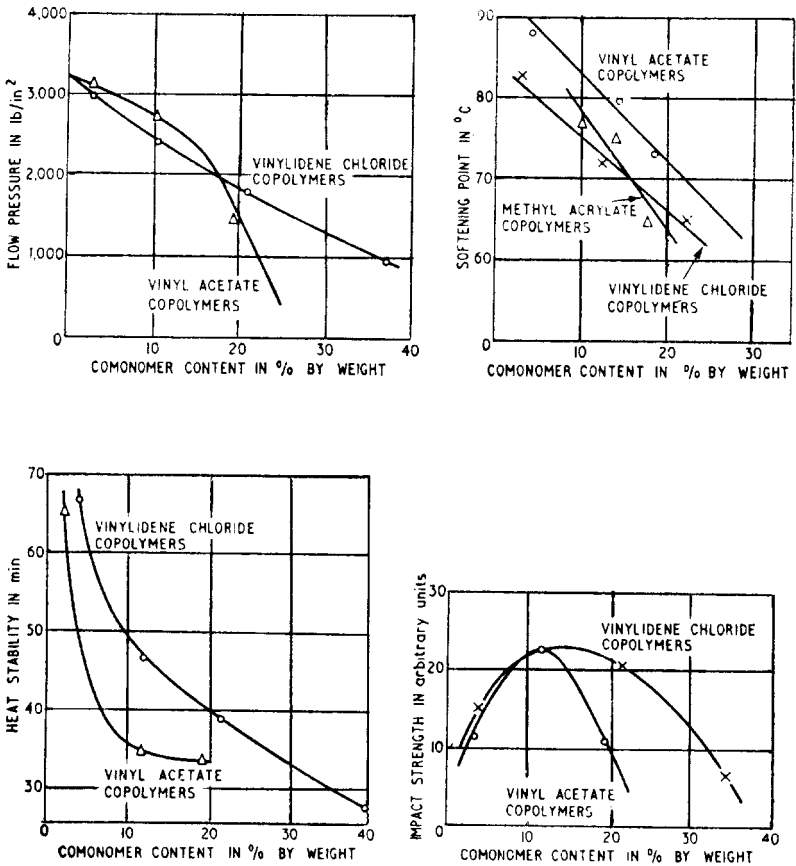


Figure 12.22. Effect of copolymerisation of vinyl chloride with other monomers on the properties of unplasticised compounds. (After Weldon¹⁹)

those used for analogous homopolymer compounds. The copolymers have better vacuum-forming characteristics, are soluble in ketones, esters and certain chlorinated hydrocarbons but have generally an inferior long-term heat stability. The effect of percentage comonomer on the properties of a copolymer are illustrated in Figure 12.22¹⁹.

12.7 PROCESSING

Consideration of the methods of processing vinyl chloride polymers is most conveniently made under the following divisions:

- (1) Melt processing of plasticised PVC.
- (2) Melt processing of unplasticised PVC.
- (3) Processing of pastes.
- (4) Processing of latices.
- (5) Copolymers.

12.7.1 Plasticised PVC

The melt processing of plasticised PVC normally involves the following stages:

- (1) Pre-mixing polymer and other ingredients.
- (2) Fluxing the ingredients.
- (3) Converting the fluxed product into a suitable shape for further processing, e.g. granulating for injection moulding or extrusion.
- (4) Heating the product to such an extent that it can be formed by such processes as calendaring, etc. and cooling the formed product before removal from the shaping zone.

The many possible variations and modifications to this sequence have been admirably summarised by Matthews²⁰ (see Figure 12.23).

In most of these routes, premixing is carried out in a trough mixer at room temperature to give a damp powdery mass or 'mush'. This may then be fluxed on a two-roll mill, in an internal mixer, or in a continuous compounder such as the Werner and Pfleiderer Plastificator. For many operations the compounded mass

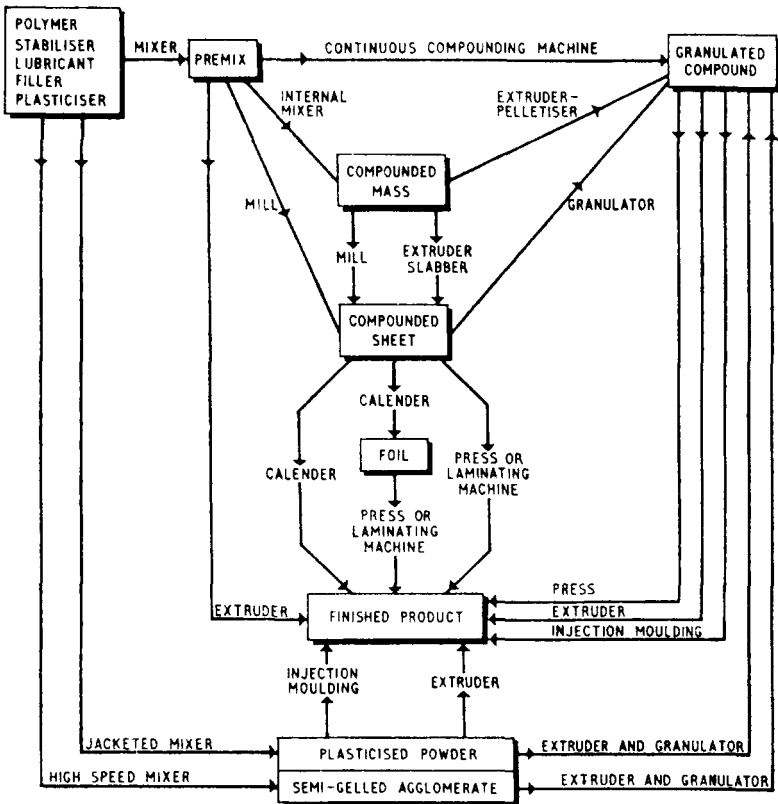


Figure 12.23. Routes from raw materials to finished products illustrating different compounding techniques with PVC compounds²⁰

is then granulated or pelleted. This can be carried out as part of the continuous compounding process, whereas a mass mixed in an internal mixer may be either fed to an extruder–pelletiser, which extrudes strands which are then cut up into pellets, to an extruder–slabber, which produces a sheet subsequently fed to a dicing machine, or to a two-roll mill, which also provides a sheet for subsequent dicing. Sheet may also be fed directly to a calender whilst still hot and it may also be used for pressing into sheet.

Over the years dry blending techniques have become more popular. In these processes the mixture of ingredients is either subjected to vigorous stirring, gentle heating or both. As a result of such treatment the plasticiser is absorbed into the polymer particles to give dry free-flowing powders. This process is most easily worked with easy-processing polymers. Although the intensity of mixing is not so great as in an internal mixer, mixing is taken to a stage where it can be subsequently completed during the plasticising stage of an extrusion operation. The important advantage of this process is that it frees the polymer from subjection to one high-temperature process and thus reduces risk of decomposition and of deterioration in electrical insulation properties. For successful use of dry blending processes it is important to ensure an adequate degree of mixing in the product. This involves not only care in the development of the mixing process but also care in the choice of extrusion machinery and conditions.

Extrusion operations are involved in making cables, garden hose-pipes and sections. It is necessary to ensure the following conditions:

- (1) That the compound is dry. (This is not normally a problem and special predrying operations are rarely necessary if the material has been properly stored.)
- (2) That the compound is not allowed to stagnate in heated zones of the extruder and thus decompose. The 'life' of many compounds at processing temperatures is little more than the normal residence time of the material in the extruder.
- (3) That there is a good means of temperature control.

It is not possible to give detailed recommendations of processing conditions as these will depend on the nature of the product, the formulation of the compound used and the equipment available. However, the temperature is generally of the order of 130°C at the rear of the barrel and this increases to about 170–180°C at the die. Screw speeds are of the order of 10–70 rev/min. A typical screw would have a length/diameter ratio of about 15:1 and a compression ratio of 2:1. It is, however, possible to extrude plasticised PVC on extruders with lower length/diameter ratios and compression ratios, particularly with extruders of screw diameters in excess of 5 cm. In some cases it may, however, be necessary to improve the degree of homogenisation by use of stainless steel mesh screens behind the breaker plate and by the use of screw cooling water. Higher length–diameter screws are often preferred for dry blends in order to ensure adequate mixing.

A large amount of plasticised PVC is fabricated by calendering techniques using calenders of either the inverted–L or, preferably, of the inclined–Z type. A major problem is the control of gauge (thickness). Transverse variations due to bowl bending may be reduced or partially compensated for by the use of bowls of greater diameter/width ratio, by cambering the bowls, by bowl cross-alignment or by deliberate bowl bending. Longitudinal variation may be largely

eliminated by preloading the bowls to prevent the journals floating in their bearings. For technical reasons it is more convenient to preload on Z-type calenders than on L- and inverted L-type calenders. Bowl temperatures are in the range 140–200°C. Large-scale leathercloth manufacture is today commonly carried out using calendering techniques.

Plasticised PVC was not easily injection moulded in ram-operated machines. This is because it is difficult to bring compound furthest from the cylinder wall to a temperature which gives the compound adequate flow without decomposing the material nearest to the cylinder wall. The introduction of preplasticising machines, which amongst other advantageous characteristics do not rely on heat transfer solely by conduction, has largely overcome this problem. A number of special low-pressure machines have been especially developed for use in the manufacture of PVC shoes and shoe soles. For these purposes, compounds based on lower molecular weight homopolymers (K -value 55–60) or copolymers are frequently employed.

Fluidised-bed techniques, pioneered with low-density polyethylene, have been applied to PVC powders. These powders can be produced by grinding of conventional granules, either at ambient or sub-zero temperatures or by the use of dry blends (plasticised powders). The fluidised bed process is somewhat competitive with some well-established paste techniques, and has the advantage of a considerable flexibility in compound design.

12.7.2 Unplasticised PVC

The processing of unplasticised PVC (UPVC) is more critical than that of the plasticised material since UPVC only becomes processable in the temperature range at which decomposition occurs at a measurable rate. Any unnecessary heating, either through a needless processing stage, by undue frictional working of the viscous melts, by too high temperature settings on the equipment or by poor flow lines which cause hold-up of the polymer in processing machines, should be avoided. At the same time the polymer compound should be designed so that it has a low melt viscosity (by the use of polymers with low ISO number and the incorporation of internal lubricants and process aids) and of a high degree of thermal stability such as is provided by the newer organo-tin stabilisers.

Due consideration of these principles has made it possible to process unplasticised PVC by all the standard melt processes, including injection moulding and bottle blowing, a state of affairs hardly conceivable in the 1950s.

Most UPVC compounds are prepared by dry blending of powders. Not only does this avoid unnecessary heating in internal mixers, mills and granulating equipment but it also leads to substantial economies. The fine powders do, however, cause problems of dust and contamination of hydraulic systems of processing plant unless particular care is taken. High-speed mixers are preferred, frictional heating causing a temperature rise bringing the PVC above its T_g and thus facilitating rapid absorption of liquid and semi-solid additives. Too early addition of lubricants may retard the heat build-up and the point of their addition can be critical. The blends continue to increase in temperature as mixing proceeds, causing agglomeration and an increase in bulk density. This leads to increasing output in, for example, extruders but also reduces the thermal stability of the compound.

Twin-screw extruders now dominate the extrusion field, particularly because of their positive pumping action which is so important with PVC in powder form.

(This is probably because efficient pumping of the granules or powder in a single-screw extruder depends on the adhesion of the polymer to a hot barrel being greater than that of the polymer to a cooler screw. With PVC there is a much lower temperature coefficient of adhesion than with other polymers.) In some cases the desired compression ratio (of about 2:1) is achieved by using tapered barrels. Dies must be designed so that there is no chance of polymer stagnation and all flow path cross-sections should only change slowly, with narrow lead-in angles to the die parallels. Accurate temperature control is also clearly important. As previously mentioned the selection of lubricant is critical in that it controls the point of gelation in the extruder barrel; too early a gelation leads to unnecessary working and frictional heat, too late a gelation leads to imperfect extrudates.

Because PVC evolves corrosive hydrochloric acid on heating, care should be taken in the choice of metals for machine construction and the use of plating and/or special steels is widely practised.

Extrusion blow moulding of bottles has been successfully accomplished in recent years by attention to the points mentioned above. It is to be noted here that UPVC has a much lower average specific heat between the processing temperature and room temperature than polyethylene and, being essentially amorphous, no latent heat of fusion. This leads to much less heat needing to be removed on cooling of mouldings and very short cycle times are possible.

Injection moulding of unplasticised PVC was only really made possible by the advent of the in-line screw preplasticising machines. As with extrusion the main points to bear in mind are the high melt viscosity, the need to avoid overheating and steel corrosion by hydrochloric acid evolved during processing. In practice this demands good control of operating conditions, short runners, reasonably generous gates and mould cavities which, preferably are either chrome or gold plated. Although it is possible to extrude rigid PVC sheet, it is commonly made by compression moulding techniques, either by laminating hide from a sheeting or mixing mill or by moulding granules. Such sheet may be welded using hot gas welding guns to produce chemical plant and other industrial equipment. The sheet may be shaped by heating and subjecting it to mechanical or air pressure. The methods used are similar to those originally developed to deal with poly(methyl methacrylate).

UPVC film or sheet may also be made by the Luvitherm process using a technique used only with PVC. High molecular weight PVC (ISO No. 145–165) is compounded and partly agglomerated in an extruder-mixer. The heated mix is then fed to an L-type calender (a vertical three-roll calender with a fourth roll horizontally aligned with the bottom roll of the three-roll stack). The hot calender rolls simply partly consolidate the granules so that the resulting film or sheet is strong enough to be drawn over a train of heated drums which are well above the fluxing temperature of the compound. The PVC is therefore subjected to only a very short but intense heating process. The resulting films with the high mechanical properties consequent on the use of high molecular weight polymers are used for magnetic tapes and for packaging applications.

12.7.3 Pastes

As explained in Section 12.4.1 a paste is obtained when the voids between particles are completely filled with a plasticiser so that the polymer particles are suspended in it. It has also been pointed out that to ensure a stable paste there is

an upper and a lower limit to the order of particle size. Finally it has been stressed that both the flow and fluxing characteristics of a paste are, to no small extent, dependent on the particle shape, size and size distribution.

A number of basic paste types may be distinguished. The most important classes are the plastisols, the organosols, plastisols incorporating filler polymers (including the rigisols), plastigels, hot melt compounds, and compounds for producing cellular products.

The first four types are most conveniently distinguished by reference to formulations A to D in *Table 12.5*. Formulation A is a conventional *plastisol*. The viscosity of the paste is largely controlled by the choice of type and amount of polymer and plasticiser. In order to achieve a sufficiently low viscosity for processing, large quantities of plasticiser must be added, thereby giving a product of lower hardness, modulus, tensile strength and other mechanical properties than would be the case if less plasticiser could be used. In many applications this is not a serious problem and plastisols are of some considerable importance commercially.

Table 12.5

	A	B	C	D
Paste-making polymer	100	100	55	100
Filler polymer	—	—	45	—
Plasticiser (e.g. DOP)	80	30	80	80
Filler (e.g. china clay)	10	10	10	10
Stabiliser (e.g. white lead)	4	4	4	4
Naphtha	—	50	—	—
Aluminium stearate	—	—	—	4

The influence of plasticiser content on viscosity is shown in *Figure 12.24*. It is also to be noted that because of plasticiser absorption the viscosities of pastes do invariably increase on storage. The rate of increase is a function of the plasticiser used (*Figure 12.25*).

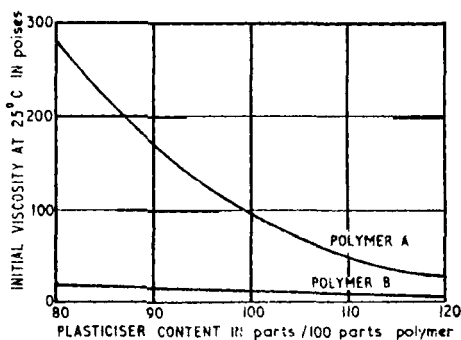


Figure 12.24. Effect of plasticiser (diaphanyl phthalate) on initial paste viscosity with two commercial paste polymers

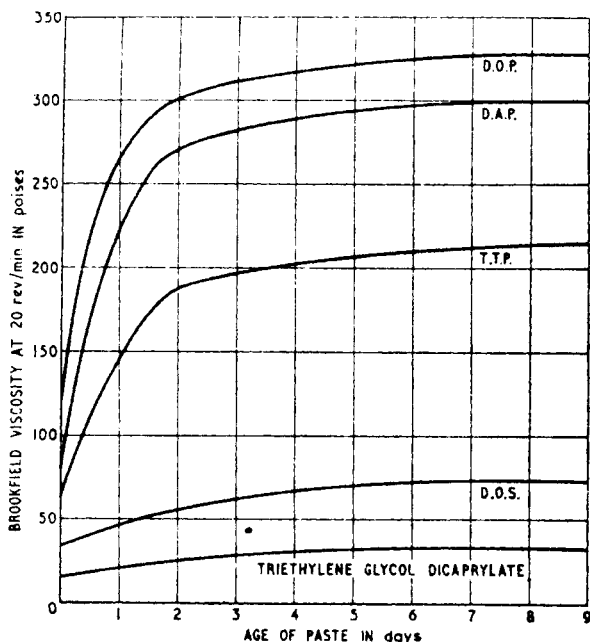


Figure 12.25. Effect of storage on the viscosity of PVC pastes using different plasticisers¹⁵. (The Distillers Company Ltd.)

Plastisols are converted into tough rubbery products by heating at about 160°C. At this temperature plasticiser diffusion occurs to give a molecular mixture of plasticiser and polymer. In some processes the paste is only partially fluxed initially to give a 'cheesy' pregel, full gelation being carried out at some later stage.

Organosols (Mix B, Table 12.5) are characterised by the presence of a volatile organic diluent whose function is solely to reduce the paste viscosity. After application it is necessary to remove the diluent before gelling the paste. Organosols are therefore restricted in use to processes in which the paste is spread into a thin film, such as in the production of leathercloth. Because of the extra processes involved, organosols have not been widely used, in Europe at least.

One way of obtaining low-viscosity pastes with a minimum of plasticiser is to use filler polymers (Table 12.5, mix C). As explained in Section 12.4.1 these materials reduce the voids and thus make more plasticiser available for particle lubrication, thus reducing paste viscosity. It has been found that a good filler polymer must have a low plasticiser absorption and a high packing density.²¹ The effect of partial replacement of a paste-making polymer by a filler polymer is shown in Figure 12.26. The use of filler polymer has increased considerably in recent years and greatly increased the scope of PVC pastes. The term *rigisol* is applied to pastes prepared using filler polymers and only small quantities (approx. 20 parts per 100 parts polymer) of plasticiser.

Mix D is a typical *plastigel*. The incorporation of such materials as fumed silicas, certain bentonites or aluminium stearate gives a paste which shows pronounced Bingham Body behaviour (i.e. it only flows on application of a shearing stress above a certain value). Such putty-like materials, which are also

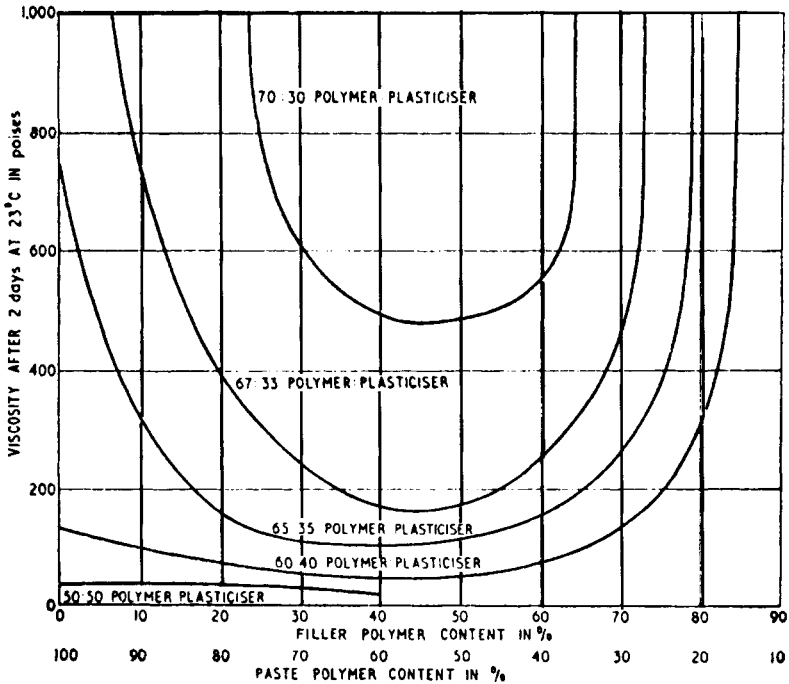


Figure 12.26. Effect on viscosity of partial replacement of a PVC paste polymer (Breon P130/1) in a PVC paste with a non-porous suspension polymer of high packing density¹⁵. (The Distillers Company Ltd.)

usually thixotropic, may be hand shaped and subsequently gelled. Plastigels are often compared with *hot melt compositions*. These latter materials are prepared by fluxing polymer with large quantities of plasticisers and extenders. They melt and become very fluid at elevated temperatures so that they may be poured. These materials are extensively used for casting and prototype work. Formulations for making expanded PVC compounds are of different types and are considered later.

Many different types of equipment are used for mixing PVC pastes, of which sigma-blade trough mixers are perhaps the most popular. To facilitate dispersion it is common practice to mix the dry ingredients initially with part of the plasticiser in order to keep shearing stresses high enough to break down aggregates. The product is then diluted with the remainder of the plasticiser. Before final processing the mix is preferably deaerated to remove occlusions developed during the mixing operation.

Much PVC paste is used in the manufacture of leathercloth by spreading techniques. Cloth is drawn between a roller or endless belt and a doctor blade against which there is a rolling bank of paste. A layer of paste is thus smeared on to the cloth and the paste is gelled by passing through a heated tunnel or underneath infrared heaters. Whilst it is still hot, embossing operations may be carried out using patterned rollers. The cloth is then cooled and wound up. Where a flexible leathercloth is desired a dilatant paste compound is employed so that 'strike-through' is reduced to a minimum. Conversely where it is desired that the paste should enter the interstices of the cloth a shear-thinning paste is employed.

In recent years there has been an increased interest in cellular leathercloth using modified spreading techniques. In some leathercloth formulations the surface has an undesirable tackiness. In such cases this can be overcome by applying a PVC-acrylic lacquer.

Many useful products can be made by dipping heated formers into PVC paste, allowing part of the paste to pregel on to the former, withdrawing the former (and pregel) from the paste and heating in an oven to complete gelation. It is not difficult to produce objects up to $\frac{1}{8}$ in thick in this way, the thickness depending on the temperature of the former, its heat capacity (mass \times specific heat), the time of immersion and the compound formulation. Metal objects may be permanently coated by the same technique.

The slush moulding process is in principle very similar. Paste is poured into a hot mould, some of which pregels and adheres to the walls of the mould cavity. Express paste is poured out and the mould is then heated to complete the gelation of the adhering paste in an oven at about 155–170°C. Both the hot dipping and slush moulding processes involve repeated heating of paste and care must be taken to avoid formation of lumps. Uneven wall thicknesses can occur due to drainage but this may be reduced by the use of the so-called thixotropic fillers, such as fumed silicas, bentonites and aluminium stearate.

In recent years rotational casting methods have made the slush moulding process virtually obsolete. In these processes an amount of material equal to the weight of the finished product is poured into a mould. The mould is then closed and rotated slowly about two axes so that the paste flows easily over the cavity walls in an oven at about 200–250°C. When the compound has gelled, the moulds are cooled and the moulding removed. Compared with the slush moulding process there is no wastage of material, little flash, and more even wall thickness. Completely enclosed hollow articles such as playballs are most conveniently made.

Paste injection moulding processes have also been developed. In one technique used for applying PVC soles to shoe uppers the paste is injected by gas under pressure into a hot mould, the last and shoe upper forming the top half of the mould. The paste gels in the mould, adheres to the upper in the presence of a suitable adhesive and is stripped hot from the mould.

A number of methods have been devised for producing cellular products from PVC pastes. One approach is to blend the paste with carbon dioxide, the latter either in the solid form or under pressure. The mixture is then heated to volatilise the carbon dioxide to produce a foam which is then gelled at a higher temperature. Flexible, substantially open-cell structures may be made in this way. Closed-cell products may be made if a blowing agent such as azodiisobutyronitrile is incorporated into the paste. The paste is then heated in a filled mould to cause the compound to get and the blowing agent to decompose. Because the mould is full, expansion cannot take place at this stage. The mould is then thoroughly cooled and the as yet unexpanded block removed and transferred to an oven where it is heated at about 100°C and uniform expansion occurs.

12.7.4 Copolymers

Vinyl chloride-vinyl acetate copolymers may be processed at lower temperatures than those used for the homopolymer. Their main applications were in gramophone records and flooring. Gramophone record compositions are unfilled

and contain only stabiliser, lubricant, pigment, and, optionally, an antistatic agent. Preheated compound is normally moulded in compression presses at about 130–140°C. Flooring compositions contain about 30–40 parts plasticiser per 100 parts copolymer and about 400 parts filler (usually a mixture of asbestos and chalk). Internal mixer discharge temperatures are typically about 130°C whilst calender roll temperatures are usually some 10–20°C below this.

12.7.5 Latices

Poly(vinyl chloride) is commercially available in the form of aqueous colloidal dispersions (latices). They are the uncoagulated products of emulsion polymerisation process and are used to coat or impregnate textiles and paper. The individual particles are somewhat less than 1 μm in diameter. The latex may be coagulated by concentrated acids, polyvalent cations and by dehydration with water-miscible liquids.

Compounding ingredients are of two types:

- (1) Surface active agents which modify the properties of the latex.
- (2) Ingredients that modify the properties of the end-product.

An example of the first type is the emulsion stabiliser as exemplified by sodium oleyl sulphate, cetyl pyridinium chloride and poly(ethylene oxide) derivatives. For a number of applications it is desirable that the latex be thickened before use, in which case thickening agents such as water-soluble cellulose ethers or certain alginates or methacrylates may be employed. Antifoams such as silicone oils are occasionally required.

Fillers are often employed to reduce the surface tack of the final product. Examples are talc and china clay. If powdered materials are added directly to a latex they compete for the emulsion stabiliser present and tend to coagulate the latex. They are therefore added as an aqueous dispersion prepared by ball milling the filler with water and a dispersing agent, for example a naphthalene formaldehyde sulphonate at a concentration of about 1% of the water content. Heat and light stabilisers which are solids must be added in the same way.

Liquid ingredients, such as plasticisers, are usually added as an emulsion using ammonium oleate as an emulsifying agent. The oleate is formed *in situ* by mixing together the plasticiser and oleic acid and adding this to water containing some ammonia. The emulsion may then be stirred into the latex.

Unplasticised latexes will not form a coherent film on drying and about 25% plasticiser is required before such a film is produced. As with paste it is necessary to flux the compound at about 150–160% in order to produce a useful product.

12.8 APPLICATIONS

PVC might be considered as the material that succeeded in spite of itself. As indicated in the first sentence of this chapter, PVC is one of the least stable of commercially available polymers. The material also has a history which is not entirely to its credit.

The polymer first became well known during World War II as a substitute for natural rubber for wire insulation and for waterproof sheeting. After the war it

retained some of these applications and found additional uses in the areas of flexible sheeting, hose piping and small mouldings. In many instances poor formulation gave the material a bad reputation which took some years to eradicate. Over the years many of the additives came under scrutiny concerning their toxicity but the discovery that the monomer had a number of undesirable toxic characteristics caused considerable alarm and revision of manufacturing procedures in the 1970s. More recently there have been worries concerning the use of plasticisers in applications requiring contact with food. In addition there has been concern about the nature of the decomposition products of fire and of composting. Finally, as a long-established material it was first used in a more utilitarian age so that many of its early applications may be considered to be downmarket or, indeed, obsolescent. Not surprisingly, it has been subject to increasing substitution by newer polymers.

In spite of these problems it was estimated in late 1997 that consumption at the end of the century would be about 24×10^6 t.p.a., second only to polyethylene (@ 46×10^6 t.p.a.) and just ahead of polypropylene (@ 20×10^6 t.p.a.). Global manufacturing capacity of about 28×10^6 t.p.a., is widely distributed around the world with large production capacities not only in North America (6.4×10^6 t.p.a.), Western Europe (6.1×10^6 t.p.a.) and the Western Pacific Rim (10.5×10^6 t.p.a.) but also in South America, Australia, the Indian Sub-continent, and Eastern Europe. Growth rates of some 4.5–5% during the 1980s and 1990s are commensurate with a mature polymer finding difficulty in growing as fast as that of plastics materials in general and losing some long-held markets.

Over 80% of the market is accounted for by suspension homopolymer, 13% by emulsion and paste-forming homopolymer, and the rest is mainly bulk homopolymer and vinyl chloride–vinyl acetate copolymer. In Western Europe about two-thirds of consumption is in the field of unplasticised PVC.

One reason for the success of PVC is its formulation versatility. Products range from rigid piping and window frames to soft flexible foams, with such diverse materials as vinyl leathercloth, flexible sheeting and playballs somewhere in between.

The principal advantages of UPVC are:

- (1) Low cost.
- (2) Good resistance to burning, which may be further enhanced by appropriate selection of additives.
- (3) Excellent weathering behaviour (if correctly formulated).
- (4) Good clarity (if correctly formulated).
- (5) Very good chemical resistance—particularly to hydrocarbons.
- (6) Rigidity and toughness (if correctly formulated).

The largest single use area for UPVC is for pipes and fittings. One particular area here is in chemical plant. It is of course necessary to check that all of the components of the PVC compound will be resistant to any of the chemicals with which the plant is liable to come into contact (at the appropriate temperatures) and also that additives will not be leached out by these chemicals. Particular uses are in acid recovery plant and in plant for handling hydrocarbons.

The second largest market is that of profiles, particularly for the building industry. UPVC has become well established for guttering, waste piping and conduits, where economies arise not just in basic product costs but also in transportation and installation costs. Unlike with cast iron products, corrosion and maintenance is less of a problem, although UPVC products are more liable

to damage. UPVC is widely used for soil pipes and for drainage, with pipes up to 60 cm in diameter being not uncommon. After many years of steady development and careful formulation, UPVC has become widely accepted for window frames. UPVC profiles have also been used for shiplap wall cladding, fencing and bench-type seating, although in many of these cases UPVC materials have not proved sufficiently robust.

UPVC sheet is widely used in building applications. Corrugated sheet is extensively employed in roofing and flat sheet for wall cladding of buildings, particularly where exposed to corrosive chemical atmospheres. Sheet is also used for lining chemical and food processing plant, for thermoforming and for road signs. Transparent film is used for packaging and adhesive tape but in recent years has been increasingly substituted by polypropylene.

Substantial quantities of UPVC are also used for blow moulded containers for such diverse materials as consumable liquids such as fruit squashes, liquids for household use such as detergents and disinfectants, cosmetics and toiletries, and pharmaceuticals. For most of these applications UPVC is in competition with at least one other polymer, particularly poly(ethylene) terephthalate (Chapter 25), polyethylene (Chapter 10), polypropylene (Chapter 11) and, to a small extent, the nitrile resins (Chapter 15). The net result is that in recent years there has been some replacement of PPVC in these areas, in part because of problems of waste disposal.

Plasticised PVC, referred to below as PPVC, is used in a wide variety of applications. Originally a substitute for natural rubber when the latter material became difficult to obtain during World War II, it is frequently the first material to consider where a flexible, even moderately rubbery, material is desired. This arises from the low cost of the compounds, their extreme processing versatility, their toughness and their durability.

The long-established use in wire and cable insulation remains the largest single application area. This is a result of the durability, toughness, reasonable heat resistance and fire resistance and low cost of the compounds. Although the material is of limited use in high-frequency work, it is of great value as an insulator for direct current and low-frequency alternating current carriers. It has almost completely replaced rubber-insulated wire for domestic flex and is widely used industrially. PPVC sheathing may also be used in cables and TV downleads where polyethylene is used as the insulator. It may be noted that in some applicational areas for insulation there has been concern about the generation of toxic and aggressive halogen-containing degradation products in fire situations in closed environments, for example in subways, submarines, ships and aircraft, and this may restrict the use of PPVC insulation.

The market for PPVC film and sheet is only slightly less than for wire and cable insulation. Uses are as diverse as seepage barriers, factory doors, inflatables, baby pants, car trim, covering materials for book bindings and document cases and shower curtains. UPVC film has also been widely used for packaging of food, particularly for shrink-wrap purposes, but this market has been subject to some substitution by polypropylene.

PPVC has also retained a substantial market as a leathercloth, where it is more durable than earlier cellulose-based products. In the 1950s and 1960s it largely replaced leather as a car upholstery material on grounds of cost and durability but was never very popular with consumers. As a result, since the 1970s it has been largely replaced by various fabric materials which have, to this writer at least, proved very durable and preferable in terms of comfort.

Table 12.6 Consumption breakdown of PVC for Western Europe 1997 (source *Modern Plastics* January 1998)

	'000t	%
<i>Unplasticised pvc</i>		
Pipes and conduit	1475	26.5
Profiles	1145	20.5
Film and sheet	605	10.8
Bottles	340	6.1
Injection mouldings	45	0.8
Other	115	2.1
Total UPVC	3725	66.8
<i>Plasticised pvc</i>		
Wire and cable	455	8.2
Film and sheet	380	6.8
Flooring	285	5.1
Coated fabrics	225	4.0
Tube and profiles	215	3.9
Other	280	5.0
Total plasticised pvc	1840	33.0
<i>Other applications</i>		
<i>Adhesives, coatings etc</i>	10	0.2
Grand Total	5575	100

Tubes and profiles remain a small but important market for PPVC, with garden hose being one well-known end-use. Other examples are trim and edging strips for furniture.

UPVC manufactured by paste processes is used not only for leathercloth but for sports equipment and playballs, sheathings and protective covers. PVC is widely used for the manufacture of 'vinyl-coated wallpaper'. Coated fabric is also used in the manufacture of conveyor belting although the reduction in coal mining activities has reduced the demand for this outlet. Furthermore, the comments regarding concern for aggressive, toxic fire degradation products mentioned above with respect to insulation products are equally relevant here. The use of PVC for *foam* has decreased in recent years although the material continues to find some use in rigid cellular applications.

For many years vinyl chloride–vinyl acetate copolymers had two main uses, in flooring compositions and for long playing gramophone records. Whereas the former application remains strong, the use in gramophone records has dropped sharply, particularly since the widespread acceptance of polycarbonate-based compact discs.

The main application areas for PVC are indicated in *Table 12.6*.

Table 12.6 gives a consumption breakdown for Western Europe in 1997. There are three points to be made which are not expressed in the figures. First the clear predominance of rigid or unplasticised pvc is a reversal of the situation of the 1960s when plasticised pvc provided the bulk of the market, particularly in the United States and in Britain. Secondly the grand total figure is only about 10% higher than that given in the 6th edition of this book for the corresponding 1993 figure inferring an annual growth rate of only about 2%. Finally it may be noted that the breakdown in the main consumption areas is similar to the 1993 data, the main differences being a reduction in the importance of the bottles market and the disappearance of consumption for gramophone records as a separate item.

12.9 MISCELLANEOUS PRODUCTS

This chapter has so far dealt with the major fields of use of vinyl chloride polymers, namely plasticised PVC homopolymer, unplasticised PVC, including impact-modified grades, and copolymers particular based on vinyl acetate. There are, however, five particular special forms of vinyl chloride polymer which merit separate consideration, namely crystalline PVC, after-chlorinated PVC (often known as CPVC) and certain graft copolymers and two vinyl-chloride-based copolymers.

12.9.1 Crystalline PVC

The development of stereoregular polyolefins and polydienes as the result of the discovery of Ziegler–Natta-type catalysts not surprisingly stimulated attempts to produce vinyl chloride polymers of increased stereo regularity. Whilst the Ziegler–Natta catalysts cannot be used because they react with both monomer and polymer, low-temperature free-radical polymerisation using γ -radiation and active substances such as alkylboranes has been found to be feasible. Whereas conventional PVC is about 55% syndiotactic and about 5% crystalline, materials polymerised at -50°C are about 65% syndiotactic and 20% crystalline. The T_g also increases steadily with decrease in polymerisation temperature, with a value of about 105°C for PVC polymerised at -50°C . Melting occurs over a range and it has been estimated that the T_m for 100% syndiotactic material would be about 273°C .

It is interesting to note that these crystalline materials do not dissolve in tetrahydrofuran or cyclohexanone at room temperature, indicating that PVC is too weak a proton donor to overcome extensive crystallisation. Crystalline PVC has a greater tensile strength and creep resistance than conventional polymer. It is, however, brittle, and whilst most conventional impact modifiers appear ineffective, EVA polymers are said to be quite useful. Plasticised compounds may also be prepared although mixing temperatures of up to 190°C are necessary.

12.9.2 Chlorinated PVC

The process of post-chlorinating PVC was carried out during World War II in order to obtain polymers soluble in low-cost solvents and which could therefore be used for fibres and lacquers. The derivate was generally prepared by passing chlorine through a solution of PVC in tetrachloroethane at between 50°C and 100°C . Solvents for the product included methylene dichloride, butyl acetate and acetone. These materials were of limited value because of their poor colour, poor light stability, shock brittleness and comparatively low softening point.

In the 1960s materials became available which are said to have been obtained by chlorination at lower temperatures. In one process the reaction is carried out photochemically in aqueous dispersion in the presence of a swelling agent such as chloroform. At low temperatures and in the presence of excess chlorine the halogen adds to the carbon atom that does not already have an attached chlorine. The product is therefore effectively identical with a hypothetical copolymer of vinyl chloride and symmetrical dichloroethylene. An increase in the amount of post-chlorination increases the melt viscosity and the transition temperature. Typical commercial materials have a chlorine content of about 66–67% (c.f. 56.8% for PVC) with a T_g of about 110°C (c.f. approx. 80°C for PVC).

The main applications for CPVC arise from the fact that the material has a softening point of about 100°C and very good chemical resistance. Particular interest has been shown in waste and soil systems which may pass hot water effluents. Calendered sheet may be vacuum formed for uses where hot filling techniques are employed, for example in jam packing.

12.9.3 Graft Polymers Based on PVC

Graft polymerisation techniques have been lately employed in an attempt to obtain improvements in toughness and thermal stability of PVC. Commercial quantities of vinyl chloride grafted on to ethylene–vinyl acetate copolymer and vinyl chloride grafted on to a butadiene–acrylonitrile copolymer have become available as impact modifiers, the latter material being notable in providing tough, transparent blends with only a low tendency to stress-whitening. Vinyl chloride–EVA graft copolymers are used in blends with PVC homopolymers in unplasticised PVC compounds for outdoor service, such as window frames, where good weatherability and impact resistance at low temperature are important. In addition to blending materials, a number of ready-to-use high-impact PVC materials based on graft polymers have become available recently. For example, B 6805 (Lonza Werke) is a graft polymer of vinyl chloride on polyacrylates, whilst Pantalast L (Pantasote Inc.), Vinnol K (Wacker Chemie) and Vestolit BAU (Hüls) are obtained by grafting vinyl chloride onto EVA. In the Rucodor polymers (Hooker), vinyl chloride is grafted onto EPDM. Data on these materials have been collated (ref.22). Grafts of vinyl chloride with ethylene–propylene rubbers have also given polymers of high impact strength. Finally one would mention a recent claim that grafting with *cis*-1,4-polybutadiene substantially improved the thermal stability of PVC.

12.9.4 Vinyl Chloride–Propylene Copolymers

Copolymers of vinyl chloride with 2–10% propylene became available in the USA in 1973 (Sta-Flow by Air Products and Chemicals Inc.). Compared with the vinyl chloride homopolymer these copolymers have a reduced tendency to dehydrochlorination and thus improved heat stability. This is of importance both in application and during processing, and one particular claim made for these products is their ease of moulding.

Typical products have a specific gravity of 1.3–1.4, a tensile strength of 50 MPa and a flexural modulus of 2500 MPa. ASTM Izod impact strengths range from 1 to 25 ft lbf/in of notch according to formulation whilst melt flow may also be varied 100-fold in a similar manner.

Uses reported include motor housings for portable fans, food blender bases, tape storage housings, tough, clear toys, injection blow moulded products and thermoformed packages.

12.9.5 Vinyl Chloride–*N*-cyclohexylmaleimide Copolymers

Attempts to improve the heat deformation resistance of PVC by chlorination or by manufacture of more crystalline grades (see Sections 12.9.1 and 12.9.2) results in a need for much higher processing temperatures and thus reduced processing stability. There may also be a loss in clarity. By copolymerising vinyl chloride with a small amount of *N*-cyclohexylmaleimide the softening point can

be raised without serious detriment to these properties. The improvement is small, 5% of the comonomer raising the Vicat softening point from 80 to 87°C. This is, however, sufficient for the material to be of interest in applications involving short-term exposure to elevated temperature, e.g. filling hot foodstuffs into containers. Such a copolymer has been introduced by Hoechst (Hostalit LP HT 5060).

References

1. REGNAULT, V., *Ann.*, **15**, 63 (1835); *Ann Chim.*, **II**, **59** 358 (1835)
2. REBOUL, N. E., *Jahresber.*, 304 (1872)
3. *German Patent*, 278, 249 (F. Klatt)
4. BAUMANN, E., *Ann.*, **163**, 312 (1872)
5. OSTROMISLENSKY, I., *Chem Zentral.*, **1**, 1980 (1912)
6. *U.S. Patent*, 2, 188, 396
7. *European Chem. News*, **4** (89), 35 (1963)
8. *British Patent*, 842, 690
9. SMALL, P. A., *J. Appl. Chem.*, **3**, 71 (1953)
10. MARVEL, C. S., SAMPLE, J. H., and ROY, M. F., *J. Am. Chem. Soc.*, **61**, 3241 (1939)
11. FLORY, P. J., *J. Am. Chem. Soc.*, **61**, 1518 (1939)
12. FULLER, C. S., *Chem. Rev.*, **26**, 162 (1940)
13. NAITA, G., and CARRADINI, P. *J. Polymer Sci.*, **20**, 262 (1956)
14. MATTHEWS, G. A. R., *Vinyl and Allied Polymers Vol. II, Vinyl Chloride and Vinyl Acetate Polymers*, Iliffe, London (1972).
15. Technical Trade Literature, British Geon Ltd., London
16. JACOBSON, U., *Brit. Plastics*, **34**, 328 (1961)
17. BRAMFITT, J. E., and HEAPS, J. M. *Advances in P. V. C. Compounding and Processing* (Ed. KAUFMAN, M.), Maclaren, London, p. 41 (1962)
18. SKINNER, S. J., and BOLAM, S. E., *Rubber and Plastics Age*, **37**, 169 (1956)
19. WELDON, L. H. P., *Trans. Plastics Inst.*, **24**, 303 (1956)
20. MATTHEWS, G. A. R. *Advances in P. V. C. Compounding and Processing* (Ed. KAUFMAN, M.), Maclaren, London, p. 53 (1962)
21. STOCKER, J. H. J., A. P. I. Project Thesis (1960)
22. ELIAS, H.-G. and VOHWINKEL, F. (Eds.), *New Commercial Polymers—2* (Chapter 2), Gordon and Breach, New York, London (1986)

Bibliography

- BURGESS, R. H. (Ed.), *Manufacture and Processing of PVC*, Applied Science Publishers, London, New York (1981)
- CHEVASSUS, F., and DE BROUTELLES, R., *The Stabilisation of Polyvinyl Chloride*, Edward Arnold, London (1963)
- DUX, J. P., Chapter in *Encyclopedia of Polymer Science and Technology*, Vol. 14, pp. 305–483 (Eds MARK, H. F. and GAYLORD, N. G.), Wiley-Interscience, New York (1971)
- FELGER, H. K. (Ed.), *Kunststoff Handbuch (Bands I and II)—Polyvinylchloride*, Carl Hanser Verlag, München, Wien (1985)
- HENSON, J. H. L., and WHELAN, A. (Eds.), *Development in PVC Technology*, Applied Science, London (1973)
- KAUFMAN, M., *The History of P.V.C.* Maclaren, London (1969)
- KAUFMAN, M. (ED.), *Advances in P.V.C. Compounding and Processing*, Maclaren, London (1962)
- KOLESKA, J. V., and WARTMAN, L. H., *Poly(vinyl chloride)*, Macdonald, London (1969)
- KREKELER, K., and WICK, G., *Kunststoff-Handbuch (Band II)—Polyvinyl chloride*, Hanser, Munich, Pts. I and II (1963) (see also FELGER above)
- MATTHEWS, G. A. R., *Vinyl and Allied Polymers*, Vol. II *Vinyl Chloride and Vinyl Acetate Polymers*, Iliffe, London (1972)
- Multicomponent Polymer Systems* (Advances in Chemistry Series No. 99). American Chemical Society, Washington (1971)
- NASS, L. I., *Encyclopaedia of PVC* Marcel Dekker, New York; Vol. (1976); Vol. 2 (1977)
- OWEN, E. D. (Ed.), *Degradation of Stabilisation of PVC*, Elsevier Applied Science, London–New York (1984)

SARVETNICK, H. A. *Polyvinyl Chloride*, Van Nostrand-Reinhold, New York (1969)

SARVETNICK, H. A. (Ed.), *Plastisols and Organosols*, Van Nostrand-Reinhold, New York (1972)

SEDLACEK B. (Ed.), *Polyvinyl Chloride: Its Formation and Properties* (IUPAC Symposium), Butterworths, London (1971)

TITOW, W. V., *PVC Technology*, 4th edition, Elsevier Applied Science Publishers, London, New York (1984)

WHELAN, A., and CRAFT, J. L. (Eds), *Developments in PVC Production and Processing—I*, Applied Science, London (1977)

Reviews

BIRKNER, H. and NEUNDORF, U., *Kunststoffe*, **77**, 954–9 (1987)

FRANK, A., *Kunststoffe* **80**, (10), 1070–5 (1990)

REHM, T. AND WERNER, R. *Kunststoffe*, **86**(10), 1474–76 (1996)

Fluorine-containing Polymers

13.1 INTRODUCTION

The high thermal stability of the carbon-fluorine bond has led to considerable interest in fluorine-containing polymers as heat-resistant plastics and rubbers. The first patents, taken out by IG Farben in 1934, related to polychlorotrifluoroethylene¹ (PCTFE) (*Figure 13.1* (a)), these materials being subsequently manufactured in Germany and the United States. PCTFE has been of limited application and it was the discovery of polytetrafluoroethylene (PTFE) (*Figure 13.1* (b)) by Plunkett² in 1938 which gave an impetus to the study of fluorine-containing polymers.

The inability to process PTFE by conventional thermoplastics techniques has nevertheless led to an extensive search for a melt-processable polymer but with similar chemical, electrical, non-stick and low-friction properties. This has resulted in several useful materials being marketed, including tetrafluoroethylene-hexafluoropropylene copolymer, poly(vinylidene fluoride) (*Figure 13.1*(d)), and, most promisingly, the copolymer of tetrafluoroethylene and perfluoropropyl vinyl ether. Other fluorine-containing plastics include poly(vinyl fluoride) and polymers and copolymers based on CTFE.

The fluororubbers also form an important class of speciality elastomers and although the market is dominated by the vinylidene fluoride-hexafluoropropylene copolymers a wide range of materials has been produced over the past 40 years.

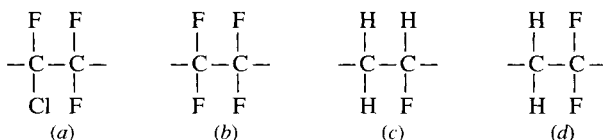


Figure 13.1. (a) Polychlorotrifluoroethylene (PCTFE), (b) Polytetrafluoroethylene (PTFE), (c) Poly(vinyl fluoride), (d) Poly(vinylidene fluoride)

World-wide capacity for fluoropolymers in the late 1990s has been estimated at 90 000 t.p.a. divided roughly equally between Western Europe, North America and the rest of the world. This total is dominated by PTFE although this has decreased from about 80% of the total in 1980 to about 60% in the late 1990s.

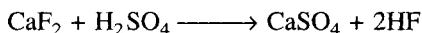
13.2 POLYTETRAFLUOROETHYLENE

In addition to the presence of stable C—F bonds, the PTFE molecule possesses other features which lead to materials of outstanding heat resistance, chemical resistance and electrical insulation characteristics and with a low coefficient of friction. It is today produced by a number of chemical manufacturers such as Du Pont (Teflon), ICI (Fluon), Hoechst (Hostaflon TF), Rhône-Poulenc (Soreflon), Montecatini (Algoflan), Nitto Chemical-Japan (Tetraflon) and Daikin Kogyo-Japan (Polyflon).

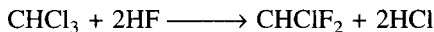
13.2.1. Preparation of Monomer

Tetrafluoroethylene was first prepared in 1933. The current commercial syntheses are based on fluorspar, sulphuric acid and chloroform.

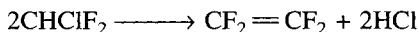
The reaction of fluorspar (CaF_2) and sulphuric acid yields hydrofluoric acid



Treatment of chloroform, obtained by reacting methanol and chlorine, with the hydrofluoric acid yields monochlorodifluoromethane, also used as a refrigerant, which is a gas boiling at -40.8°C .



The monochlorodifluoromethane may be converted to tetrafluoroethylene by pyrolysis, for example by passing through a platinum tube at 700°C .



Other fluorine compounds are produced during pyrolysis, including some highly toxic ring structures. Since very pure monomer is required for polymerisation, the gas is first scrubbed to remove any hydrochloric acid and then distilled to separate other impurities. Tetrafluoroethylene has a boiling point of -76.3°C . For safe storage under pressure the oxygen content should be below 20 ppm. Traces of compounds which react preferentially with oxygen such as 0.5% dipentene, benzaldehyde or methyl methacrylate may be added as stabilisers.

13.2.2 Polymerisation

Pure uninhibited tetrafluoroethylene can polymerise with violence, even at temperatures initially below that of room temperature. There is little published information concerning details of commercial polymerisation. In one patent³ example a silver-plated reactor was quarter-filled with a solution consisting of 0.2 parts ammonium persulphate, 1.5 parts borax and 100 parts water, and with a pH of 9.2. The reactor was closed and evacuated, and 30 parts of monomer

were let in. The reactor was agitated for one hour at 80°C and after cooling gave an 86% yield of polymer.

PTFE is made commercially by two major processes, one leading to the so called 'granular' polymer and the second leading to a dispersion of polymer of much finer particle size and lower molecular weight. One method of producing the latter⁴ involved the use of a 0.1% aqueous disuccinic acid peroxide solution. The reactions were carried out at temperatures up to 90°C. It is understood that the Du Pont dispersion polymers, at least, are produced by methods based on the patent containing the above example.

13.2.3 Structure and Properties

Polytetrafluoroethylene is a linear polymer free from any significant amount of branching (*Figure 13.2*).

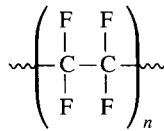


Figure 13.2

Whereas the molecule of polyethylene is in the form of planar zigzag in the crystalline zone this is sterically impossible with that of PTFE due to the fluorine atoms being larger than those of hydrogen. As a consequence the molecule takes up a twisted zigzag, with the fluorine atoms packing tightly in a spiral around the carbon-carbon skeleton. A complete turn of the spiral will involve over 26 carbon atoms below 19°C and 30 above it, there being a transition point involving a 1% volume change at this temperature. The compact interlocking of the fluorine atoms leads to a molecule of great stiffness and it is this feature which leads to the high crystalline melting point and thermal form stability of the polymer.

The intermolecular attraction between PTFE molecules is very small, the computed solubility parameter being $12.6 \text{ (MJ/m}^3\text{)}^{1/2}$. The polymer in bulk does not thus have the high rigidity and tensile strength which is often associated with polymers with a high softening point.

The carbon-fluorine bond is very stable. Further, where two fluorine atoms are attached to a single carbon atom there is a reduction in the C—F bond distance from 1.42 Å to 1.35 Å. As a result bond strengths may be as high as 504 kJ/mole. Since the only other bond present is the stable C—C bond, PTFE has a very high heat stability, even when heated above its crystalline melting point of 327°C.

Because of its high crystallinity and incapability of specific interaction, there are no solvents at room temperature. At temperatures approaching the melting point certain fluorinated liquids such as perfluorinated kerosenes will dissolve the polymer.

The properties of PTFE are dependent on the type of polymer and the method of processing. The polymer may differ in particle size and/or molecular weight. The particle size will influence ease of processing and the quantity of voids in the finished product whilst the molecular weight will influence crystallinity and

hence many physical properties. The processing techniques will also affect both crystallinity and void content.

The weight average molecular weights of commercial polymers appear to be very high and are in the range 400 000 to 9 000 000. ICI report that their materials have a molecular weight in the range 500 000 to 5 000 000 and a percentage crystallinity greater than 94°C as manufactured. Fabricated parts are less crystalline. The degree of crystallinity of the finished product will depend on the rate of cooling from the processing temperatures. Slow cooling will lead to high crystallinity, with fast cooling giving the opposite effect. Low molecular weight materials will also be more crystalline.

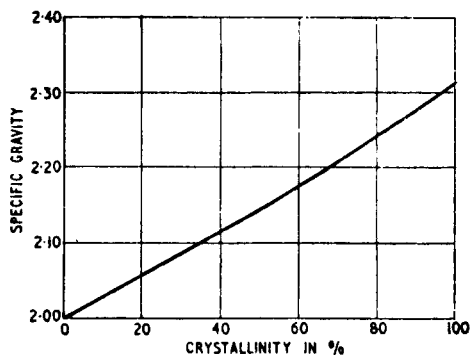


Figure 13.3. Density as a function of crystallinity in PTFE (After Thomas et al.⁵)

Figure 13.3 shows the relationship between percentage crystallinity and specific gravity at 23°C. By measuring the specific gravity of mouldings prepared under rigorously controlled conditions Thomas⁵ and co-workers were able to obtain a measure of molecular weight which they were able to calibrate with results obtained by end-group and infrared analysis (Figure 13.4).

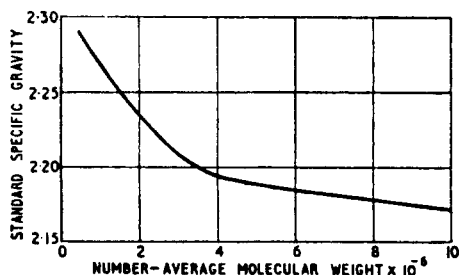


Figure 13.4. Standard specific gravity of PTFE as a function of molecular weight. (After Thomas et al.⁵)

It is observed that the dispersion polymer, which is of finer particle size and lower molecular weight, gives products with a vastly improved resistance to flexing and also distinctly higher tensile strengths. These improvements appear to arise through the formation of fibre-like structures in the mass of polymer during processing.

There has been some recent interest in polymers containing very small proportions (<2000 ppm) of a second comonomer. These can interfere with crystallisation and the resulting products are claimed to have improved compression strength, electrical insulation properties, weldability and transparency compared with the unmodified homopolymers.

13.2.4 General Properties

PTFE is a tough, flexible, non-resilient material of moderate tensile strength but with excellent resistance to heat, chemicals and to the passage of an electric current. It remains ductile in compression at temperatures as low as 4K (-269°C).

Table 13.1 lists some typical values of PTFE mouldings compared with other fluorine-containing thermoplastics.

As with other plastics materials, temperature has a considerable effect on mechanical properties. This is clearly illustrated in Figure 13.5 in the case of stress to break and elongation at break. Even at 20°C unfilled PTFE has a measurable creep with compression loads as low as 300 lbf/in² (2.1 MPa).

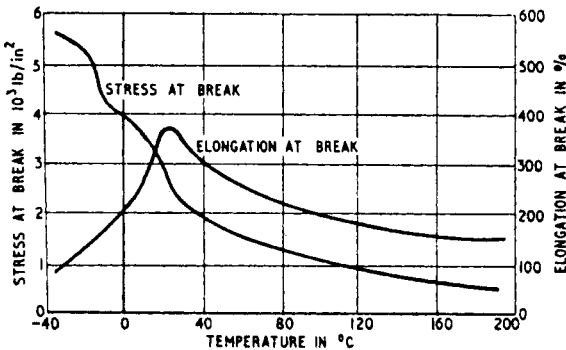


Figure 13.5. Effect of temperature on the stress at break and elongation at break of PTFE.⁶ (Reproduced by permission of ICI Plastics Division)

The coefficient of friction is unusually low and stated to be lower than that of any other solid. A number of different values have been quoted in the literature but are usually in the range 0.02–0.10 for polymer to polymer.

PTFE is an outstanding insulator over a wide range of temperature and frequency. The volume resistivity (100 s value) exceeds 10²⁰ Ω m and it appears that any current measured is a polarisation current rather than a conduction current. The power factor is negligible in the temperature range -60°C to +250°C at frequencies up to 10¹⁰ Hz. The polymer has a low dielectric constant similarly unaffected by frequency. The only effect of temperature is to alter the density which has been found to influence the dielectric constant according to the relationship

$$\text{Dielectric constant} = \frac{1 + 0.238D}{1 - 0.119D}$$

where D = specific gravity

Table 13.1 Properties of PTFE and other fluorine-containing thermoplastics

<i>Property</i>	<i>ASTM test</i>	<i>PTFE</i>	<i>PCTFE</i>	<i>PVF^c</i>	<i>PVDF</i>	<i>TFE-HFP</i>	<i>TFE-ethylene</i>	<i>PFA</i>
Specific gravity	D.792	2.1–2.3	2.1	1.38–1.57*	1.76	2.16	1.70	2.15
Tensile strength at 23°C (lbf/in ²)	D.638	2 500–3 800	4 300–5 700	9.16–19 × 10 ³ *	7 000	2 700–3 100	6 500	4 200
(MPa)	—	17–21	30–39	66–131	48	19–22	45	29
Elongation at break at 23°C (%)	D.638	200–300	100–200	110–260*	100–300	250–350	150	300
Izod impact strength at 23°C (ft lbf in ⁻¹)	D.256	2.0	1.2–1.3	—	3.5	2.9	—	—
Deflection temp. Under load of 66 lbf/in ² (°C)	D.648	121	58	—	150	88	104	74
Water absorption (%)	D.570	0.005	negligible	<0.5	0.04	negligible	<0.02	0.03
Coefficient of friction ²	—	0.09–0.12	0.4	—	—	0.08–0.425	0.4	—
Power of factor 60 Hz	D.150	<0.0003	0.010	0.01 (100c/s)	0.049	<0.0003	0.0006	0.0002
Power factor 10 ⁶ Hz	D.150	<0.0003	0.010	0.08 (10 ⁴ c/s)	0.17	<0.0003	0.005	—
Dielectric constant 60 Hz	D.150	2.1	3.0	6.8–8.5 (10 ³ c/s)	8.4	2.1	2.6	—
Dielectric constant 10 ⁶ Hz	D.150	2.1	2.5	—	6.6	2.1	2.6	2.1
Volume resistivity (Ω m)	D.257	>10 ²⁰	10 ²⁰	10 ¹⁵ –10 ¹⁶	10 ¹⁶	>10 ²⁰	>10 ¹⁶	10 ¹⁸
Dielectric strength ^b (V/0.001 in)	D.149	400–500	530	3 000–6 000*	260	500–600	—	1150

a Polymer to metal.

b short time on 0.080 in thick sheet.

c Tests on Tedlar film. Different test methods involved where marked*

PFA – perfluoroalkoxy resin.

Figure 13.6 shows the influence of temperature on specific volume (reciprocal specific gravity). The exact form of the curve is somewhat dependent on the crystallinity and the rate of temperature change. A small transition is observed at about 19°C and a first order transition (melting) at about 327°C. Above this temperature the material does not exhibit true flow but is rubbery. A melt viscosity of 10^{10} – 10^{11} poises has been measured at about 350°C. A slow rate of decomposition may be detected at the melting point and this increases with a further increase in temperature. Processing temperatures, except possibly in the case of extrusion, are, however, rarely above 380°C.

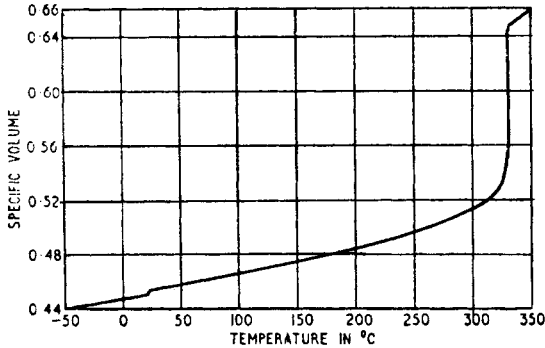


Figure 13.6. Variation of specific volume of PTFE with temperature.⁶ (Reproduced by permission of ICI Plastics Division)

The chemical resistance of PTFE is exceptional. There are no solvents and it is attacked at room temperature only by molten alkali metals and in some cases by fluorine. Treatment with a solution of sodium metal in liquid ammonia will sufficiently alter the surface of a PTFE sample to enable it to be cemented to other materials using epoxide resin adhesives.

Although it has good weathering resistance, PTFE is degraded by high-energy radiation. Exposure to a dosage of 70 Mrad will halve the tensile strength of a given sample. The polymer is not wetted by water and does not measurably absorb it. The permeability to gases is low, the water vapour transmission rate being approximately half that of low-density polyethylene and poly(ethylene terephthalate).

13.2.5 Processing

PTFE is normally available in three forms:

- (1) Granular polymers with median particle size of 300 and 600 μm .
- (2) Dispersion polymer obtained by coagulation of a dispersion. It consists of agglomerates with an average diameter of 450 μm made up of primary particles 0.1 μm in diameter.
- (3) Dispersions (latices) containing about 60% polymer in particles with an average diameter of about 0.16 μm .

The exceptionally high melt viscosity above the melting point (about 10^{10} – 10^{11} poises at 350°C) prevents the use of the usual techniques for

processing thermoplastics. In the case of granular polymers, methods allied to those used with ceramics and in powder metallurgy are employed instead. In principle this involves preforming the powder, usually at room temperature, sintering at a temperature above the melting point, typically at about 370°C, and then cooling.

Preforming is carried out by compressing sieved powder that has been evenly loaded into a mould. It has been shown⁷ that if the pressure is too low there is an excessively large void content whereas if the pressure is too high cleavage planes are produced by one portion of polymer sliding over another. Best results are obtained using a pressure of about 1 tonf/in² (16 MPa). If the powder is preheated at 100°C immediately before preforming, optimum results are obtained at performing pressures of 3.5 tonf/in² (54 MPa). Mouldings made from reforms prepared in this way, i.e. using preheated powder, are found to have tensile strengths appreciably higher than those using cold powder (e.g. 2800 lbf/in² (19 MPa) compared with about 2000 lbf/in² (14 MPa)).

For many applications it is found that the technique of free sintering is quite satisfactory. This simply involves heating the preform in an oven at about 380°C for a time of 90 minutes plus a further 60 minutes for every 0.25 in (0.65 cm) thickness. For example a sample 0.5 in (1.25 cm) thick will require sintering for 3.5 hours. The ovens should be ventilated to the open air to prevent toxic decomposition products accumulating in the working area.

After sintering, the moulding is cooled. Thin sections, i.e. less than $\frac{3}{16}$ in (0.5 cm) thick, may be removed from the oven and allowed to cool naturally or may be quenched by placing between cold flat metal plates and light pressure applied. Sections up to 1 in (2.5 cm) thick are preferably cooled in an oven, cooling at a rate of 20°C/h when maximum dimensional stability is required. Thicker sections are usually cooled under pressure. In this case the preform can be sintered in the preform mould and the mould and moulding then transferred to a press in which they are cooled under a gradually increased pressure. It is necessary that this should reach the preforming pressure as the sample goes through the transition temperature (327°C) and it should be maintained until the sample reaches room temperature.

Shrinkage of about 5–10% occurs at right angles to the direction of the preforming force. The amount of shrinkage is mainly dependent on the rate of cooling, but also to a minor extent, on the preforming pressure.

The above process is limited to simple shapes whose principal dimension is not more than four times, and preferably less than twice, that of the next largest dimension. More intricate shapes must be made by machining or in some instances by a coining operation which involves stamping a sintered moulding of the same weight and approximate dimensions as the finished part at 320°C.

Granular polymer may also be extruded, albeit at very low rates (1–6 in/min, 2.5–16 cm/min), by means of both screw and ram extruders. In both machines the extruder serves to feed cold powder into a long, heated sintering die whose overall length is about 90 times its internal diameter. The polymer, preferably a presintered grade of 600 μm particle size, is compacted, sintered and partially cooled before leaving the die. Since compacting is still taking place as the polymer enters the sintering zone it is possible to obtain extrudates reasonable free from voids, a factor which is reflected in their high tensile strength and elongation.

PTFE mouldings and extrudates may be machined without difficulty. Film may be obtained by peeling from a pressure sintered ring and this may be welded to similar film by heat sealing under light pressure at about 350°C.

Dispersion polymer, which leads to products with improved tensile strength and flex life, is not easily fabricated by the above techniques. It has, however, been found possible to produce preforms by mixing with 15–25% of a lubricant, extruding and then removing the lubricant and sintering. Because of the need to remove the lubricant it is possible to produce only thin-section extrudates by this method.

In a typical process a preform billet is produced by compacting a mixture of 83 parts PTFE dispersion polymer and 17 parts of petroleum ether (100–120°C fraction). This is then extruded using a vertical ram extruder. The extrudate is subsequently heated in an oven at about 105°C to remove the lubricant, this being followed by sintering at about 380°C. By this process it is possible to produce thin-walled tube with excellent flexing fatigue resistance and to coat wire with very thin coatings or polymer.

Tape may be made by a similar process. In this case the lubricant selected is a non-volatile oil. The preform is placed in the extruder and a rod extruded. The rod is then passed between a pair of calender rolls at about 60–80°C. The unsintered tape is often used for lapping wire and for making lapped tube. Sintering is carried out after fabrication. The current most important application of unsintered tape is in pipe-thread sealing.

If sintered tape is required, the product from the calender is first degreased by passing through boiling trichlorethylene and then sintered by passing through a salt bath. This tape is superior to that made by machining from granular polymer mouldings.

PTFE dispersions⁸ may be used in a variety of ways. Filled PTFE moulding material may be made by stirring fillers into the dispersion, coagulating with acetone, drying at 280–290°C and disintegrating the resulting cake of material. Asbestos and glass cloth fabrics may be impregnated with PTFE by passing through the dispersion, drying and sintering the polymer. Glass-cloth PTFE laminates may be produced by plying-up layers of impregnated cloth and pressing at about 330°C. The dispersions are also used for coating PTFE on to metal to produce surfaces which are non-adhesive and which have a very low coefficient of friction.

Whenever PTFE is used in a sintered form there are two points that should always be borne in mind. Firstly, at sintering temperatures toxic cyclic fluorinated compounds are formed and it is thus necessary to ventilate ovens and to use fume hoods whenever fumes of such toxic compounds are produced. It is particularly important that dust should not contaminate cigarettes or tobacco since the smoker will inhale the decomposition products. Secondly, scrupulous standards of cleanliness are necessary to prevent dust, which is frequently organic in nature, contaminating PTFE products before sintering. If this did happen organic dust would carbonise on sintering leaving a product both unsightly and with inferior electrical properties.

13.2.6 Additives

Because of the high processing temperatures there are few pigments suitable for use with PTFE. A number of inorganic pigments, particularly the cadmium compounds, iron oxides and ultramarines, may, however, be used.

The resistance of PTFE to creep can be improved by blending in up to 25% of glass or asbestos fibre using PTFE dispersions as mentioned in the previous section. By the same technique alumina, silica and lithia may be incorporated to

give compounds of improved dimensional stability coupled with good electrical insulation properties. Molybdenum disulphide and graphite improve dimensional stability without losing the low coefficient of friction whilst the use of barium ferrite will produce a material that can be magnetised. The incorporation of titanium dioxide serves to increase the dielectric constant whilst certain compounds of boron increase the resistance to neutron bombardment.

13.2.7 Applications

The use of PTFE in a great diversity of applications may be ascribed to the following properties:

- (1) Chemical inertness.
- (2) Exceptional weathering resistance. Samples exposed in Florida for 10 years showed little change in physical properties.
- (3) The excellent electrical insulation characteristics.
- (4) The excellent heat resistance.
- (5) The non-adhesive properties.
- (6) The very low coefficient of friction.

However, world production is only about 55 000 tonnes per annum and this is a reflection of the high volume cost, the rather specialised techniques involving lengthy processing times and to a smaller extent the high creep rate under load.

Because of its chemical inertness over a wide temperature range it is used in a variety of seals, gaskets, packings, valve and pump parts and in laboratory equipment.

Its excellent electrical insulation properties lead to its use in wire insulation, in valve holders, in insulated transformers, in hermetic seals for condensers, in laminates for printed circuitry and for many other miscellaneous electrical applications.

PTFE is used for lining chutes and coating other metal objects where low coefficients of friction or non-adhesive characteristics are required. Because of its excellent flexing resistance, inner linings made from dispersion polymer are used in flexible steam hose. A variety of mouldings are used in aircraft and missiles and also in other applications where use at elevated temperatures is required.

Table 13.2 Consumption of fluorine-containing plastics for Western Europe 1991

	<i>PTFE</i>		<i>Thermoplastic fluoro materials</i>	
	<i>Consumption (t.p.a.)</i>	<i>%</i>	<i>Consumption (t.p.a.)</i>	<i>%</i>
Chemical industry	3 900	35	1 500	42
Motor construction	2 700	25		
Electrical engineering	1 700	15		
Wire/cable insulation			830	22
Coating			900	25
Other	2 700	25	370	11
Total	11 000		3 600	

Because of its high volume cost PTFE is not generally used to produce large objects. In many cases, however, it is possible to coat a metal object with a layer of PTFE and hence meet the particular requirement.

One significant development in recent years has been the widespread treatment of clothing fabrics to give a measure of water and stain resistance. Mention may also be made of the expression 'Teflon-coated' (Teflon is the DuPont trade name for PTFE) to describe a person, usually a politician, to whom no dirt (i.e. scandal) sticks, a reflection of the non-stick characteristics of the polymer!

Some indication of the relative importance of the various applications is given by the consumption breakdown for fluorine-containing plastics in Western Europe in 1991 is (*Table 13.2*).

13.3 TETRAFLUOROETHYLENE–HEXAFLUOROPROPYLENE COPOLYMERS

These materials were first introduced by Du Pont in 1956 and are now known as Teflon FEP resins. (FEP = fluorinated ethylene–propylene.) Subsequently other commercial grades have become available (Neoflon by Daikin Kogyo and Teflex by Niitechim, USSR). These copolymers may be regarded as the first commercial attempt to provide a material with the general properties of PTFE and the melt processability of the more conventional thermoplastics.

The commercial polymers are mechanically similar to PTFE but with a somewhat greater impact strength. They also have the same excellent electrical insulation properties and chemical inertness. Weathering tests in Florida showed no change in properties after four years. The material also shows exceptional non-adhesiveness. The coefficient of friction of the resin is low but somewhat higher than that of PTFE. Films up to 0.010 in thick show good transparency.

The maximum service temperature is about 60°C lower than that of PTFE for use under equivalent conditions. Continuous service at 200°C is possible for a number of applications. The polymer melts at about 290°C.

Injection moulding and extrusion may be carried out at temperatures in the range of 300–380°C. The polymer has a high melt viscosity and melt fracture occurs at a lower shear rate (about 10^2 s^{-1}) than with low-density polyethylene (about 10^3 s^{-1}) or nylon 66 (about 10^5 s^{-1}). Extruders should thus be designed to operate at low shear rates whilst large runners and gates are employed in injection moulds.

The advantage of being able to injection mould and extrude these copolymers has perhaps had a less marked effect than might have been expected. This is because the fabrication of PTFE has been developed by firms closely related to the engineering industries rather than by the conventional plastics fabricators. The PTFE fabricators, because they do not normally possess conventional injection moulding and extrusion machines, would see no obvious advantage in melt processability. At the same time the conventional plastics fabricators, if they wished to enter the field of fabricated fluorine-containing thermoplastics, would have to modify their existing machinery in order to cope with the processing temperatures and high melt viscosity. In spite of these retarding influences the use of FEP copolymers has grown steadily.

At the present time they are used for a variety of electrical and chemically resistant mouldings, for corrosion-resistant linings, for coatings, for flexible printed circuits and for wire insulation. One particular growth area arising from

the inherent flame retardancy has been for wire and cable insulation, particularly for data networks and for optical fibre insulation.

In the mid-1980s Hoechst introduced a related material, Hostafion TFB, a terpolymer of tetrafluoroethylene, hexafluoropropene and vinylidene fluoride.

13.4 TETRAFLUOROETHYLENE–ETHYLENE COPOLYMERS (ETFE)

A second melt-processable copolymer containing tetrafluoroethylene residues was introduced by Du Pont in 1972 as Tefzel. This material is similar in many properties to the TFE–HFP copolymers but claimed to have exceptional abrasion resistance for a fluorine-containing plastics material. It also has very high impact strength and does not fracture in a notched Izod test at room temperature when subjected to impact stresses as high as $20 \text{ ft lbf in}^{-1}$ ($10.9 \text{ kgf m cm}^{-1}$). Unlike PTFE it cross-links during irradiation. It also differs from PTFE in that glass fibre actually reinforces the polymer, giving tensile strengths as high as $12\,000 \text{ lb/in}^2$ (85/MPa).

This copolymer has proved particularly suitable for wire and cable insulation, with many grades being rated at 155°C for 20 000 h continuous exposure. It is extensively used in electrical systems for aircraft, underground railways, computers, telecommunications installations and heating circuits. Because of its toughness combined with its heat and chemical resistance it also finds use for lining pumps and valves and other equipment for the chemical industry and for laboratory ware.

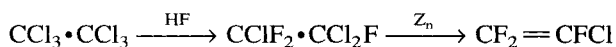
Typical physical properties are listed in *Table 13.1*.

Whereas Tefzel is said to be an internally stabilised copolymer of TFE and ethylene, other copolymers that are compounds of similar copolymers with stabilisers of antioxidants are now also available (Hostafion ET by Hoechst and Aflon by Asahi Glass Co.). Glass-fibre-filled grades are also available.

13.5 POLYCHLOROTRIFLUOROETHYLENE POLYMERS (PCTFE) AND COPOLYMERS WITH ETHYLENE (ECTFE)

Polychlorotrifluoroethylene was the first fluorinated polymer to be produced on an experimental scale and polymers were used in Germany and in the United States early in World War II. PCTFE was used, in particular, in connection with the atomic bomb project in the handling of corrosive materials such as uranium hexafluoride.

The monomer may conveniently be produced from hexachloroethane via trichlorotrifluoroethane



Polymerisation may be carried out by techniques akin to those used in the manufacture of PTFE. The preparation of polymers in yields of up to 88% are described in one patent.⁹ Water was used as a diluent in concentrations of from one to five times the weight of the monomer, a gas with boiling point of -27.9°C . Solid polymers were formed with reaction temperatures of 0 – 40°C ; at higher reaction temperatures liquid polymers are formed.

Pressures varied from 20 to 1500 lbf/in² (0.14 to 10.5 MPa) and reaction times were of the order of 5–35 hours. Reaction promoters included peroxides and salts of persulphuric and perphosphoric acids. ‘Activators’, ‘accelerators’ and buffering agents were also discussed in the patent. The process of manufacture of Kel-F is understood to be based on this patent.

The major differences in properties between PTFE and PCTFE can be related to chemical structure. The introduction of a chlorine atom, which is larger than the fluorine atom, breaks up the very neat symmetry which is shown by PTFE and thus reduces the close chain packing. It is still, however, possible for the molecules to crystallise, albeit to a lower extent than PTFE. The introduction of the chlorine atom in breaking up the molecular symmetry appears to increase the chain flexibility and this leads to a lower softening point. On the other hand the higher interchain attraction results in a harder polymer with a higher tensile strength. The unbalanced electrical structure adversely affects the electrical insulation properties of the material and limits its use in high-frequency applications.

Because of the lower tendency to crystallisation it is possible to produce thin transparent films.

The chemical resistance of PCTFE is good but not as good as that of PTFE. Under certain circumstances substances such as chlorosulphonic acid, molten caustic alkalis and molten alkali metal will adversely affect the material. Alcohols, acids, phenols and aliphatic hydrocarbons have little effect but certain aromatic hydrocarbons, esters, halogenated hydrocarbons and ethers may cause swelling at elevated temperatures.

The polymer melts at 216°C and above this temperature shows better cohesion of the melt than PTFE. It may be processed by conventional thermoplastics processing methods at temperatures in the range 230–290°C. Because of the high melt viscosity high injection moulding pressures are required.

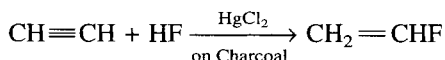
PCTFE is more expensive than PTFE and its use is comparatively limited. With the advent of FEP copolymers, TFE–ethylene copolymers and the perfluoroalkoxy polymers the advantage of melt processability is no longer, alone, a sufficient justification for its use. The particular advantages of the material are its transparency in thin films and its greater hardness and tensile strength as compared to PTFE and FEP copolymers. Examples of its use include gas-tight packaging film for medical and military applications (the main use), transparent windows for chemical and other apparatus where glass or other materials cannot be used, seals, gaskets and O-rings and some electrical applications such as hook-up wire and terminal insulators. Consumption, estimated at 350–400 tonnes per annum, is only about 1% that of PTFE.

PCTFE is marketed by Hoechst as Hostaflon C2 and in the United States by Minnesota Mining and Manufacturing (Kel-F) and Allied Chemical (Halon). Typical values for various physical properties are given in *Table 13.1*.

Copolymers of chlorotrifluoroethylene and ethylene were introduced by Allied Chemicals under the trade name Halar in the early 1970s. This is essentially a 1:1 alternating copolymer compounded with stabilising additives. The polymer has mechanical properties more like those of nylon than of typical fluoroplastic, with low creep and very good impact strength. Furthermore the polymers have very good chemical resistance and electrical insulation properties and are resistant to burning. They may be injection moulded or formed into fibres.

13.6 POLY(VINYL FLUORIDE) (PVF)

Poly(vinyl fluoride) was first introduced in the early 1960s, in film form, by Du Pont under the trade name Tedlar. Details of the commercial method of preparing the monomer have not been disclosed but it may be prepared by addition of hydrogen fluoride to acetylene at about 40°C.



It may also be prepared by pyrolysis of 1,1-difluoroethane at 725°C over a chromium fluoride catalyst in a platinum tube or by the action of zinc dust on bromodifluoroethane at 50°C.

The polymers were first described by Newkirk.¹⁰ Polymerisation may be brought about by subjecting acetylene-free vinyl fluoride to pressures to up to 1000 atm at 80°C in the presence of water and a trace of benzoyl peroxide.

Although poly(vinyl fluoride) resembles PVC in its low water absorption, resistance to hydrolysis, insolubility in common solvents at room temperature and a tendency to split off hydrogen halides at elevated temperatures, it has a much greater tendency to crystallise. This is because the fluorine atom (c.f. the chlorine atom) is sufficiently small to allow molecules to pack in the same way as polythene.

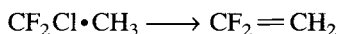
PVF has better heat resistance than PVC and exceptionally good weather resistance. It will burn slowly. Instability at processing temperatures makes handling difficult but this problem has been sufficiently overcome for Du Pont to be able to market their Tedlar film.

PVF film is now being used in the manufacture of weather-resisting laminates, for agricultural glazing and in electrical applications.

13.7 POLY(VINYLLIDENE FLUORIDE)

This melt-processable homopolymer was first introduced in 1961 as Kynar by the Pennsalt Chemical Corporation (the company name being subsequently changed to Pennwalt). Other companies now manufacturing similar polymers are Dynamit Nobel (Dyflor), Kureha (KF), Solvay (Solef) and Atochem (Forafilon).

The monomer is a gas boiling at -84°C which may be made by dehydrochlorination of 1-chloro-1,1-difluoroethane:



or by dechlorination of 1,2-dichloro-1,1-difluoroethane:



Poly(vinylidene fluoride) is a crystalline polymer melting at 171°C. Amongst the melt-processable fluoroplastics the polymer is of interest because of its good mechanical properties and relatively low price. Tensile and impact strengths are good and the material is flexible in thin sections. Although it has generally good chemical resistance, strongly polar solvents such as dimethyl acetamide tend to

dissolve the polymer whilst some strongly basic primary amines such as *n*-butylamine tend to cause embrittlement and discolouration. The polymer is also attacked by some concentrated acids. A further disadvantage of the material is that its dielectric properties are frequency dependent and this limits its use as an electrical insulator. The high dielectric constant is a particular feature.

Of greater interest in recent years have been the peculiar piezoelectric properties¹¹⁻¹³ of poly(vinylidene fluoride). In 1969 it was observed¹¹ that stretched film of the polymer heated to 90°C and subsequently cooled to room temperature in a direct current electric field was 3–5 times more piezoelectric than crystalline quartz. It was observed that the piezoelectric strain coefficients were higher in the drawn film and in the normal directions than in the direction transverse to the film drawing.

The piezoelectric phenomena have been used to generate ultrasonic waves up to microwave frequencies using thin poly(vinylidene fluoride) transducers. In the audio range a new type of loudspeaker has been introduced using the transverse piezoelectric effect on a mechanically biased membrane. This development has been of considerable interest to telephone engineers and scientists.

Poly(vinylidene fluoride) also has interesting pyroelectric properties showing a stable and reversible polarisation which persists after several heating cycles. In consequence the film is used in pyroelectric detectors. PVDF has a wide processing window in that there is a big difference between the melt temperature and the decomposition temperature. Thermal stability may, however, be drastically affected by contaminants, and scrupulous cleanliness is important when processing. The generation of HF should decomposition occur during processing is an obvious hazard. Typical melt temperatures are in the range 240–260°C, with mould temperatures being anything from 30 to 120°C.

The polymer, like many fluorine-containing polymers has very good weathering resistance and may also be used continuously up to 150°C. Outside of the electrical field it finds use in fluid handling, in hot water piping systems, in packaging and in chemical plant. A widely used specific application for PVDF is in ultra-pure water systems for the semiconductor industry.

13.8 OTHER PLASTICS MATERIALS CONTAINING TETRAFLUOROETHYLENE

In 1972 Du Pont introduced Teflon PFA, a copolymer of tetrafluoroethylene and perfluoro(propyl vinyl ether) ($\text{CF}_2 = \text{CFOCF}_2\text{CF}_2\text{CF}_3$). Similar materials are now also produced by Asahi Glass, Daikin, Hoechst and Monteflos and are commonly referred to as PFA fluoropolymers. In 1994 Hoechst introduced Hostafion PFA-N, claimed to have significantly lower melt viscosities than earlier grades of material.

Properties are similar to those of PTFE, and PFA fluoropolymers are generally considered to be the best melt-processable alternative to PTFE yet available. They are, however, more expensive than PTFE. Compared with the TFE–FEP copolymers such as Teflon FEP the PFA fluoropolymers:

- (1) Have a higher melting point (300–310°C).
- (2) Have better processability.
- (3) Retain a higher proportion of their room temperature stiffness and strength at elevated temperatures.

In addition, the polymers are noted for their outstanding flex life, toughness and stress cracking resistance.

PFA fluoropolymers may be processed by injection moulding, extrusion, extrusion blow moulding and transfer moulding. All machine parts coming into contact with the melt should be made from highly corrosion-resistant high nickel content alloys. Processing melt temperatures can be as high as 420°C and mould temperatures may be in the range 50–250°C.

Applications include high-performance insulation for wire and cables (particularly heater cables), and corrosion-resistant linings for pumps, valves, pipes and other chemical equipment. Its availability in the form of film and tubing has led to its demand for both corrosion protection and antistick applications.

Somewhat between PTFE and PFA materials is the product Hostaflon TFM, which is a copolymer of TFE and a small amount of the perfluoro(propyl vinyl ether). It has improved impact strength and weldability and has been promoted as a suitable material for forming into bottles. Yet another TFE–perfluoroalkoxy copolymer was introduced by Du Pont in 1979 as Teflon EPE. This material had a somewhat lower melting point (295°C) than the more common PFA fluoropolymers but it is no longer marketed.

In 1989 Du Pont introduced Teflon AF, said to be a copolymer of tetrafluoroethylene and trifluoromethyldifluorodioxol. This amorphous fluoropolymer has a similar heat and chemical resistance to PTFE but possesses several notable properties, including:

- (1) High optical clarity (>95% in the visible range extending into the near infrared together with a good level of transparency to ultraviolet light).
- (2) A very low refractive index (1.29–1.31).
- (3) The lowest dielectric constant (1.83–1.93) of any known plastics material. (It is to be noted that this is in spite of the fact that the dielectric constant is more than the square of the refractive index, indicating that polarisations other than electronic polarisations are present—see Section 6.3).
- (4) Limited solubility in selected perfluorinated solvents (unique amongst commercial fluoropolymers), enabling solution-cast ultra-thin coatings in the submicrometre thickness range.
- (5) A high coefficient of friction.
- (6) At about £1500/lb it is one of the most expensive plastics materials commercially available.

At the time of writing two grades of the material were available with different comonomer ratios. Typical properties are given in *Table 13.3*.

Table 13.3 Typical properties of Teflon AF amorphous fluoropolymers

<i>Grade</i>	<i>ASTM Method</i>	<i>AF1600</i>	<i>AF2400</i>
T_g (°C)	D3418	160	240
Tensile strength (MPa)	D1708	27	24.6
Ultimate elongation (%)	D1708	20.5	6.1
Tensile modulus (GPa)	D1708	1.55	1.54
Specific gravity	D792	1.78	1.67
Melt viscosity (Pa.s) (at 100 ⁻¹)	D3835	2657 at 250°C	540 at 350°C

The AF polymers are of potential interest in a number of high-technology applications, including the following:

- (1) For coating optical devices for use in chemically aggressive environments.
- (2) Fibre optics applications.
- (3) Semiconductor and dielectric applications.
- (4) Release film coatings of very low thickness.
- (5) Corrosion-resistant coatings and high-permeability separation membranes.

13.9 HEXAFLUOROISOBUTYLENE-VINYLLIDENE FLUORIDE COPOLYMERS

A 50:50 mol/mol copolymer of hexafluoroisobutylene ($\text{CH}_2=\text{C}(\text{CF}_3)_2$) and vinylidene fluoride was made available by Allied Chemical in the mid-1970s as CM-1 Fluoropolymer. The polymer has the same crystalline melting point as PTFE (327°C) but a much lower density (1.88 g/cm^3). It has excellent chemical resistance, electrical insulation properties and non-stick characteristics and, unlike PTFE, may be injection moulded (at $\sim 380^\circ\text{C}$). It is less tough than PTFE.

13.10 FLUORINE-CONTAINING RUBBERS

Fluorine-containing rubbers were originally developed during the search for fluid-resisting elastomers which could be used over a wide temperature range. Much of the initial developmental work was a result of contracts placed by the US Army and Air Force. Whilst the current commercial materials are very expensive compared with general purpose rubbers they find a number of both military and non-military applications, particularly in the area of seals and O-rings.

In order to produce a rubbery material the polymer must have a flexible backbone, be sufficiently irregular in structure to be non-crystalline and also contain a site for cross-linking. These are of course requirements applicable equally to any potential elastomer whether or not it contains fluorine.

The first material to be marketed, Fluoroprene, was introduced by Du Pont in 1948. A polymer of 2-fluorobuta-1,3-diene it was the fluoro analogue of polychloroprene. However, its properties were far from outstanding and production was soon discontinued.

In the early 1950s the fluoroacrylate polymers Poly-1F4 and Poly-2F4 (known initially as PolyFBA) and PolyFMFPA were introduced. These materials had the structures given in *Figure 13.7*. These materials are also no longer of commercial significance.

Much greater success has been achieved with fluororubbers based on vinylidene fluoride (see *Table 13.4*). The copolymer of VDF with hexafluoropropylene (HFP) (typified by Viton A) and the terpolymer of VDF, HFP and TFE (typified by Viton B) are of similar importance and between them probably hold about 95% of the fluororubber market. The terpolymers have better long-term heat resistance, better resistance to swelling in oils and better resistance to chemical degradation, particularly from oil additives. On the other hand, the copolymers have a good balance of properties with a better retention of tensile strength after high-temperature aging, and some copolymer grades have outstanding compression set resistance. Polymers containing hydropenta-

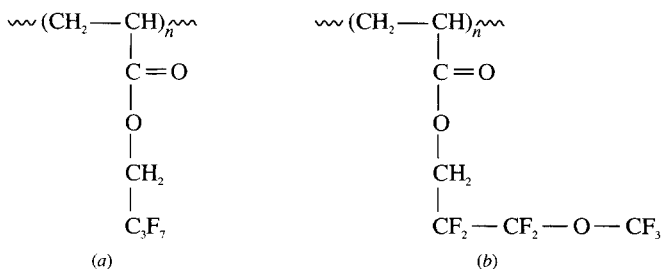


Figure 13.7. (a) Poly 1F4, (b) Poly 2F4

fluoropropylene (early grades of Tecnoflon) appear to have been introduced primarily to circumvent patents but are no longer of importance. On the other hand DuPont have introduced Viton GLT, a terpolymer of tetrafluoroethylene, vinylidene fluoride and perfluoromethyl ether. All of the materials referred to in this paragraph are collectively classified by ASTM as FKM rubbers.

Since their appearance in the 1950s the main developments with these materials have been in their method of vulcanisation. Being saturated rubbers they cannot be vulcanised with sulphur but they could be cross-linked by irradiation or the use of peroxides. Until the 1970s, however, the only agents of commercial importance were diamines and certain of their derivatives. Typical of these materials were ethylenediamine carbamate, hexamethylenediamine carbamate and *N,N'*-dicinnamylidenehexane-1,6-diamine. Amongst the disadvantages of these systems were the high level of compression set shown by the vulcanisates, the generation of double bonds during vulcanisation providing a possible site of degradation, and the generation of up to 2% of water during cure which can cause both porosity and some de-vulcanisation.

Reduction in compression set began to be achieved in the late 1960s when it was found that tropolene and phenanthroline not only accelerated amine cures but were also effective with certain bisnucleophiles such as resorcinol, hydroquinone and bis-phenol AF. In due course even better results were obtained with quaternary ammonium or phosphonium salts being used in conjunction with aromatic dihydroxy compounds.

As with the amine systems such systems still suffered the disadvantage that water was split out during cure. This led to the availability in the late 1970s of peroxide-curable materials containing a cure site of enhanced receptivity to attack by aliphatic radicals. These peroxide-cured elastomers are claimed to have superior resistance to steam, hot water and mineral acids than the earlier systems.

It has been estimated that about 75% of FKM consumption is for O-rings, packings and gaskets for the aerospace industry, whilst automotive and other mechanical goods accounts for about 12%. Although the parts are expensive, motor manufacturers, are nowadays more appreciative of the demand by customers for reliability and increased service intervals. For this reason FKM is now used in valve stem seals, heavy duty automatic and pinion seals, crankshaft seals and cylinder liner O-rings for diesel engines. Other uses include seals for diesel engine glow plugs, seals for pilot-operated slide valves, protective suiting and flue duct expansion joints.

As will be seen from Table 13.4 elastomers are also available which are copolymers of vinylidene fluoride and chlorotrifluoroethylene. These materials

Table 13.4 Commercial fluoroelastomers

<i>Composition</i>	<i>Trade name</i>	<i>Manufacturer</i>	<i>Comments</i>
1. Vinylidene fluoride–hexafluoropropylene copolymer	Viton A Fluorel Tecnoflon	Du Pont MMM	Usually 60–85°C VDF. Most important fluororubber in tonnage terms
2. Vinylidene fluoride–hexafluoropropylene–tetrafluoroethylene terpolymer	Viton B Daiei	Du Pont Daikin Kogyo	Superior heat, Chemical and solvent resistance
3. Vinylidene fluoride– 1-hydropentafluoropropylene	Tecnoflon SL	Montecatini	
4. Vinylidene fluoride– 1-hydropentafluoropropylene– tetrafluoroethylene terpolymer	Tecnoflon T	Montecatini	Superior oil, chemical and solvent resistance
5. Vinylidene fluoride–chlorotrifluoroethylene copolymer	Kel-F 3700 Kel-F 5500 SKF-32	MMM MMM Russia	30% CTFE 50% CTFE
6. Tetrafluoroethylene–perfluoro(methyl vinyl ether) + cure site monomer terpolymer	Kalrez	Du Pont	~40% perfluoro(methyl vinyl ether) Ex. air oxidation resistance to 315°C
7. Substituted poly(phosphonitrilic chloride)	Eypel F	Ethyl Corporation	
8. Tetrafluoroethylene–propylene + cure site monomer terpolymer	Aflas	Asahi Glass	Lower cost alternative to 6
9. Tetrafluoroethylene–propylene–vinylidene fluoride	Fluorel II	MMM	Intermediate between FKM and Aflas
10. Fluorosilicones	LS53 etc.	Dow Corning	Good strength at elevated temperatures

are notable for their superior resistance to oxidising acids such as fuming nitric acid. Elastomeric copolymers of vinylidene fluoride and hypodentafluoroplyene have also been marketed (Tecnoflon by Montedison).

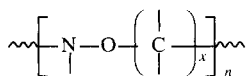
In attempts to further improve the stability of fluorine-containing elastomers Du Pont developed a polymer with no C—H groups. This material is a terpolymer of tetrafluoroethylene, perfluoro(methyl vinyl ether) and, in small amounts, a cure site monomer of undisclosed composition. Marketed as Kalrez in 1975 the polymer withstands air oxidation up to 290–315°C and has an extremely low volume swell in a wide range of solvents, properties unmatched by any other commercial fluoroelastomer. This rubber is, however, very expensive, about 20 times the cost of the FKM rubbers and quoted at \$1500/kg in 1990, and production is only of the order of 1 t.p.a. In 1992 Du Pont offered a material costing about 75% as much as Kalrez and marketed as Zalak. Structurally, it differs mainly from Kalrez in the choice of cure-site monomer.

A terpolymer of tetrafluoroethylene, propylene and a cure site monomer (suggested as triallyl cyanurate by one commentator) has now been marketed by Asahi Glass as Aflas. This rubber may be cross-linked by peroxides to give vulcanisates that swell only slightly in inorganic acids and bases but strongly in chloroform, acetone and hydrocarbons. Compared with the Du Pont material Kalrez, this rubber has a higher T_g (–2°C, c.f. –12°C) and a lower long time heat distortion temperature (less than 200°C) and thus has a narrower temperature range of application. It is stated to be significantly cheaper.

The excellent chemical resistance of Aflas has led to important applications in oilfields and, more recently, in the car industry in place of FKM rubbers because of the better resistance to new types of engine oils, transmission fluids, gear lubricants and engine coolants.

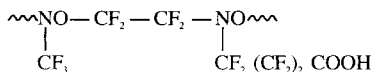
In 1991 MMM announced Fluorel II, a terpolymer of tetrafluoroethylene, vinylidene fluoride and propylene. As might be expected from the structure, this is intermediate between FKM and Aflas, having better resistance to many newer automotive oils, lubricants and transmission fluids than the former but better heat resistance than the latter.

In 1955 Barr and Haszeldine, working in Manchester, prepared nitroso-fluoroelastomers of the general type:



Interest has continued with these materials because of their non-inflammable nature (they will not burn, even in pure oxygen), their excellent chemical resistance, including that of nitrogen tetroxide and chlorine trifluoride, a low T_g of –51°C and an extremely low solubility parameter of 10.6 MPa^{1/2}.

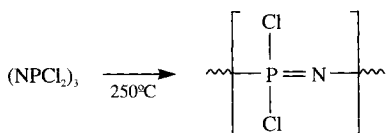
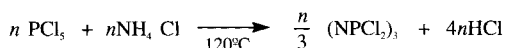
The earliest materials were copolymers of tetrafluoroethylene and trifluoronitrosomethane but they were cross-linked with difficulty and the vulcanisates had little strength. Somewhat better results were obtained using carboxynitrosopolymers of the type



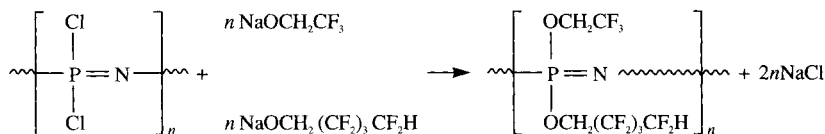
in which perfluoro(nitrosobutyric acid) was used as the cure site monomer.

In general the nitroso rubbers also suffer from a poor resistance to ionising radiation, sensitivity to degradation by organic bases, highly toxic degradation products and an exceptionally high cost. The advent of the rubbers based on perfluoro(methyl vinyl ether) considered above and of the phosphonitrilic elastomers considered below would appear to put the commercial future of these materials in extreme doubt.

These last named materials may be considered as derivatives of the inorganic rubber, polyphosphonitrilic chloride, discovered by Stokes in 1895. This was prepared by the reaction of phosphorus pentachloride with ammonium chloride as follows:



This material had poor hydrolytic stability and was no more than a laboratory curiosity. Treatment with sodium trifluoroethoxide and heptafluorobutoxide has recently been found to yield a useful fluorophosphazene polymer:



The rubber has a very low T_g of -68°C , excellent hydrolytic stability and excellent resistance to ozone, solvents and acids. In addition the rubber does not burn even in an oxidising atmosphere. Although its properties are virtually unchanged in the range -75 to $+120^\circ\text{C}$ it does not possess the heat resistance of other fluoroelastomers. This polymer was marketed by Firestone in the mid-1970s as PNF rubber, but in 1983 the Ethyl Corporation obtained exclusive rights to the Firestone patents and the polymer is now marketed as Eypel F.

In addition to the elastomers already described, others, have been produced on an experimental scale. These include the perfluoroalkylenetriazines with their unsurpassed thermal oxidative stability for an elastomer but with many offsetting disadvantages, and poly(thiocarbonyl fluoride). It is probably true to say that material does not have any outstanding desirable property that cannot now be matched by an alternative and commercially available material.

13.11 THERMOPLASTIC FLUOROELASTOMERS

Over the past 40 years there have been a number of developments that have resulted in the availability of rubbery materials that are thermoplastic in nature and which do not need chemical cross-linking (vulcanisation or setting) to generate elastomeric properties (see also Section 11.8 and 31.2). This approach has been extended to the fluoroelastomers.

The Japanese company Daikin Industries has marketed block copolymers of the ABA type where B is a soft segment that is a terpolymer of vinylidene fluoride, hexafluoropropene and tetrafluoroethylene and A is a hard segment which is either a polyvinylidene fluoride segment or an ethylene, tetrafluoroethylene, hexafluoropropene copolymer. If desired, in order to enhance the properties, the soft segment may be thermoset either by radiation or chemical curing mechanisms. These polymers are made by free radical polymerisation of the B monomers in the presence of organic iodides. At the end of this reaction monomer(s) for the hard segment are charged into the reactor and the terminal iodines cleaved by radicals leaving free radical ends which can initiate chain extension polymerisation of the A segment monomers.

The polymers are marketed under the name Dai-el. Dai-el T530 has a hard segment based on ethylene, tetrafluoroethylene and hexafluoropropene which has a melting point of 220°C, tensile strength of 12 MPa, a resilience of 10% and a 24 h compression set @ 50°C of 11%. Dai-el T630, with the hard segment based on vinylidene fluoride has a lower melting point of 160°C, a tensile strength of only 2 MPa and a compression set (24 h @ 50°C) of 80%.

13.12 MISCELLANEOUS FLUOROPOLYMERS

In addition to the fluoroplastics and fluororubbers already described other fluoropolymers have been marketed. Polymers of hexafluoropropylene oxide are marketed by Du Pont (Krytox). These materials have a low molecular weight (2000–7000) and are either oils or greases. The oils are used as lubricants, heat transfer fluids and non-flammable oils for diffusion pumps. The greases are also used as lubricants. They have good heat and oil resistance but it is said that explosions may result from contact with the surfaces aluminium or magnesium cuttings.

Another Du Pont material (XR-resin) is prepared by copolymerisation of tetrafluoroethylene and the following sulphonyl fluoride vinyl ether:



Saponification to the sulphonic acid yields the product marketed as Nafion. This material is said to be permselective in that it passes cations but not anions. It is used as a membrane material in electrochemical processes, in for example the manufacture of sodium hypochlorite.

Very similar materials have been produced by Asahi Glass which are copolymers of tetrafluoroethylene and ω -carbalkoxy-perfluoroalkoxy vinyl ethers of the general structure



Films of the copolymers are, as with Nafion, saponified and used for permselective membranes. They have a much higher tensile strength than the Du Pont material and are also claimed to have a higher ion exchange capacity.

An interesting aromatic fluoro compound is polytrifluoromethylstyrene, which is claimed to have excellent optical properties (ref. 14).

References

- 1 German Patent, 677,071; French Patent, 796, 026; British Patent, 465, 520 (IG Farben)
2. U.S. Patent, 2,230,654 (Kinetic Chemicals Inc.)
3. U.S. Patent, 2,393,967 (Du Pont)
4. U.S. Patent, 2,534,058 (Du Pont)
5. THOMAS, P. E., LONTZ, J. F., SPERATIC, C. A., and MCPHERSON, J. L., *Soc. Plastics Engrs J.*, **12**,(5) 89 (1956)
6. Technical Trade Literature, ICI Ltd. (Plastics Division), Welwyn Garden City
7. BOWLEY, G. W., *Plastics Progress 1957* (Ed. P. Morgan), Iliffe, London (1958)
8. WHITCUT, H. M., *Plastics Progress 1955* (Ed. P. Morgan) Iliffe, London, p. 103 (1956)
9. U.S. Patent, 2,689,241 (M. W. Kellogg)
10. NEWKIRK, A. E., *J. Am. Chem. Soc.*, **68**, 2467 (1946)
11. KAWNI, H., *Japan J. Appl. Phys.*, **8**, 975 (1969)
12. ZIMMERMAN, R. L., SUCHICITAL, C., and FUKADA, E., *J. Appl. Polymer Sci.*, **19**, 1373 (1975)
13. SUSSNER, H., and DRANSFELD K., *J. Polymer Sci. (Phys.)*, **16** 529 (1978)
14. BÖMER, B. and HAGEMANN, H., *Angew. Makromol. Chem.*, **109-110**, 285 (1982)

Bibliography

- BRYDSON, J.A., *Rubbery Materials and their Compounds*, Applied Science, London (1988)
- COOK, D. and LYNN, M., *Fluoroelastomers – Properties and Applications (RAPRA Review Report 32 (Vol. 3, No. 8) 1990*
- RUDNER, M.A., *Fluorocarbons*, Reinhold, New York (1958)
- SCHILDKNECHT, C.E., *Vinyl and Related Polymers*, John Wiley, New York (1952)
- SHERRATT, S., Contribution to *Encyclopedia of Chemical Technology*, Vol. 9, Interscience, New York, 2nd Edn, pp. 805–831 (1966)
- WALL, L.A. (Ed.), *Fluoropolymers* (High Polymer Series Vol. 25), Wiley-Interscience, New York (1972)
- Technical Service Note F. 12: Physical Properties of Polytetrafluoroethylene*, ICI Ltd. (Plastics Division), Welwyn Garden City (1966)

Reviews

- FITZ, H., *Kunststoffe*, **77**, 1016–19 (1987)
- KORINEK, P. M. *Kunststoffe*, **80**, 1137–41 (1990)
- NIERATSCHKER, J., *Kunststoffe*, **86**, 1524–1528 (1996)

Poly(vinyl acetate) and its Derivatives

14.1 INTRODUCTION

Because of its high cold flow, poly(vinyl acetate) is of little value in the form of mouldings and extrusions. However, because of its good adhesion to a number of substrates, and to some extent because of its cold flow, a large quantity is produced for use in emulsion paints, adhesives and various textile finishing operations. A minor proportion of the material is also converted into poly(vinyl alcohol) and the poly(vinyl acetal)s which, are of some interest to the plastics industry.

The IUPAC systematic name for poly(vinyl acetate) is poly-(1-acetoxyethylene) and that for poly(vinyl alcohol) is poly-(1-hydroxyethylene). As with other common polymers the IUPAC names are not in general use.

In addition to the above materials a number of copolymers containing vinyl acetate have been marketed. Ethylene–vinyl acetate (EVA) copolymers are discussed in Chapter 11 and vinyl chloride–vinyl acetate copolymers in Chapter 12. On the other hand, the commercial ethylene–vinyl alcohol copolymers, although derived from EVA, are considered briefly in this chapter since in weight terms the ethylene component is usually the minor one.

14.2 POLY(VINYL ACETATE)

14.2.1 Preparation of the Monomer

Vinyl acetate was originally prepared industrially¹ by the reaction of acetylene with acetic acid or by oxidation of ethylene.

The first reaction may be carried out either in the liquid or vapour phase although the liquid phase route is now commercially obsolete. In a typical liquid phase preparation, acetylene is passed through an agitated solution of glacial acetic acid and acetic anhydride containing mercuric sulphate, preferably formed *in situ*, in a finely divided state as catalyst.

Owing to the tendency for ethylidene diacetate to be formed at elevated temperatures, care is taken for the rapid removal of vinyl acetate from the reaction vessel as soon as it is formed (*Figure 14.1*).

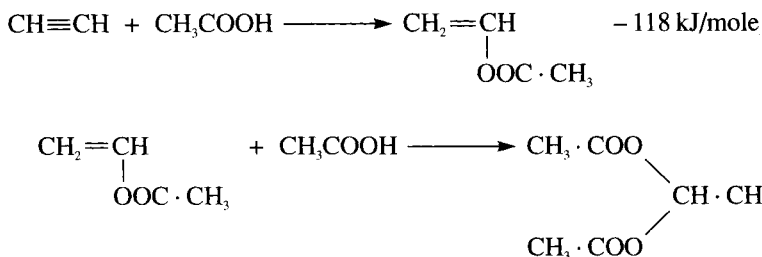


Figure 14.1

In a typical system the reaction vessel is at 75–80°C and the vinyl acetate formed is swept out into a condenser at 72–74°C by means of circulating excess acetylene. This prevents distillation of higher boiling components but allows the vinyl acetate and acetylene through. The former is separated out by cooling and the acetylene recycled.

Vapour phase synthesis may be carried out by passing a mixture of acetylene and acetic acid through a reaction tube at 210–215°C. Typical catalysts for this reaction are cadmium acetate, zinc acetate and zinc silicate. The monomer in each of the above mentioned processes is purified by distillation.

Purified monomer is usually inhibited before shipment by such materials as copper resinate, diphenylamine or hydroquinone, which are generally removed before polymerisation. The monomer is a sweet-smelling liquid partially miscible with water and with the following properties: boiling point at 760 mmHg, 72.5°C; specific gravity at 20°C, 0.934; refractive index n_D^{20} , 1.395; vapour pressure at 20°C, 90 mmHg.

In 1953 the Celanese Corporation of America introduced a route for the production of vinyl acetate from light petroleum gases. This involved the oxidation of butane which yields such products as acetic acid and acetone. Two derivatives of these products are acetic anhydride and acetaldehyde, which then react together to give ethylidene diacetate (Figure 14.2.)

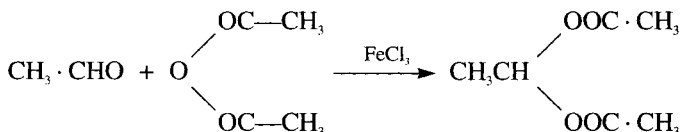
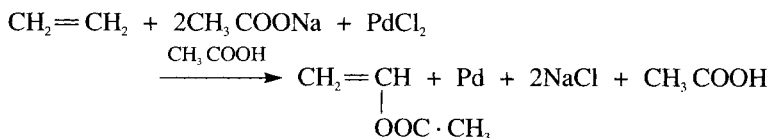


Figure 14.2

Exposure of the ethylidene diacetate to an aromatic sulphonic acid in the presence of five times its weight of acetic anhydride as diluent at 136°C will yield the following mixture: 40% vinyl acetate; 28% acetic acid; 20% acetic anhydride; 4% ethylidene diacetate; 8% acetaldehyde.

The latter four products may all be reused after separation.

In recent years vinyl acetate has been prepared in large quantities by oxidation of ethylene. If ethylene is passed into a solution of palladium chloride in acetic acid containing sodium acetate, then vinyl acetate, ethylene diacetate and acetaldehyde are produced, the vinyl acetate being obtained in good yields by the reaction shown in Figure 14.3

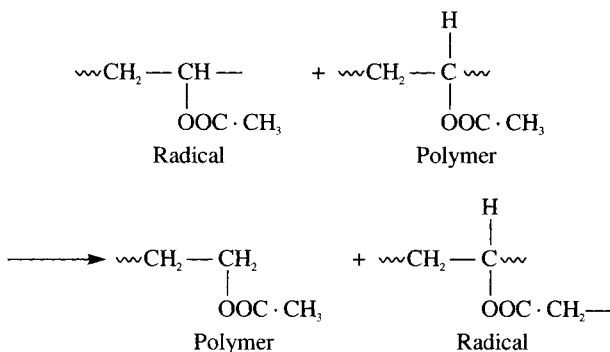
*Figure 14.3*

The ethylene oxidation process can be carried out in either a liquid or a vapour phase but the latter method is often preferred because it avoids corrosion problems and the use of solvents.

A one-stage process for producing vinyl acetate directly from ethylene has also been disclosed. In this process ethylene is passed through a substantially anhydrous suspension or solution of acetic acid containing cupric chloride and copper or sodium acetate together with a palladium catalyst to yield vinyl acetate.

14.2.2 Polymerisation

Vinyl acetate may be easily polymerised in bulk, solution, emulsion and suspension. At conversions above 30%, chain transfer to polymer or monomer may occur. In the case of both polymer and monomer transfer two mechanisms are possible, one at the tertiary carbon, the other (illustrated in *Figure 14.4*) at the acetate group.

*Figure 14.4*

The radical formed at either the tertiary carbon atom or at the acetate group will then initiate polymerisation and form branched structures.

Since poly(vinyl acetate) is usually used in an emulsion form, the emulsion polymerisation process is commonly used. In a typical system, approximately equal quantities of vinyl acetate and water are stirred together in the presence of a suitable colloid-emulsifier system, such as poly(vinyl alcohol) and sodium lauryl sulphate, and a water-soluble initiator such as potassium persulphate.

Polymerisation takes place over a period of about 4 hours at 70°C. The reaction is exothermic and provision must be made for cooling when the batch size exceeds a few litres. In order to achieve better control of the process and to

obtain particles with a smaller particle size, part of the monomer is first polymerised and the rest, with some of the initiator, is then steadily added over a period of 3–4 hours. To minimise the hydrolysis of vinyl acetate or possible comonomers during polymerisation, it is necessary to control the pH throughout reaction. For this purpose a buffer such as sodium acetate is commonly employed.

14.2.3 Properties and Uses

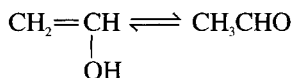
Poly(vinyl acetate) is too soft and shows excessive 'cold flow' for use in moulded plastics. This is no doubt associated with the fact that the glass transition temperature of 28°C is little above the usual ambient temperatures and in fact in many places at various times the glass temperature may be the lower. It has a density of 1.19 g/cm³ and a refractive index of 1.47. Commercial polymers are atactic and, since they do not crystallise, transparent (if free from emulsifier). They are successfully used in emulsion paints, as adhesives for textiles, paper and wood, as a sizing material and as a 'permanent starch'. A number of grades are supplied by manufacturers which differ in molecular weight and in the nature of comonomers (e.g. vinyl maleate) which are commonly used (see Section 14.4.4)

The polymers are usually supplied as emulsions which also differ in the particle size, the sign of the charge on the particle, the pH of the aqueous phase and in other details.

Being an amorphous polymer with a solubility parameter of 19.4 MPa^{1/2}, it dissolves in solvents with similar solubility parameters (e.g. benzene $\delta = 18.8$ MPa^{1/2}, chloroform $\delta = 19.0$ MPa^{1/2}, and acetone $\delta = 20.4$ MPa^{1/2}).

14.3 POLY(VINYL ALCOHOL)

Vinyl alcohol does not exist in the free state and all attempts to prepare it have led instead to the production of its tautomer, acetaldehyde.



Poly(vinyl alcohol) is thus prepared by alcoholysis of a poly(vinyl ester) and in practice poly(vinyl acetate) is used (*Figure 14.5*).

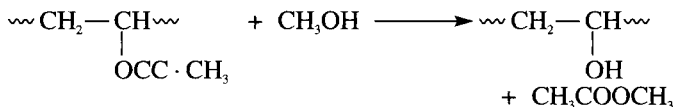


Figure 14.5

The term hydrolysis is sometimes incorrectly used to describe this process. In fact water does not react readily to yield poly(vinyl alcohol)s and may actually retard reaction where certain catalysts are used.

Either methanol or ethanol may be used to effect alcoholysis but the former is often preferred because of its miscibility with poly(vinyl acetate) at room

temperature and its ability to give products of better colour. Where methanol is employed, methyl acetate may be incorporated as a second solvent. It is also formed during reaction. The concentration of poly(vinyl acetate) in the alcohol is usually between 10 and 20%.

Either acid or base catalysis may be employed. Alkaline catalysts such as caustic soda or sodium methoxide give more rapid alcoholysis. With alkaline catalysts, increasing catalyst concentration, usually less than 1% in the case of sodium methoxide, will result in decreasing residual acetate content and this phenomenon is used as a method of controlling the degree of alcoholysis. Variations in reaction time provide only a secondary means of controlling the reaction. At 60°C the reaction may take less than an hour but at 20°C complete 'hydrolysis' may take up to 8 hours.

The use of acid catalysts such as dry hydrochloric acid has been described in the literature but are less suitable when incompletely 'hydrolysed' products are desired as it is difficult to obtain reproducible results.

Commercial poly(vinyl alcohol) (e.g. Gelvatol, Elvanol, Mowiol and Rhodoviol) is available in a number of grades which differ in molecular weight and in the residual acetate content. Because alcoholysis will cause scission of branched polymers at the points where branching has proceeded via the acetate group, poly(vinyl alcohol) polymer will have a lower molecular weight than the poly(vinyl acetate) from which it is made.

14.3.1 Structure and Properties

Poly(vinyl acetate) is an atactic material and is amorphous. Whilst the structure of poly(vinyl alcohol) is also atactic the polymer exhibits crystallinity and has essentially the same crystal lattice as polyethylene. This is because the hydroxyl groups are small enough to fit into the lattice without disrupting it.

The presence of hydroxyl groups attached to the main chain has a number of significant effects. The first effect is that the polymer is hydrophilic and will dissolve in water to a greater or lesser extent according to the degree of 'hydrolysis' and the temperature. Polymers with a degree of 'hydrolysis' in the range of 87–89% are readily soluble in cold water. An increase in the degree of 'hydrolysis' will result in a reduction in the ease of solubility and fully 'hydrolysed' polymers are only dissolved by heating to temperatures above 85°C.

This anomalous effect is due to the greater extent of hydrogen bonding in the completely 'hydrolysed' polymers. Hydrogen bonding also leads to a number of other effects, for example, unplasticised poly(vinyl alcohol) decomposes below its flow temperature. The polymer also has a very high tensile strength and is very tough. Films cast from high molecular weight grades, conditioned to 35% humidity, are claimed² to have tensile strengths as high as 18 000 lbf/in² (125 MPa).

The properties will be greatly dependent on humidity; the higher the humidity, the more the water absorbed. Since water acts as a plasticiser there will be a reduction in tensile strength but an increase in elongation and tear strength. *Figure 14.6* shows the relationship between tensile strength, percentage 'hydrolysis' and humidity.

Because of its high polarity, poly(vinyl alcohol) is very resistant to hydrocarbons such as petrol. Although the polymer will dissolve in lower alcohol-water mixtures, it does not dissolve in pure alcohols. As it is crystalline as well as

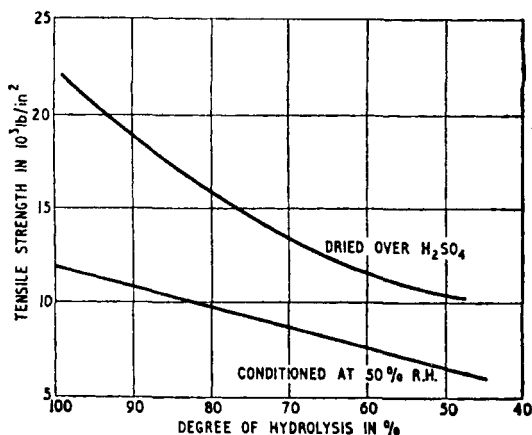


Figure 14.6. Relation between tensile strength and degree of 'hydrolysis' for unplasticised poly(vinyl alcohol) film. (After Davidson and Sittig²)

highly polar only a few organic solvents, such as diethylenetriamine and triethylenetetramine, are effective at room temperature. As might be expected, the hydroxyl group is very reactive and many derivatives have been prepared.

The polymer may be plasticised by polar liquids capable of forming hydrogen bonds with the hydroxyl groups. Glycerin has been used for this purpose.

14.3.2 Applications

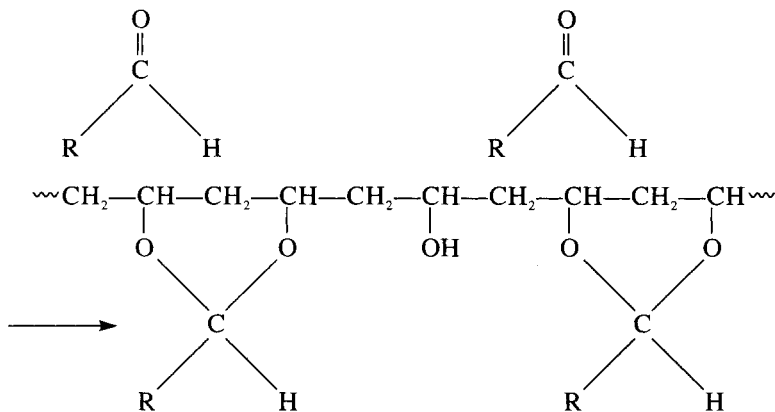
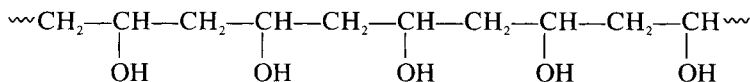
Poly(vinyl alcohol) is employed for a variety of purposes. Film cast from aqueous alcohol solution is an important release agent in the manufacture of reinforced plastics. Incompletely 'hydrolysed' grades have been developed for water-soluble packages for bath salts, bleaches, insecticides and disinfectants. Techniques for making tubular blown film, similar to that used with polyethylene, have been developed for this purpose. Moulded and extruded products which combine oil resistance with toughness and flexibility are produced in the United States but have never become popular in Europe.

Poly(vinyl alcohol) will function as a non-ionic surface active agent and is used in suspension polymerisation as a protective colloid. In many applications it serves as a binder and thickener in addition to an emulsifying agent. The polymer is also employed in adhesives, binders, paper sizing, paper coatings, textile sizing, ceramics, cosmetics and as a steel quenchant.

Japanese workers have developed fibres from poly(vinyl alcohol). The polymer is wet spun from warm water into a concentrated aqueous solution of sodium sulphate containing sulphuric acid and formaldehyde, the latter insolubilising the alcohol by formation of formal groups.

14.4 THE POLY(VINYL ACETALS)

Treatment of poly(vinyl alcohol) with aldehydes and ketones leads to the formation of poly(vinyl acetals) and poly(vinyl ketals), of which only the former products are of any commercial significance (Figure 14.7).



A Poly(Vinyl Acetal)

Figure 14.7

The products are amorphous resins whose rigidity and softening point depend on the aldehyde used. Poly(vinyl butyral), with the larger side chain, is softer than poly(vinyl formal). Since the reaction between the aldehyde and the hydroxyl groups occurs at random, some hydroxyl groups become isolated and are incapable of reaction. A poly(vinyl acetal) molecule will thus contain:

- (1) Acetal groups.
- (2) Residual hydroxyl groups.
- (3) Residual acetate groups, due to incomplete 'hydrolysis' of poly(vinyl acetate) to poly(vinyl alcohol).

14.4.1 Poly(vinyl formal)

The poly(vinyl acetals) may be made either from poly(vinyl alcohol) or directly from poly(vinyl acetate) without separating the alcohol. In the case of poly(vinyl formal) the direct process is normally used.

In a typical process, 100 parts of poly(vinyl acetate) are added to a mixture of 200 parts acetic acid and 70 parts water, which has been warmed to about 70°C, and stirred to complete solution. Sixty parts of 40% formalin and 4 parts sulphuric acid (catalyst) are added and reaction is carried out for 24 hours at 70°C. Water is added to the mixture with rapid agitation to precipitate the granules, which are then washed free from acid and dried.

A number of grades of poly(vinyl formal) are commercially available (Formvar, Mowital) which vary in degree of polymerisation, hydroxyl content and residual acetate content.

*Table 14.1*³ shows the influence of these variables on some properties. The residual hydroxyl content is expressed in terms of poly(vinyl alcohol) content and residual acetate in terms of poly(vinyl acetate) content.

Table 14.1 Influence of structure variables on the properties of poly(vinyl formal)

	ASTM test	Various grades of poly(vinyl formal)				
Av. D. of P.	—	500	500	350	430	350
Poly(vinyl alcohol) (%)	—	5–6	7–9	7–9	5–7	5–7
Poly(vinyl acetate) (%)	—	9.5–13	9.5–13	9.5–13	20–27	40–50
Flow temperature (°C)	D.569–48T	160–170	160–170	140–145	145–150	—
Deflection temperature under load	D.648–49T	88–93	88–93	88–93	75–80	50–60
Tensile strength (10^{-3} lbf/in ²)	D.638–41T	10	10	10	10	10
(MPa)	—	69	69	69	69	69
Elongation (%)	D.638–41T	7–20	10–50	10–50	4–5	3–4
Impact strength (Izod $\frac{1}{2}$ in $\times \frac{1}{2}$ in) (ft lbf in ⁻¹)	D.256–43T	1.2–2.0	1.2–2.0	1.0–1.4	0.5–0.7	0.4–0.6
Water absorption (%)	D.570–40T	0.75	1.1	1.1	1.5	1–5

It will be observed that molecular weight has little effect on mechanical properties but does influence the flow temperature.

The hydroxyl content of commercial material is kept low but it is to be observed that this has an effect on the water absorption. Variation in the residual acetate content has a significant effect on heat distortion temperature, impact strength and water absorption. The incorporation of plasticisers has the usual influence on mechanical and thermal properties.

The polymer, being amorphous, is soluble in solvents of similar solubility parameter, grades with low residual acetate being dissolved in solvents of solubility parameter between 19.8 and 22 MPa^{1/2}.

The main application of poly(vinyl formal) is as a wire enamel in conjunction with a phenolic resin. For this purpose, polymers with low hydroxyl (5–6%) and acetate (9.5–13%) content are used. Similar grades are used in structural adhesive (e.g. Redux) which are also used in conjunction with phenolic resin. Poly(vinyl formal) finds some use as a can coating and with wash primers. Injection mouldings have no commercial significance since they have no features justifying their use at current commercial prices.

14.4.2 Poly(vinyl acetal)

Poly(vinyl acetal) itself is now of little commercial importance. The material may be injection moulded but has no particular properties which merit its use. It is occasionally used in conjunction with nitrocellulose in lacquers, as a vehicle for wash primers and as a stiffener for fabrics.

14.4.3 Poly(vinyl butyral)

As a safety glass interleaver, poly(vinyl butyral) (Butacite, Saflex) is extensively used because of its high adhesion to glass, toughness, light stability, clarity and moisture insensitivity.

It also finds miscellaneous applications in textile and metal coatings and in adhesive formulations. Where it is to be used as a safety glass interleaver, a very pure product is required and this is most conveniently prepared from

poly(vinyl alcohol) rather than by the direct process from poly(vinyl acetate).

In a typical process 140 parts of fully 'hydrolysed' poly(vinyl alcohol) are suspended in 800 parts of ethanol; 80 parts of butyraldehyde and 8 parts of sulphuric acid are added and the reaction is carried out at about 80°C for 5–6 hours.

The solution of poly(vinyl butyral) is diluted with methanol and the polymer precipitated by the addition of water during vigorous agitation. The polymer is then stabilised, washed and dried.

Highly 'hydrolysed' poly(vinyl alcohol) is normally used as a starting point. For safety glass applications about 25% of the hydroxyl groups are left unreacted. In this application the polymer is plasticised with an ester such as dibutyl sebacate or triethylene glycol di-2-ethyl butyrate, about 30 parts of plasticiser being used per 100 parts of polymer. The compound is then calendered to a thickness of 0.015 in and coated with a layer of sodium bicarbonate to prevent blocking. To produce safety glass the film is washed and dried and then placed between two pieces of glass which are then subjected to mild heat and pressure. Bulletproof glass is made by laminating together several layers of glass and poly(vinyl butyral) film.

Laminated safety glass has now become standard for automobile wind-screens and is used for aircraft glazing.

14.5 ETHYLENE-VINYL ALCOHOL COPOLYMERS

If ethylene is copolymerised with vinyl acetate, and the vinyl acetate component 'hydrolysed' to vinyl alcohol, a material is produced which is in effect a copolymer of ethylene and vinyl alcohol.

The material is produced by Kuraray and Nippon Gohsei in Japan and was also produced up until 1993 by Du Pont. Global nameplate capacity has increased from about 30 000 t.p.a. early in the 1990s to 60 000 t.p.a. at the end of the millenium. The material is commonly referred to in the abbreviated form EVOH but occasionally also as EVAL and EVOL.

Certain copolymers of this type have been found to have excellent gas barrier properties, with the dry polymer having an oxygen permeability only about 1/10th that of polyvinylidene chloride. Unsurprisingly, the copolymer has a high moisture absorption and a high moisture vapour transmission rate. Where the material is swollen by water, gas permeability is also higher.

For reasons explained below, the effect of increasing the 'vinyl alcohol' content in EVOH is quite different to that of increasing the vinyl acetate content in EVA. In the case of ethylene-vinyl acetate (EVA) copolymers, increasing the vinyl acetate content up to about 50% makes the materials less crystalline and progressively more flexible and then rubbery. In the range 40–70% vinyl acetate content the materials are amorphous and rubbery, whilst above 70% the copolymers become increasingly rigid and brittle.

Commerical grades of EVOH typically have 'vinyl alcohol' contents in the range 56–71%, but in contrast to the corresponding EVA materials these copolymers are crystalline. Furthermore, an increase in the 'vinyl alcohol' content results in an *increase* in such properties as crystalline melting point, tensile strength and tensile modulus together with a decrease in oxygen permeability. This is a reflection of the fact that the ethylene and vinyl alcohol units in the chain are essentially isomorphous (see Sections 4.4 and 14.3.1).

Table 14.2 Typical properties of EVOH copolymers (For purposes of comparison the grades selected all have a MFI (2.16 kg, 190°C) of 1.7–1.8. Grades with other MFI values are also available)

	Ethylene content (mole %)			
	29	32	38	44
Specific gravity	1.21	1.19	1.17	1.14
T_m (by DSC) (°C)	188	183	173	164
T_g (by DSC) (°C)	62	61	58	55
Tensile strength (MPa)	96	89	75	62
Elongation at break (%)	75–150	100–200	>180	>280
Tensile modulus (MPa)	3900	3700	3100	2700
Oxygen permeability cc.20 μm^2 24 h atm.				
0% RH, 20°C	0.23	0.30	0.53	1.20
25% RH, 25°C	0.8	0.9	1.4	2.6

Some typical properties of some commercial EVOH polymers (Soarnol—Nippon Gohsei) are given in *Table 14.2*.

As is to be expected, the table shows that as the humidity is increased, causing swelling and an increase in the interchain separation, so the oxygen permeability increases. Also, as expected, the percentage increase is greater the higher the vinyl alcohol content.

Because of the excellent gas barrier properties, EVOH is of interest as a packaging material. However, because of its high water absorption it is usually used as an internal layer in a co-extruded film, sheet, bottle or tube. For example, the system HDPE–EVOH–EVA may be used as a barrier film for packaging cereals, and the system polystyrene–EVOH–polystyrene for packaging coffee and cream, whilst the system polystyrene–EVOH–polyethylene has the additional advantage of heat sealability.

In the case of EVOH being used as an interlayer with polyethylene or polystyrene, it is necessary to use additional adhesive layers such as an ethylene–vinyl acetate–maleic anhydride terpolymer (e.g. Orevac—Atochem).

While EVOH is of interest primarily for food packaging applications attention is now being turned to non-food outlets such as automotive fuel tanks, floor heating pipes and toothpaste tubes.

14.6 POLY(VINYL CINNAMATE)

Poly(vinyl cinnamate) is not used in the traditional areas of plastics technology but its ability to cross-link on exposure to light has led to important applications in photography, lithography and related fields as a photoresist.

The concept of a *photoresist* is of great antiquity and has a number of features of interest relating to plastics. In Ancient Egypt mummies were wrapped in linen cloths dipped in a solution of oil of lavender containing high molecular mass bituminous material (Chapter 30) which was known variously as Syrian Asphalt or Bitumen of Judea. On exposure to light the product hardened and became insoluble. The evidence is that some form of cross-linking occurred.

At the beginning of the nineteenth century, an amateur Egyptologist, J. Nicéphore Niepce, became interested in the process and in 1822 he adapted it to produce the first permanent photograph. It also played an important role in the development of lithography. In essence surfaces exposed to light become insoluble and cannot be removed by solvents whilst unexposed surfaces remain soluble and can be so removed. This is the concept of a negative photoresist. (There also exist positive photoresists, including some phenolic resins, which become more soluble on exposure to light). Today photoresists are used in the fabrication of solid-state electronic components and integrated circuits and poly(vinyl cinnamate) is one of the longest established materials of this type.

As with poly(vinyl alcohol), poly(vinyl cinnamate) is prepared by chemical modification of another polymer rather than from 'monomer'. One process is to treat poly(vinyl alcohol) with cinnamoyl chloride and pyridine but this is rather slow. Use of the Schotten Baumann reaction will, however, allow esterification to proceed at a reasonable rate. In one example⁴ poly(vinyl alcohol) of degree of polymerisation 1400 and degree of saponification of 95% was dissolved in water. To this was added a concentrated potassium hydroxide solution and then cinnamoyl chloride in methyl ethyl ketone. The product was, in effect a vinyl alcohol-vinyl cinnamate copolymer (*Figure 14.8*)

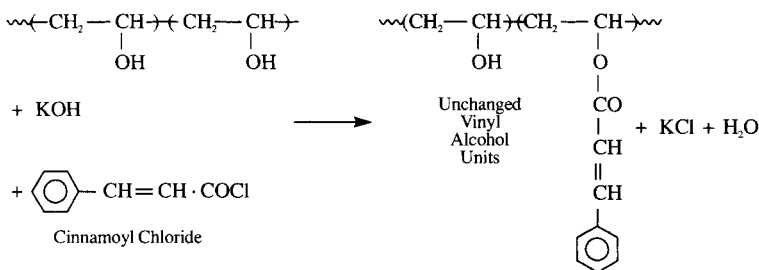


Figure 14.8

To make a photoresist poly(vinyl cinnamate), or a high vinyl cinnamate copolymer, is dissolved in a solvent such as methylene dichloride and the solution is coated uniformly over the substrate by a process such as spin casting. After evaporation of the solvent a masking material (which in the case of a simple demonstration could be a paper clip) is placed on the resist and the assembly is exposed to ultraviolet light. The exposed surfaces are then insolubilised. After exposure the mask is removed and soluble matter dissolved in a solvent such as cellosolve acetate and this exposes the substrate in the shape of the mask. This may then be etched or otherwise treated as required. By the use of appropriate sensitisers such as 1,2-benzanthraquinone or Michler's ketone the cross-linking may be brought about by visible light. The cross-linking is believed to involve the production of a four-membered cyclobutane ring (*Figure 14.9*).

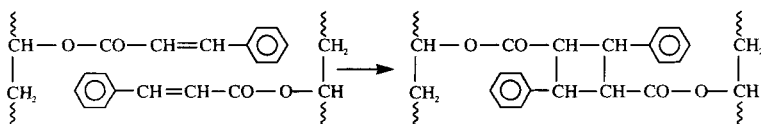


Figure 14.9

14.7 OTHER ORGANIC VINYL ESTER POLYMERS

Polymers from many other vinyl esters, such as vinyl propionate, vinyl caproate, vinyl benzoate, vinyl stearate and vinyl laurate, have been prepared on a commercial scale. As is to be expected, increasing the length of the side chain reduces the softening point of the polymer so that polymers similar in many ways to the higher acrylates and methacrylates may be obtained. It is also of interest to note that, as with acrylates and methacrylates, the glass transitions of the polymers go through a minimum with about twelve carbon atoms in the side chain, side-chain crystallisation becoming important with higher homologues.

Of the higher vinyl ester homopolymers only poly(vinyl propionate) is currently believed to be of commercial value, being marketed as Propiofan (BASF) for surface coating application where greater alkali resistance is possible than with the normal vinyl acetate based copolymers.

Whilst vinyl acetate is reluctant to copolymerise it is in fact usually used today in copolymers. Two of particular interest to the plastics industry are ethylene-vinyl acetate (Chapter 11) and vinyl chloride-vinyl acetate copolymers (Chapter 12). In surface coatings internal plasticisation to bring the T_g to below ambient temperatures and thus facilitate film forming is achieved by the use of ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate and dialkyl maleates and fumarates.

References

1. HORN, O., *Chem. Ind.*, 1749 (1955)
2. DAVIDSON, R.L., and SITTING, M., *Water-soluble Resins*, Reinhold, New York (1962)
3. FITZHUGH, A.F., and LAVIN, E., *J. Electrochem. Soc.*, **100** (8), 351 (1953)
4. DELZENNE, G.A., *Encyclopaedia of Polymer Science and Technology, Supplement*, Vol.1, p.401, Wiley, New York (1976)

Bibliography

General

- KAINER, F., *Polyvinylalkohole*, Enka, Stuttgart (1949)
- LEONARD, E. C. (Ed.), *Vinyl and Diene Monomers* (High Polymers Series Vol. 24), Wiley-Interscience, New York (1971)
- SCHILDKNECHT, C.E., *Vinyl and Related Polymers*, John Wiley, New York (1952)
- Encyclopaedia of Polymer Science and Technology* Vols. 14 and 15, Wiley-Interscience, New York (1971)

Polyvinyl Acetate

- WHEELER, O.L., LAVIN, E., and CROZIER, R.N., *J. Polymer Sci.*, **9**, 157 (1952)

Polyvinyl Alcohol

- Brit. Plastics*, **16**, 77, 84, 122 (1944)
- DAVIDSON, R.L., and SITTING, M., *Water-soluble Resins* (2nd Ed.), Reinhold, New York (1968)
- FINCH, C.A. (Ed.), *Polyvinyl alcohol: Properties and Applications*, Wiley New York (1973)
- PRITCHARD, J.G., *Poly(Vinyl alcohol): Basic Properties and Uses*, Macdonald, London (1970)
- Properties and Applications of Polyvinyl Alcohol* (SCI Monograph No. 30), Society of the Chemical Industry, London (1968)

Polyvinyl Acetals

- FITZHUGH, A.F. and LAVIN, E., *J. Electrochem. Soc.*, **100** (8), 351 (1953)
- PLATZER, N. *Mod. Plastics*, **28**, 142 (1951)

Acrylic Plastics

15.1 INTRODUCTION

Poly(methyl methacrylate) (*Figure 15.1, I*) is, commercially, the most important member of a range of *acrylic* polymers which may be considered structurally as derivatives of acrylic acid (*II*).

This family includes a range of polyacrylates (*III*), polymethacrylates (*IV*) and the important fibre-forming polymer, polyacrylonitrile (*V*).

Methyl, ethyl and allyl acrylate were first prepared in 1873 by Caspary and Tollens,¹ and of these materials the last was observed to polymerise. In 1880 Kahlbaum² reported the polymerisation of methyl acrylate and at approximately the same time Fittig^{3,4} found that methacrylic acid and some of its derivatives readily polymerised.

In 1901 Otto Röhm reported on his studies of acrylic polymers for his doctoral dissertation. His interest in these materials, however, did not cease at this stage and eventually in 1927 the Röhm and Hass concern at Darmstadt, Germany commenced limited production of poly(methyl acrylate) under the trade names

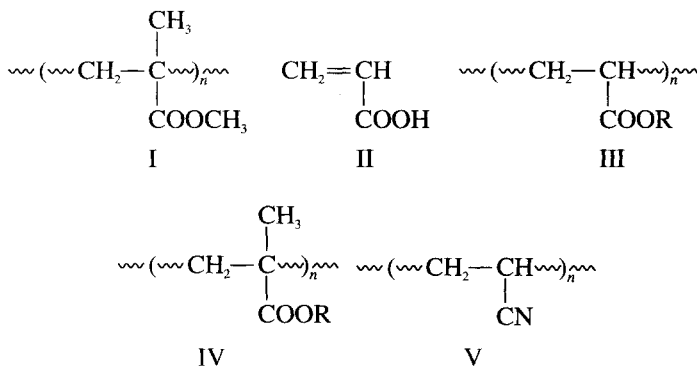


Figure 15.1

Acryloid and Plexigum. These were soft gummy products of interest as surface coatings rather than as mouldable plastics materials. About 1930 R. Hill in England and W. Bauer in Germany independently prepared poly(methyl methacrylate) and found it to be a rigid, transparent polymer, potentially useful as an aircraft glazing material.⁵

The first methacrylic esters were prepared by dehydration of hydroxyisobutyric esters, prohibitively expensive starting points for commercial synthesis. In 1932 J. W. C. Crawford⁶ discovered a new route to the monomer using cheap and readily available chemicals—acetone, hydrocyanic acid, methanol and sulphuric acid—and it is his process which has been used, with minor modifications, throughout the world. Sheet poly(methyl methacrylate) became prominent during World War II for aircraft glazing, a use predicted by Hill in his early patents, and since then has found other applications in many fields.

Examples of commercial poly(methyl methacrylate) sheet are Perspex (ICI), Oroglas and Plexiglas (Atoglas). Poly(methyl methacrylate) moulding powders include Diakon (ICI), Acry-ace (Fudow Chemical Co., Japan), Lucite (Du Pont) and Vedril (Montecatini).

In addition to poly(methyl methacrylate) plastics and polyacrylonitrile fibres, acrylic polymers find widespread use. First introduced in 1946, acrylic rubbers have become established as important special purpose rubbers with a useful combination of oil and heat resistance. Acrylic paints have become widely accepted particularly in the car industry whilst very interesting reactive adhesives, including the well-known 'super-glues' are also made from acrylic polymers.

During the 1970s there was considerable interest for a time in copolymers with a high acrylonitrile content for use as barrier resins, i.e. packaging materials with low permeability to gases. Problems associated with free acrylonitrile have, however, led to the virtual disappearance of these materials from the market.

Other developments in recent years have been the appearance of tough and heat-resistant materials closely related to poly(methyl methacrylate) and to interesting cross-linked polymers. Amongst these are the so-called hydrophilic polymers used in the making of soft contact lenses.

Today a very wide range of acrylic materials is available with a broad property spectrum. The word *acrylic*, often used as a noun as well as an adjective in everyday use, can mean quite different things to different people. In the plastics industry it is commonly taken to mean poly(methyl methacrylate) plastics, but the word has different meanings, to the fibre chemist and to those working in the paint and adhesives industries. Unless care is taken this may be a source of some confusion.

As with other major plastics materials, there is at present little use of the IUPAC systematic nomenclature, which is based on the nature of the repeating unit rather than the monomer used. The following names may, however, be noted:

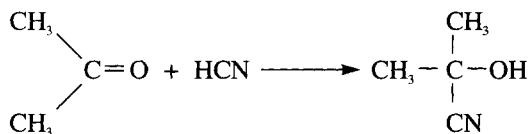
<i>Trivial name</i>	<i>IUPAC name</i>
Poly(acrylic acid)	Poly-[l-(carboxy)ethylene]
Poly(acrylonitrile)	Poly-[l-(cyano)ethylene]
Poly(methyl acrylate)	Poly-[l-methoxycarbonyl]ethylene]
Poly(methyl methacrylate)	Poly-[l-methoxycarbonyl]-l-methylethylene]

15.2 POLY(METHYL METHACRYLATE)

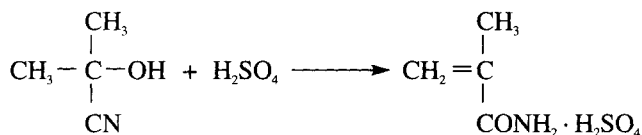
15.2.1 Preparation of Monomer

This successful commercial utilisation of poly(methyl methacrylate) is due in no small measure of the process of producing the monomer from acetone developed by Crawford of ICI which enabled the polymer to be produced at a competitive price. Some details of the process as operated by the Röhm and Hass Company of Philadelphia have been disclosed.⁷

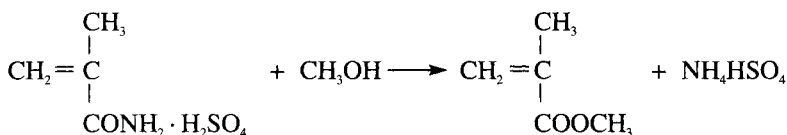
Acetone is first reacted with hydrogen cyanide to give acetone cyanohydrin (*Figure 15.2*)

*Figure 15.2*

The cyanohydrin is then treated with 98% sulphuric acid in a cooled hydrolysis kettle to yield methacrylamide sulphate (*Figure 15.3*)

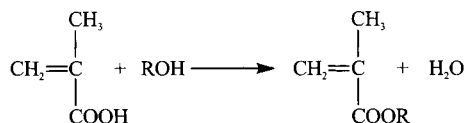
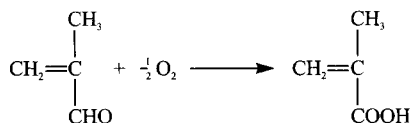
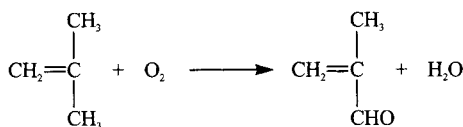
*Figure 15.3*

The sulphate is not isolated from the reaction mixture, which passes into an esterification kettle and reacts continuously with methanol (*Figure 15.4*).

*Figure 15.4*

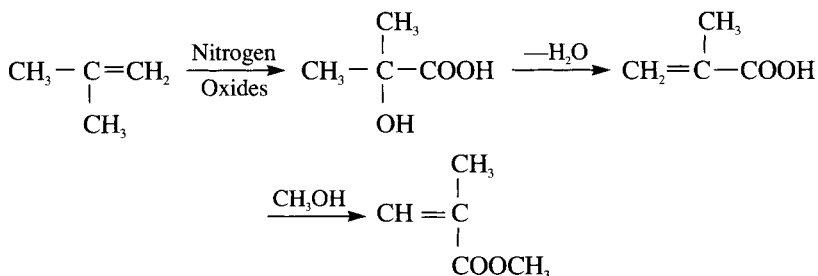
The esterified stream, which may contain inhibitors to prevent premature polymerisation, is then passed to a stripping column which separates the methyl methacrylate, methanol and some water from the residue made up of sulphuric acid, ammonium bisulphate and the remainder of the water. The methyl methacrylate is subsequently separated and purified by further distillation.

Because of limitations on the ready availability of HCN, particularly in Japan, processes involving the oxidation of C₄ intermediates have been developed and are now replacing the older route developed by Crawford. One important process is based on the two-stage oxidation of isobutylene or *t*-butyl alcohol to methacrylic acid, which is then separated and esterified (*Figure 15.5a*).



(a)

(Japan Koka 74117425, 7795609, 79300008, 78109889, USP 3 928 462)



(b)

Figure 15.5

This process appears to be very similar to the process developed by the Escambia Chemical Company which has been known for over 30 years and mentioned in all the previous editions of this book (Figure 15.5b).

The monomer is a mobile liquid with a characteristic sweet odour and with the following properties:

Boiling point (760 mmHg)	100.5°C
Density D_4^{20}	0.936–0.940 g/cm ³
Refractive index n_D^{20}	1.413–1.416
Heat of polymerisation	48.5 kJ/mole

15.2.2 Polymerisation

Methyl methacrylate will polymerise readily and the effect may be observed with non-inhibited samples of monomers during storage. In commercial practice the monomer is supplied with up to 0.10% of an inhibitor such as hydroquinone, which is removed before polymerisation, either by distillation under reduced pressure or, in some cases, by washing with an alkaline solution.

Free-radical polymerisation techniques involving peroxides or azodi-isobutyronitrile at temperatures up to about 100°C are employed commercially. The presence of oxygen in the system will affect the rate of reaction and the nature of the products, owing to the formation of methacrylate peroxides in a side reaction. It is therefore common practice to polymerise in the absence of oxygen, either by bulk polymerisation in a full cell or chamber or by blanketing the monomer with an inert gas.

It has been observed that in the polymerisation of methyl methacrylate there is an acceleration in the rate of conversion after about 20% of the monomer has been converted. The average molecular weight of the polymer also increases during polymerisation. It has been shown that these results are obtained even under conditions where there is a negligible rise in the temperature (<1°C) of the reaction mixture.

The explanation for this effect (known variously as the gel effect, Tromsdorff effect or auto-acceleration effect) is that the chain termination reaction slows down during conversion and, as can be seen by reference to equations (2.5) and (2.6), a decrease in the termination rate constant leads to an increase in both overall rate and molecular weight. The reason for the drop in termination rate is that as the reaction mixture becomes more viscous the radical ends of the polymer chains find increased difficulty in diffusing towards each other, leading to the important mutual termination reaction. Small monomer molecules on the other hand find little difficulty in diffusion at moderate conversion so that propagation reactions are relatively little affected, until the material becomes semi-solid, when the propagation rate constant also decreases. It is of interest to note that the gel effect may be induced by the addition of already formed poly(methyl methacrylate) or even another polymer such as cellulose tripropionate because such additions increase the viscosity of the system.

The auto-acceleration effect appears most marked with polymers that are insoluble in their monomers. In these circumstances the radical end becomes entrapped in the polymer and termination reactions become very difficult. It has been suggested that, in thermodynamic terms, methyl methacrylate is a relatively poor solvent for poly(methyl methacrylate) because it causes radicals to coil while in solution. The termination reaction is then determined by the rate at which the radical ends come to the surface of the coil and hence become available for mutual termination.

Polymerisation in bulk

Bulk polymerisation is extensively used in the manufacture of the sheet and to a lesser extent rod and tube. In order to produce a marketable material it is important to take the following factors into account:

- (1) The exotherm developed during cure.
- (2) The acceleration in conversion rate due to increasing viscosity.
- (3) The effect of oxygen.
- (4) The extensive shrinkage in conversion from monomer to polymer (~20%).
- (5) The need to produce sheet of even thickness.
- (6) The need to produce sheet of constant quality.
- (7) The need to produce sheet free from impurities and imperfections.

In order to reduce the shrinkage in the casting cell, and also to reduce problems of leakage from the cell, it is normal practice to prepare a 'prepolymer'. In a typical process monomer freed from inhibitor is heated with agitation for about 8 minutes at 90°C with 0.5% benzoyl peroxide and then cooled to room temperature. Plasticiser, colouring agents and ultraviolet light absorbers may be incorporated at this stage if required. The resulting syrup, consisting of a solution of polymer in monomer, is then filtered and stored in a refrigerator if it is not required for immediate use. The heating involved in making the prepolymer may also be of assistance in removing oxygen dissolved in the monomer.

The preparation of a prepolymer requires careful control and can be somewhat difficult in large-scale operations. An alternative approach is to prepare a syrup by dissolving some polymer in the monomer and adding some peroxide to the mixture. As in the case of a prepolymer syrup, such a syrup will cause less shrinkage on polymerisation and fewer leakage problems.

Acrylic sheet is prepared by pouring the syrup into a casting cell. This consists of two plates of heat-resistant polished glass provided with a separating gasket round the edges. The gasket commonly consists of a hollow flexible tube made from a rubber, or from plasticised poly(vinyl alcohol). The cell is filled by opening up the gasket at a corner or edge and metering in the syrup, care being taken to completely fill the cell before closing up the gasket. The cell is held together by spring-loaded clamps or spring clips so the plates will come closer together as the reacting mixture shrinks during polymerisation. This technique will enable the sheet to be free of sink marks and voids.

It is important to use rigid glass sheet and to apply pressure to the plates in such a manner that they do not bow out as this would lead to sheet of uneven thickness.

The filled cells are then led through a heating tunnel. In a typical system the time to pass through the tunnel is about 16 hours. For the first 14 hours the cell passes through heating zones at about 40°C. Under these conditions polymerisation occurs slowly. Any acceleration of the rate due to either the rise in temperature through the exothermic reaction or due to the viscosity-chain termination effect will be small. It is particularly important that the temperature of any part of the syrup is not more than 100°C since this would cause the monomer to boil. By the end of this period the bulk of the monomer has reacted and the cell passes through the hotter zones. After 15 hours (total time) the cell is at about 97°C, at which temperature it is held for a further half-hour. The sheet is then cooled and removed from the cell. In order to reduce any internal stresses the sheet may be annealed by heating to about 140°C and, before being dispatched to the customer, the sheet is masked with some protective paper using gelatine or, preferably, with a pressure-sensitive adhesive.

When casting large blocks, the exotherm problem is more severe and it may be necessary to polymerise inside a pressure vessel and thus raise the boiling point of the monomer.

In order to compensate for shrinkage, special techniques are required in the manufacture of rod. In one process, vertical aluminium tubes are filled with syrup and slowly lowered into a water bath at 40°C. As the lowest level of syrup polymerises, it contracts and the higher levels of syrup thus sink down the tube, often under pressure from a reservoir of syrup feeding into the tubes.

Acrylic tubes may be prepared by adding a calculated amount of syrup to an aluminium tube, sealing both ends, purging the air with nitrogen and then rotating horizontally at a constant rate. The whole assembly is heated and the

syrup polymerises on the wall of the rotating tube. The natural shrinkage of the material enables the casting to be removed quite easily.

An interesting modification of the sheet casting process is the band polymerisation process due to Swedlow.⁸ In this process a monomer/polymer syrup is polymerised between steel bands which pass through heating zones and which are spaced according to the sheet thickness required. Whilst there may be some economic attraction of the process in some countries with high labour costs the quality of the product is generally inferior to that of cell-cast sheet. Furthermore, where lower optical qualities are tolerable extruded sheet is generally cheaper to produce. The process, as with the cast cell process, does however allow for the possibility of cross-linked polymer sheet that cannot easily be produced by extrusion processes.

Suspension polymerisation

The average molecular weight of most bulk polymerised poly(methyl methacrylates) is too high to give a material which has adequate flow properties for injection moulding and extrusion.

By rolling on a two-roll mill the molecular weight of the polymer can be greatly reduced by mechanical scission, analogous to that involved in the mastication of natural rubber, and so mouldable materials may be obtained. However, bulk polymerisation is expensive and the additional milling and grinding processes necessary make this process uneconomic in addition to increasing the risk of contamination.

As a result the suspension polymerisation of methyl methacrylate was developed to produce commercial material such as Diakon made by ICI. Such a polymerisation can be carried out rapidly, usually in less than an hour, because there is no serious exotherm problem.

There is, however, a problem in controlling the particle size of the beads formed and further in preventing their agglomeration, problems common to all suspension-type polymerisations. The particle size of the beads is determined by the shape and size of the reactor, the type and rate of agitation and also the nature of suspending agents and protective colloids present. Suspending agents used include talc, magnesium carbonate and aluminium oxide whilst poly(vinyl alcohol) and sodium polymethacrylate are among materials used as protective colloids.

In one process described in the literature⁹ one part of methyl methacrylate was agitated with two parts of water and 0.2% benzoyl peroxide was employed as the catalyst. Eight to 18 g of magnesium carbonate per litre of reactants were added, the lower amount being used for larger beads, the larger for small beads. The reaction temperature was 80°C initially but this rose to 120°C because of the exothermic reaction. Polymerisation was complete in about an hour. The magnesium carbonate was removed by adding sulphuric acid to the mixture. The beads were then filtered off, carefully washed and dried.

Other additives that may be incorporated include sodium hydrogen phosphates as buffering agents to stabilise that pH of the reaction medium, lauryl mercaptan or trichlorethylene as chain transfer agents to control molecular weight, a lubricant such as stearic acid and small amounts of an emulsifier such as sodium lauryl sulphate.

The dried beads may be supplied as injection moulding material without further treatment or they may be compounded with additives and granulated.

15.2.3 Structure and Properties

Commercial poly(methyl methacrylate) is a transparent material, and microscopic and X-ray analyses generally indicate that the material is amorphous. For this reason the polymer was for many years considered to be what is now known as atactic in structure. It is now, however, known that the commercial material is more syndiotactic than atactic. (On one scale of assessment it might be considered about 54% syndiotactic, 37% atactic and 9% isotactic. Reduction in the temperature of free-radical polymerisation down to -78°C increases the amount of syndiotacticity to about 78%).

Substituents on the α -carbon atom restrict chain flexibility but, being relatively small, lead to a significantly higher T_g than with polyethylene. Differences in the T_g 's of commercial polymers (approx. 104°C), syndiotactic polymers (approx. 115°C) and anionically prepared isotactic polymers (45°C) are generally ascribed to the differences in intermolecular dipole forces acting through the polar groups.

In consequence of a T_g of 104°C with its amorphous nature, commercial poly(methyl methacrylate) is thus a hard transparent plastics material in normal conditions of use.

Because the polymer is polar it does not have electrical insulation properties comparable with polyethylene. Since the polar groups are found in a side chain these are not frozen in at the T_g and so the polymer has a rather high dielectric constant and power factor at temperatures well below the T_g (see also Chapter 6). This side chain, however, appears to become relatively immobile at about 20°C , giving a secondary transition point below which electrical insulation properties are significantly improved. The increase in ductility above 40°C has also been associated with this transition, often referred to as the β -transition.

The solubility of commercial poly(methyl methacrylate) is consistent with that expected of an amorphous thermoplastic with a solubility parameter of about $18.8\text{ MPa}^{1/2}$. Solvents include ethyl acetate ($\delta = 18.6$), ethylene dichloride ($\delta = 20.0$), trichloroethylene ($\delta = 19$), chloroform ($\delta = 19$) and toluene ($\delta = 20$), all in units of $\text{MPa}^{1/2}$. Difficulties may, however, occur in dissolving cast poly(methyl methacrylate) sheet because of its high molecular weight.

Since the polymers are unbranched (apart from the methyl and methacrylate side groups) the main difference between uncompounded commercial grades is in the molecular weight.

Cast material is stated to have a number average molecular weight of about 10^6 . Whilst the T_g is about 104°C the molecular entanglements are so extensive that the material is incapable of flow below its decomposition temperature (approx. 170°C). There is thus a reasonably wide rubbery range and it is in this phase that such material is normally shaped. For injection moulding and extrusion much lower molecular weight materials are employed. Such polymers have a reasonable melt viscosity but marginally lower heat distortion temperatures and mechanical properties.

15.2.4 General Properties of Poly(methyl methacrylate)

As indicated in the previous section poly(methyl methacrylate) is a hard, rigid, transparent material. Commercial grades have extremely good weathering resistance compared with other thermoplastics.

Table 15.1 Some properties of methyl methacrylate polymers

<i>Property</i>	<i>Units</i>	<i>ASTM test method</i>	<i>Acrylic sheet*</i>	<i>Moulding composition†</i>	<i>Copolymer‡</i>
Molecular weight (\bar{M}_n)	—	—	~10 ⁶	~60 000	—
Specific gravity	—	D.792	1.19	1.18	1.17
Tensile strength	10 ³ lbf/in ² MPa	D.638		10.5 (72.5)	—
Tensile modulus	10 ³ lbf/in ² MPa	—	~430 (3000)	~350 (2400)	~400 (2750)
Flexural strength	10 ³ lbf/in ² MPa	—	~20 (140)	~18 —	~18 (130)
Flexural modulus	10 ³ lbf/in ² MPa	—	~400 (2750)	~400 (2750)	—
Rockwell hardness	—	D.785	M.100	M103	—
Scratch hardness (Moh's scale)	—	—	—	2–3	—
Water absorption [% in 24 h(20°C)]	%	D.570	0.2	0.3	0.25
Izod impact strength	ft lbf in ⁻¹	(B.S.) 2782	—	0.40	—
Vicat softening point	°C	—	—	109–112	—
Heat deflection temperature(264lbf/in ²) (1.82 MPa)	°C	D.648	100	85–95	80
Refractive index n_D^{20}	—	—	1.49	1.49	1.49
Volume resistivity (20°C)	Ωm	—	>10 ¹⁶	>10 ¹⁷	—
Dielectric constant at 10 ³ Hz 60% R.H.(20°C)	—	—	3.0	3.1	—

* Persex (ICI) † Diakon M (ICI) ‡ Asterite (ICI) (withdrawn)

The properties of three types of poly(methyl methacrylate) (sheet based on high molecular weight polymer, lower molecular weight injection moulding material and a one-time commercial copolymer) are given in *Table 15.1*.

As might be expected of a somewhat polar thermoplastics material, mechanical, electrical and other properties are strongly dependent on temperature, testing 'rate' and humidity. Detailed data on the influence of these variables have been made available by at least one manufacturer and the following remarks are intended only as an illustration of the effects rather than as an attempt at providing complete data.

Figure 15.6 shows the considerable temperature sensitivity of the tensile strength of acrylic sheet whilst *Figure 15.7* shows how the fracturing stress decreases with the period of loading. Mouldings from acrylic polymers usually show considerable molecular orientation. It is observed that a moulding with a high degree of frozen-in orientation is stronger and tougher in the direction parallel to the orientation than in the transverse direction.

Poly(methyl methacrylate) is recognised to be somewhat tougher than polystyrene (after consideration of both laboratory tests and common experience) but is less tough than cellulose acetate or the ABS polymers. It is superior to untreated glass in terms of impact resistance and although it cracks, any fragments formed are less sharp and jagged than those of glass and, normally consequently less harmful. However, oriented acrylic sheet such as may result

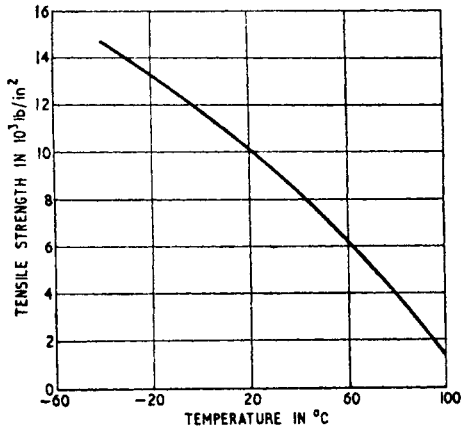


Figure 15.6. Effect of temperature on tensile strength of acrylic sheet (Perspex) at constant rate of strain (0.44% per second). (Reproduced by permission of ICI)

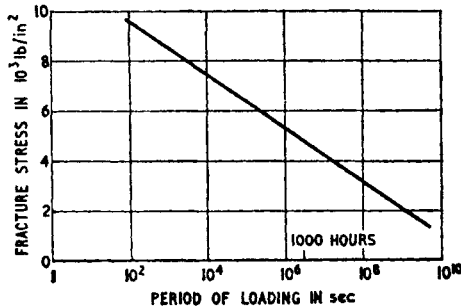


Figure 15.7. Effect of period of loading on fracturing stress at 25°C of acrylic sheet (Perspex). (Reproduced by permission of ICI)

from double curvature shaping shatters with a conchoidal fracture and fragments and broken edges can be quite sharp. Although it is harder than most other thermoplastics the scratch resistance does leave something to be desired. Shallow scratches may, however, be removed by polishing.

The optical properties of poly(methyl methacrylate) are particularly important. Poly(methyl methacrylate) absorbs very little light but there is about 4% reflection at each polymer-air interface for normal incident light. Thus the light transmission of normal incident light through a parallel sheet of acrylic material free from blemishes is about 92%. The influence of the wavelength of light on transmission is shown in *Figure 15.8*.

The interesting property of total internal reflection may be conveniently exploited in poly(methyl methacrylate). Since the critical angle for the polymer-air boundary is 42°C a wide light beam may be transmitted through long lengths of solid polymer. Light may thus be 'piped' round curves and there is little loss where the radius of curvature is greater than three times the thickness of the sheet or rod. Scratched and roughened surfaces will reduce the internal reflection. This is, normally undesirable but a roughened or cut area can also be deliberately

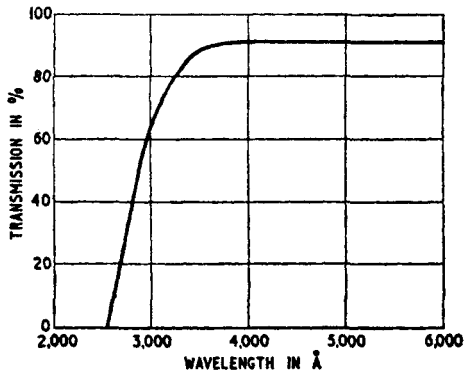


Figure 15.8. Light transmission of acrylic polymer ($\frac{1}{8}$ in thick moulded Diakon. Parallel light beam normally incident on surface). (Reproduced by permission of ICI)

incorporated to 'let out' the light at that point. The optical properties of poly(methyl methacrylate) have been exploited in the development of optical fibres.

Poly(methyl methacrylate) is a good electrical insulator for low-frequency work, but is inferior to such polymers as polyethylene and polystyrene, particularly at high frequencies. The influence of temperature and frequency on the dielectric constant is shown in Figure 15.9.

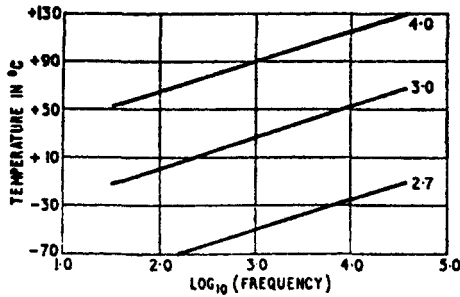


Figure 15.9. The variation of dielectric constant with temperature and frequency (Perspex) (the lines join points of equal dielectric constant). (Reproduced by permission of ICI)

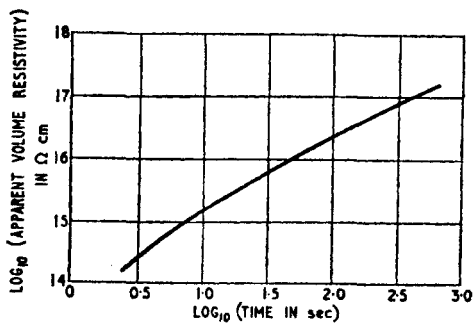


Figure 15.10. The dependence of apparent volume resistivity on time of polarisation of acrylic polymer (Perspex). (Reproduced by permission of ICI)

The apparent volume resistivity is dependent on the polarisation time (*Figure 15.10*). The initial polarisation current is effective for some time and if only a short time is allowed before taking measurements low values for volume resistivity will be obtained.

As may be expected of an amorphous polymer in the middle range of the solubility parameter table, poly(methyl methacrylate) is soluble in a number of solvents with similar solubility parameters. Some examples were given in the previous section. The polymer is attacked by mineral acids but is resistant to alkalis, water and most aqueous inorganic salt solutions. A number of organic materials although not solvents may cause crazing and cracking, e.g. aliphatic alcohols.

15.2.5 Additives

Poly(methyl methacrylate) may be blended with a number of additives. Of these the most important are dyes and pigments and these should be stable to both processing and service conditions. Two particular requirements are, firstly, that when used in castings they should not affect the polymerisation reaction and, secondly, that they should have good weathering resistance.

Plasticisers are sometimes added to the polymer, dibutyl phthalate being commonly employed in quantities of the order of 5%. Use in moulding powders will enhance the melt flow but somewhat reduce the mechanical properties of the finished product.

Further improvement in light stability may be achieved by addition of small quantities of ultraviolet absorbers. Typical examples include phenyl salicylate, 2,4-dihydroxybenzophenone, resorcinol monobenzoate, methyl salicylate and stilbene.

15.2.6 Processing

In commercial practice three lines of approach are employed in order to produce articles from poly(methyl methacrylate). They are:

- (1) Processing in the melt state such as by injection moulding and extrusion.
- (2) Manipulation of sheet, rod and tube.
- (3) The use of monomer-polymer doughs.

There are a number of general points to be borne in mind when processing the polymer in the molten state which may be summarised as follows:

- (1) The polymer granules tend to pick up moisture (up to 0.3%). Although most commercial grades are supplied in the dry condition, subsequent exposure before use to atmospheric conditions will lead to frothy mouldings and extrudates, owing to volatilisation of the water in the heating cylinders. Particular care should be taken with reground scrap.
- (2) The melt viscosities at the processing temperatures employed are considerably higher than those of polystyrene, polyethylene and plasticised PVC. This means that the equipment used must be robust and capable of generating high extrusion and injection pressures. The injection moulding of poly(methyl methacrylate) (PMMA) has been made much easier by the widespread use of the reciprocating screw in-line injection moulding

machines. The use of a screw with a decompression zone and a vented barrel may be useful both for injection moulding and extrusion, since it is possible to remove unwanted moisture and even monomer which has been produced by depolymerisation of the polymer because of overheating.

The melt viscosity is more sensitive to temperature than that of most thermoplastics (*Figure 15.11*) and this means that for accurate, consistent and reproducible results, good temperature control is required on all equipment.

- (3) Since the material is amorphous the moulding shrinkage is low and normally less than 0.008 cm/cm.

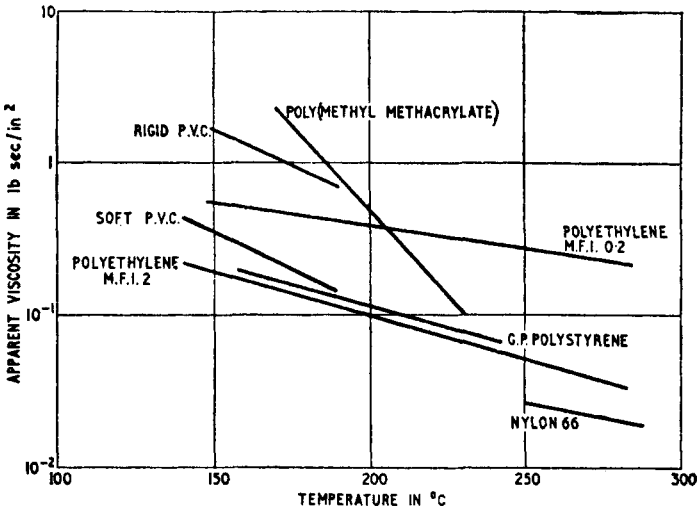


Figure 15.11. Viscosity-temperature curves for poly(methyl methacrylate) and other thermoplastics. (Reproduced by permission of ICI)

A great number of poly(methyl methacrylate) products are produced by manipulation of sheet, rod and tube. Such forms may easily be machined using drills, circular saws and bandsaws, providing care is taken not to overheat the polymer. It is very difficult to weld the sheet satisfactorily but cementing techniques have been highly developed. Acrylic parts may be joined using solvents such as chloroform or by use of solutions of polymer in a suitable solvent. Generally, however, the best results are obtained, particularly where there is a gap-filling requirement, by use of a monomer-polymer solution. Commercial cements of this type either contain a photocatalyst to allow hardening by ultraviolet light polymerisation or contain a promoter so that on addition of a peroxide, polymerisation of the monomer is sufficiently rapid at room temperature to harden the cement in less than one hour.

When heated above the glass transition temperature ($\sim 100^{\circ}\text{C}$), acrylic sheet from high molecular weight polymer becomes rubbery. The rubbery range extends for 60°C . Further raising of the temperature causes decomposition rather than melting. The reasonably wide rubbery range, c.f. cellulose acetate, high-impact polystyrene and polyethylene, enables the sheet to be heated in ovens rather than having to be heated while clamped to the shaping apparatus. Poly(methyl methacrylate) is not widely suitable for normal vacuum forming operations since the modulus of the material in the rubbery state is too great to

allow shaping of fine detail simply by atmospheric pressure. As a result a large number of techniques have been devised using air pressure, mechanical pressure, or both in combination, and sometimes also involving vacuum assistance.

The use of monomer–polymer doughs has been largely confined to the production of dentures. A plaster of Paris mould is first prepared from a supplied impression of the mouth. Polymer powder containing a suitable polymerisation initiator is then mixed with some monomer to form a dough. A portion of the dough is then placed in the mould, which is closed, clamped and heated in boiling water. After polymerisation, which usually takes less than half an hour, the mould is cooled and opened. This technique could also be usefully employed for other applications where only a few numbers-off are required but does not seem to have been exploited.

A novel technique has been developed for the manufacture of tiles and sanitary ware. A dispersion of a ground sand in methyl methacrylate monomer is prepared with a solids content of about 72% by weight. The particle size is such that the dispersion has reasonable stability but is pourable. When required for use the dispersion is blended with a free-radical initiator, usually based on a peroxide, and fed into metal moulds heated to about 70°C. As the monomer polymerises there is a shrinkage of about 11% by volume and this is compensated through a reduction in the volume of the mould cavity, with one mould half moving towards the other and into the other like a piston in a cylinder. The polymerised products have a remarkably good finish, are virtually stress free and have considerable flexibility in part design. Casting dispersions are available from ICI as Asterite (reviving a name at one time used for a now-obsolete acrylic copolymer).

15.2.7 Applications

The major uses of poly(methyl methacrylate) arise from its high light transmission and good outdoor weathering properties. It is also a useful moulding material for applications where good appearance, reasonable toughness and rigidity are requirements which are considered to justify the extra cost of the polymer as compared with the large tonnage plastics.

For many years the market growth for poly(methyl methacrylate) was much lower than for other major thermoplastics. For example, UK production in 1950 was about the same as that for polystyrene, in 1965 (when the first edition of this book was being completed) it was about 40% and by the end of the 1970s it was down to about 10%. There was, however, an upsurge in the late 1980s and early 1990s and world production capacity was estimated at 1.7×10^6 t.p.a. in 1996. This is about 17% of the capacity for polystyrene. During the late 1990s there was a considerable capacity build-up in Asia and already by 1996 this area claimed about 38% of global capacity followed by America with 34% and Europe 28%. While the overall market is roughly divided between mouldings and sheet products extruded sheet is making inroads into the cast sheet market and in 1997 in the USA it was estimated that less than 25% of PMMA products were produced from cast (mainly sheet) materials. In Western Europe the market has been assessed at auto applications 30%, illumination engineering 20–25%, building industry 15%, optical industry 10–15%, household goods 8–10%, and other 15%.

The material is eminently suitable for display signs, illuminated and non-illuminated, and for both internal and external use. The properties of importance here are weatherability, the variety of techniques possible which enable a wide range of signs to be produced and, in some cases, transparency.

In lighting fittings poly(methyl methacrylate) finds an important outlet. Street lamp housings originally shaped from sheet are now injection moulded. Ceiling lighting for railway stations, school rooms, factories and offices frequently incorporate poly(methyl methacrylate) housings. In many of these applications opalescent material is used which is effective in diffusing the light source. Poly(methyl methacrylate) is the standard material for automobile rear lamp housings.

The methacrylic polymer remains a useful glazing material. In aircraft applications it is used extensively on aircraft which fly at speeds less than Mach 1.0. They form the familiar 'bubble' body of many helicopters. On land, acrylic sheet is useful for coach roof lights, motor cycle windscreens and in do-it-yourself 'cabins' for tractors and earth-moving equipment. Injection mouldings are frequently used for plaques on the centre of steering wheels and on some fascia panelling.

Transparent guards for foodstuffs, machines and even baby incubators may be fabricated simply from acrylic sheet. It should, however, be pointed out that due to rather rapid surface deterioration and the lack of 'sparkle' the material is not ideally suited as a cover for displayed goods.

Acrylic sheet is also employed for many other diverse applications, including baths and wash-basins, which have considerable design versatility, are available in a wide range of colours, and are cheaper and much lighter than similar products from other materials.

Extruded sheet is cheaper than cast sheet but because there is some residual molecular orientation, is somewhat less satisfactory optically and more difficult to machine. On the other hand, no doubt a function of its lower molecular weight, it may be thermoformed more easily.

The energy crisis that began in the 1970s has led to much interest in solar heating. Because of its excellent weathering properties, transparency and light weight compared with glass the material is being used for the dome-shaped covers of solar collectors. In this application it is important to use a heat-resistant film between the acrylic dome and the absorbing material, both to reduce heat loss and to protect the acrylic material if there is an accumulation of heat due to failure of the liquid circulation in the absorber.

In contrast to the above use PMMA sheet has been used as the 'bed' in indoor ultraviolet lamp operated solariums. Here the ultraviolet radiation is so intense as to require the use of special formulations with adequate ultraviolet resistance.

PMMA has not been able to compete in the field of compact discs, the market having gone to the polycarbonates (see Chapter 20). It is, however, suitable for optical data storage using large video discs. Large-scale acceptance in the field of optical fibres has been held back by problems of obtaining material of an acceptable level of purity.

As described in the previous section, casting dispersions based on monomer and fine sand are now finding use in high-grade sanitary ware and tiling.

Decorative plaques are produced by injection moulding poly(methyl methacrylate) and then coating the back of the transparent moulding with a thin coat of metal by the vacuum deposition technique or with a paint by spraying. By suitable masking, more than one metal and more than one colour paint may be used to enhance the appearance. These plaques are frequently used in the centre of car steering wheels, refrigerators and other equipment where an eye-catching motif is considered desirable.

If the surface of an acrylic sheet, rod or tube is roughened or carved, less light is internally reflected and the material is often rather brighter at these non-polished surfaces. The use of this effect enables highly attractive carvings to be produced. Similarly, lettering cut into sheet, particularly fluorescent sheet, becomes 'lit-up' and this effect is useful in display signs.

The use of acrylic materials for dentures has already been mentioned.

15.3 METHYL METHACRYLATE POLYMERS WITH ENHANCED IMPACT RESISTANCE AND SOFTENING POINT

As with other rigid amorphous thermoplastic polymers such as PVC and polystyrene (see the next chapter) poly(methyl methacrylate) is somewhat brittle and, as with PVC and polystyrene, efforts have been made to improve the toughness by molecular modification. Two main approaches have been used, both of which have achieved a measure of success. They are copolymerisation of methyl methacrylate with a second monomer and the blending of poly(methyl methacrylate) with a rubber. The latter approach may also involve some graft copolymerisation.

An early approach was to use butadiene as the comonomer but the resultant copolymers have largely been used only in latex form in paper and board finishes and are no longer believed to be important.

Copolymers of methyl methacrylate and butyl acrylate gave polymers that were somewhat tougher and slightly softer than the homopolymers. Materials believed to be of this type were marketed in sheet form by ICI as Asterite for a short while in the 1960s (the name having been recently revived for another product as described in Section 15.2.6).

Rather more recently Röhm and Haas GmbH have introduced Plexidur plus which is a copolymer of acrylonitrile and methyl methacrylate. It is best considered as a glazing material for use in schools, sports halls and vehicles. The material also has good clarity, rigidity and surface hardness. Some typical properties compared with PMMA are given in *Table 15.2*.

Following the success in blending rubbery materials into polystyrene, styrene-acrylonitrile and PVC materials to produce tough thermoplastics the concept has been used to produce high-impact PMMA-type moulding compounds. These are two-phase materials in which the glassy phase consists of poly(methyl methacrylate) and the rubbery phase an acrylate polymer, usually poly(butyl acrylate). Commercial materials of the type include Diakon MX (ICI), Oroglas

Table 15.2 Some properties of a methyl methacrylate-acrylonitrile copolymer compared with a general purpose poly(methyl methacrylate) compound at 23°C and 50% R.H (German DIN tests)

<i>Property</i>	<i>Units</i>	<i>MMA-ACN copolymer</i>	<i>PMMA</i>
Tensile strength (5 mm/min strain rate)	MPa	85	80
Elongation at break (5 mm/mm strain rate)	%	60	5.5
Tension modulus	MPa	4500	3300
Impact strength	N mm mm ⁻²	40	12
Notched impact strength	N mm mm ⁻²	3	2
Light transmission	%	90	92
Vicat softening point	°C	80	115

Table 15.3 Comparison of properties of some rubber-modified polymers with poly(methyl methacrylate)

<i>Property</i>	<i>Test standard DIN</i>	<i>Unit</i>	<i>ABS</i>	<i>ASA</i>	<i>High-impact PMMA¹</i>	<i>High-impact PMMA²</i>	<i>PMMA³</i>
Gross density	53 479	g/cm ³	1.06	1.07	1.12	1.15	1.18
Vicat softening temperature 50 N, oil	53 460	°C	98	92	76	95	110
Impact strength, NKS small standard rod	53 453	N mm mm ⁻²	no fracture	no fracture	no fracture	45	18
Notched impact strength NKS small standard rod	53 453	Nmm mm ⁻²	12	14	8	3.5	2
Tensile strength	53 455	N/mm	45	44	20	40	75
Elongations at break	53 455	%	20	20	50	30	3.5
<i>E</i> -modulus	53 457	N/mm ²	2400	2300	800	1800	3300
Degree of transmission (<i>d</i> = 3 mm)	5 036	%	opaque	opaque	approx. 70	88	92

¹ Type PLEX 8535-F, manufacture Röhm GmbH(30% poly(butyl acrylate))

² Type PLEX 8558-F, manufacture Röhm GmbH(15% poly(butyl acrylate))

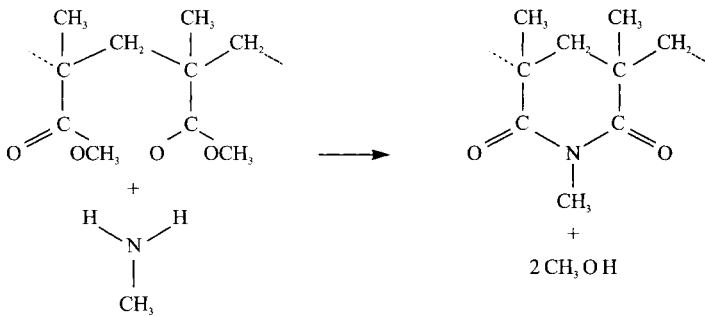
³ Type Plexiglass-moulding compound 8N, manufacture, Röhm GmbH

DR (Röhms and Haas) and Plex 8535-F (Röhms GmbH). Some typical properties of these materials compared with straight PMMA and with the competitive ABS and ASA polymers (discussed in Chapter 16) are given in *Table 15.3*.

In comparison with the styrene-based and better known ABS and ASA materials the high-impact methacrylates have generally lower values for mechanical properties such as tensile strength, impact strength and modulus. However, long-term weathering tests show the marked superiority of the methacrylates over ABS and even ASA materials to degradation. In a typical test the impact strength of unnotched high-impact PMMA rods was about sixfold that of both ABS and ASA materials.

Over the years many attempts have been made to produce commercial acrylic polymers with a higher softening point than PMMA. The usual approach was to copolymerise MMA with a second monomer such as maleic anhydride or an N-substituted maleimide which gave homopolymers with a higher T_g than PMMA. In this way copolymers with Vicat softening points as high as 135°C could be obtained.

In the early 1990s attention appeared to be focusing on the imidisation of acrylic polymers with primary amines.



As might be expected from a consideration of the factors discussed in Section 4.2, the imidisation process will stiffen the polymer chain and hence enhance T_g and thus softening points. Hence Vicat softening points (by Procedure B) may be as high as 175°C . The modulus of elasticity is also about 50% greater than that of PMMA at 4300 MPa, whilst with carbon fibre reinforcement this rises to 25 000 MPa. The polymer is clear (90% transparent) and colourless.

Such materials, known as poly(methyl methacrylimides) or PMMI, are marketed by Röhms and Haas in the USA as Kamex, and there is a small production by Röhms in Europe, where the product is marketed as Pleximid.

Hard-coated poly(methyl methacrylimide) sun-roofs have already been specified for American sports cars, whilst the polymer might be expected to make some inroads into the polycarbonate market, with one specific target being auto headlamp diffusers.

15.4 NITRILE RESINS

Poly(acrylonitrile) has found little use as a plastics material because it softens only slightly below its decomposition temperature of about 300°C . In addition it does not dissolve in its monomer so it cannot be shaped by bulk casting. It will,

however, dissolve in solvents such as dimethylformamide and tetramethylene-sulphone. In consequence poly(acrylonitrile) and closely related copolymers have found wide use as fibres (e.g. Orlon, Acrilan).

Copolymers of acrylonitrile and vinylidene chloride have been used for many years to produce films of low gas permeability, often as a coating on another material. Styrene-acrylonitrile with styrene as the predominant free monomer (SAN polymers) has also been available for a long time. In the 1970s materials were produced which aimed to provide a compromise between the very low gas permeability of poly(vinylidene chloride) and poly(acrylonitrile) with the processability of polystyrene or SAN polymers (discussed more fully in Chapter 16). These became known as *nitrile resins*.

Table 15.4 illustrates that though the nitrile resins had a gas permeability much higher than has poly(acrylonitrile) the figures for oxygen and carbon dioxide are much lower than for other thermoplastics used for packaging.

Table 15.4 Permeability (P) of nitrile resins compared with other polymers

Polymer	$10^{17} P(\text{cm}^3 \text{s g}^{-1})$	
	O ₂	CO ₂
Poly(acrylonitrile)	0.14	0.23
Nitrile resins	2.3–3.6	4.5–9
Poly(vinylidene chloride)	3.6	14–23
Poly(vinyl chloride)	23–32	40–180
High-density polyethylene	900	2000

In the mid-1970s many major plastics materials producers marketed or were actively developing materials of this type. They included American Cyanamid, Borg-Warner, Dow, Du Pont, ICI, Marbon, Monsanto, Solvay, Union Carbide and Vistron (Sohio).

The common feature of these materials was that all contained a high proportion of acrylonitrile or methacrylonitrile. The Vistron product, Barex 210, for example was said to be produced by radical graft copolymerisation of 73–77 parts acrylonitrile and 23–27 parts by weight of methyl acrylate in the presence of a 8–10 parts of a butadiene-acrylonitrile rubber (Nitrile rubber). The Du Pont product NR-16 was prepared by graft polymerisation of styrene and acrylonitrile in the presence of styrene-butadiene copolymer. The Monsanto polymer Lopac was a copolymer of 28–34 parts styrene and 66–72 parts of a second monomer variously reported as acrylonitrile and methacrylonitrile. This polymer contained no rubbery component.

The main interest in these materials lay in their potential as beverage containers although other suggested uses included such, presumably, diverse materials as barbecue sauces, pesticides and embalming fluids. However, in 1977 the US Food and Drugs Administration proposed a ban on these materials for beverage applications and suggested stringent levels of allowable acrylonitrile residual monomer migration. This led to companies withdrawing from manufacture of these resins. Shortly afterwards this particular market was penetrated by polyester resins of the poly(ethylene terephthalate) type (see Chapters 21 and

25). In 1984 the use of nitrile resins was re-approved by the Food and Drugs Administration with specific limits on the level of residual unreacted monomer.

This has resulted in some resurgence of interest in these materials. At the time of writing the only manufacturer is BP Chemicals, who acquired the rights to manufacture Barex in 1987 and doubled the manufacturing capacity to 20 000 t.p.a. in 1990. Whilst this copolymer graft has barrier properties inferior to those of poly(vinylidene chloride) and ethylene-vinyl alcohol (EVOH), it is markedly better than for polypropylene and poly(ethylene terephthalate) (PET). The ability to save some 30–40% on materials helps to offset the price of the material, which at the time of writing is about twice that of PET. The material is also attractive because of its processing versatility, with film and blow moulding operations dominating. There is some interest in the use of nitrile resins as an internal barrier layer in a co-extruded product, so that the barrier layer is not in direct contact with the foodstuff.

About 95% of material produced is used for packaging, with food packaging accounting for about 70% in the USA and 40% in Europe. This difference in usage has been ascribed to longer shelf life requirements in the USA and hence more demanding specifications. Processed meat dominates the food packaging field. The excellent chemical resistance of the material has led to uses in such diverse fields as containers for petrol (gasoline) additives, nail polishes, lemon juice, air fresheners, nicotine patches and toothpaste packs.

Another area of potential interest is in refrigerator liners. The move away from the ozone-layer-damaging chlorofluorocarbons (CFCs) to HCFCs in the USA and pentane/cyclopentane blends in Europe has not been without problems. These newer materials have an adverse effect on ABS whereas the nitrile resin appears satisfactory, if more expensive.

15.5 ACRYLATE RUBBERS

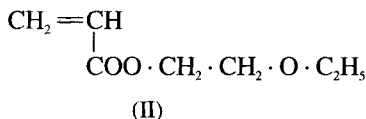
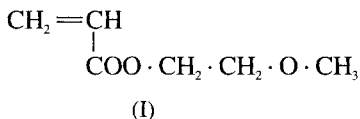
The acrylic or acrylate rubbers were first introduced in 1948 by B. F. Goodrich in consequence of earlier work carried out by the Eastern Regional Laboratory of the US Department of Agriculture. The original materials were a copolymer of ethyl acrylate with about 5% of 2-chloroethyl vinyl ether acting as a cure site monomer (eventually marketed as Hycar 4021) and a copolymer of butyl acrylate and acrylonitrile (Hycar 2121X38). These materials found some limited use in oil seals and other automotive uses where nitrile rubbers had insufficient heat resistance or tended to be cross-linked by sulphur-bearing additives in the oils. In heat resistance they are in fact superior to most rubbers, exceptions being the fluororubbers, the silicones and the fluorsilicones. Amongst the heat-resisting, oil-resisting rubbers they are, however, inferior in low-temperature properties (i.e. they stiffen at higher temperatures) to the silicones, the fluorsilicones and the epichlorhydrin rubbers.

Subsequently, several other companies have entered the acrylic rubber market (e.g. Thiokol, American Cyanamid, Goodyear, Polymer Corporation and US Rubber) and this has led to many technical developments. These may be categorised into the three main areas:

- (1) Attempts to improve low-temperature properties without loss of oil resistance.

- (2) Provision of more active cross-link sites.
- (3) Development of new cross-linking systems.

Whilst increasing the length of alkyl side chain can, to some extent, depress T_g and improve low-temperature properties this is at the expense of oil resistance. On the other hand lengthening of the side chain by incorporation of an —O— or an —S— linkage could often depress T_g and reduce swelling in hydrocarbon oils. This led to the commercial development of copolymers of either ethyl or butyl acrylate with an alkoxy acrylate comprising some 20–50% of the total composition. Typical of such alkoxy compounds are methoxyethyl acrylate (I) and ethoxyethyl acrylate (II):



Because of processing problems 2-chloroethyl vinyl ether has now been replaced with other cure site monomers. These include vinyl and allyl chloracetates and allyl glycidyl ether.

Curing systems have also radically changed. With early grades aliphatic amines and then ammonium salts were used, whilst in the late 1960s the so-called soap-sulphur systems became paramount. More recently, four-part curing systems have become more popular which contain curative, accelerator, activator and retarder. Such a typical system would be sodium stearate 3–5 (curative); 3-(3,4-dichlorophenyl)-1,1-dimethyl urea 2–6 (accelerator); high activity magnesium oxide 0–1 (activator); and stearic acid 0–3 (retarder). This system shows good scorch safety, fast cure and low compression set without causing many of the difficulties exhibited by the earlier systems. Post-curing is still advisable for optimum compression set resistance.

The changes in acrylic rubber compounds have increased the scope of these materials as heat-and oil-resisting materials able to meet many of the increasingly stringent demands being imposed on rubbers for use in automotive applications.

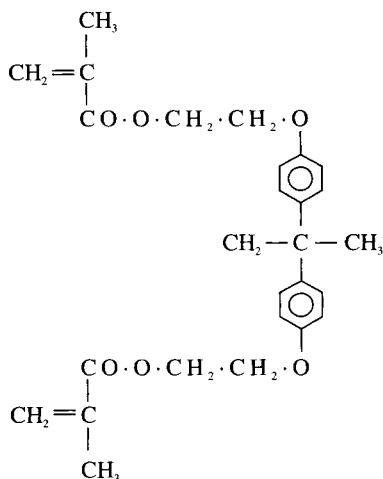
15.6 THERMOSETTING ACRYLIC POLYMERS

Acrylic and methacrylic acids and their esters are highly versatile materials in that the acid and ester side groups can partake in a variety of reactions to produce a very large number of polymerisable monomers. One particularly interesting approach is that in which two methacrylic groupings are linked together so that there are two, somewhat distant, double bonds in the molecule. In these cases it is possible to polymerise through each of these double bonds separately and this will lead eventually to a cross-linked network structure.

In recent years these materials, which as a class have been known for a very long time, have found use in two areas:

- (1) As anaerobic adhesives (see Section 15.7).
- (2) As laminating resins in competition with polyester laminating resins.

Laminating resins have been offered by Akzo (Diacryl 101), Dow (Derakane Vinyl Esters) and Showa (Spilac). Typical of these is Diacryl 101, which is manufactured by esterification of the addition product of ethylene oxide to bisphenol A with methacrylic acid. They exhibit lower curing shrinkage than the polyester laminating resins during cure. The structure of Diacryl 101 is



15.7 ACRYLIC ADHESIVES

Methyl methacrylate has been used for many years as a reactive adhesive for joining together poly(methyl methacrylate). To reduce curing shrinkage it is usually thickened with its polymer although alternative materials could be used which might be cheaper but generally cause a loss in clarity. The bond sets by polymerisation which may be brought about by ultraviolet light or by the use of peroxides. Room temperature setting with peroxides is achieved by the use of amines as promoters.

The *alkyl 2-cyanoacrylates* have become well-known adhesives, often popularly known as super-glue.

In dry air and in the presence of polymerisation inhibitors methyl and ethyl 2-cyanoacrylates have a storage life of many months. Whilst they may be polymerised by free-radical methods, anionic polymerisation is of greater significance. A very weak base, such as water, can bring about rapid polymerisation and in practice a trace of moisture on a substrate is enough to allow polymerisation to occur within a few seconds of closing the joint and excluding the air. (As with many acrylic monomers air can inhibit or severely retard polymerisation).

Cyanoacrylate adhesives are particularly valuable because of their speed of action, which allows the joining of intricate parts without the need for complex jigs and fixtures. Within very broad limits the more monomer that is used to make a joint the less will be the strength. These adhesives have in fact no gap-filling ability, nor can they be used on porous substrates. Whilst they have good heat and solvent resistance their weathering behaviour is limited and joints should not be in frequent contact with water.

The reluctance of acrylic monomers to polymerise in the presence of air has been made a virtue with the *anaerobic acrylic adhesives*. These are usually *dimethacrylates* such as tetramethylene glycol dimethacrylate. The monomers are supplied with a curing system comprising a peroxide and an amine as part of a one-part pack. When the adhesive is placed between mild steel surfaces air is excluded, which prevents air inhibition, and the iron present acts as a polymerisation promoter. The effectiveness as a promoter varies from one metal to another and it may be necessary to use a primer such as cobalt naphthenate. The anaerobic adhesives have been widely used for sealing nuts and bolts and for a variety of engineering purposes. Small tube containers are also available for domestic use.

To overcome brittleness these materials are sometimes blended with rubbery materials and with polyurethanes. These polymers may contain unsaturated groups, particularly at the chain ends, so that graft structures may be produced rather than simple mixtures.

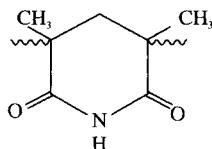
15.8 HYDROPHILIC POLYMERS

The successful development of eye contact lenses led in turn to a demand for soft contact lenses. Such a demand was eventually met by the preparation of copolymers using a combination of an acrylic ester monomer such as methyl methacrylate, a cross-linkable monomer such as a dimethacrylate, and a monomer whose homopolymer is soluble or highly swollen in water such as N-vinyl pyrrolidone. Such copolymers swell in water (hence the term *hydrophilic*), the degree of swelling being controlled by the specific type and amount of the monomers used. In use the lens is swollen to equilibrium in water, a typical soft lens having a water content of about 75%.

Such lenses may be made by machining from rod. More recently processes have been developed where the monomers are cast polymerised in tiny plastics moulds whose cavity corresponds to the dimensions of the lens and using procedures very reminiscent of those described for the manufacture of acrylic sheet (see Section 15.2.2).

15.9 POLY(METHACRYLIMIDE)

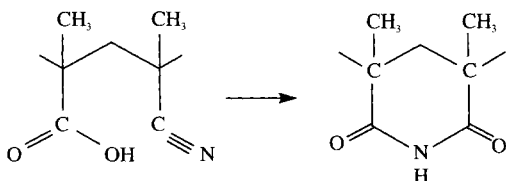
Poly(methacrylimide) has the structure



and should not be confused with poly(methyl methacrylamide) discussed in Section 15.3.

Materials containing the above structure in the polymer chain may be made from copolymers of methacrylic acid and methacrylonitrile. Ammonia-producing additives (such as urea and ammonium hydrogen carbonate) are added to the

copolymers at a temperature above T_g (~140°C) but below the decomposition temperature (~240°C)



Complete imidation will not occur but that which does will be accompanied by the formation of a cellular structure to produce a rigid cellular polymer.

The foams, marketed by Röhm as Rohacell, are stable at room temperature to hydrocarbons, ketones, chlorinated solvents and 10% sulphuric acid. They may be used under load at temperature up to 160°C. Uses quoted for these materials include bus engine covers, aircraft landing gear doors, radar domes, domes, ski cores and tennis racket cores. Their potential is in applications demanding a level of heat deformation resistance, solvent resistance and stiffness not exhibited by more well-known cellular polymers such as expanded polystyrene and the polyurethane foams.

15.10 MISCELLANEOUS METHACRYLATE AND CHLOROACRYLATE POLYMERS AND COPOLYMERS

A large number of methacrylate polymers have been prepared in addition to poly(methyl methacrylate). In many respects the properties of these materials are analogous to those of the polyolefins described in Chapter 8.

As with other linear polymers the mechanical and thermal properties are dependent on the intermolecular attraction, the spatial symmetry and the chain stiffness. If the poly-(n-alkyl methacrylate)s are compared it is seen that as the side chain length increases the molecules become spaced apart and the intermolecular attraction is reduced. Thus as the chain length increases, the softening point decreases, and the polymers become rubbery at progressively lower temperatures (*Figure 15. 12*).¹⁰ However, where the number of carbon atoms in the side chain is 12 or more, the softening point, brittle point and other properties closely related to the glass transition temperature rise with increase in chain length. As with the polyolefins this effect is due to side-chain crystallisation. It is to be noted that in the case of the polyolefins the side-chain crystallisation has a much greater effect on melting point than on the glass temperature. In studies on the methacrylates the property measured was the brittle point, a property generally more associated with the glass temperature.

A number of higher n-alkyl methacrylate polymers have found commercial usage. The poly-(n-butyl-), poly-(n-octyl-) and poly-(n-nonyl methacrylate)s have found use as leathering finishes whilst poly(lauryl methacrylate) has become useful as a pour-point depressant and improver of viscosity temperature characteristics of lubricating oils.

As is the case in the polyolefins, the polymethacrylates with branched side chains have higher softening points and are harder than their unbranched isomers. The effect of branching of Vicat Softening point is shown in *Table 15.5*.¹¹

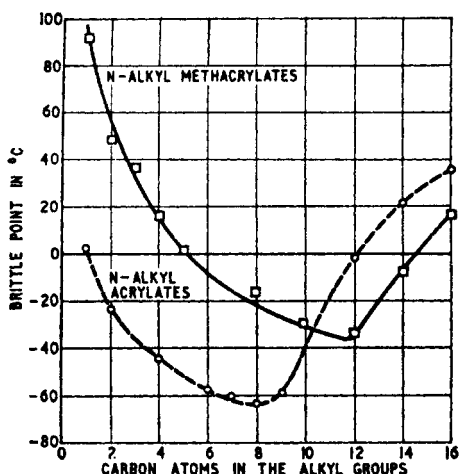


Figure 15.12. Brittle points of n-alkyl acryl acrylate and methacrylate ester polymers. (After Rehberg and Fisher,¹⁰ copyright 1948 by The American Chemical Society and reprinted by permission of the copyright owner)

This effect is not simply due to the better packing possible with the branched isomers. The lumpy branched structures impede rotation about the carbon-carbon bond on the main chain, thus giving a stiffer molecule with consequently higher transition temperature.

Methyl methacrylate has been widely copolymerised with a variety of other monomers and several of the copolymers have been commercially available. Copolymerisation with styrene gives a material with improved melt flow characteristics whilst methyl methacrylate- α -methylstyrene copolymers have improved heat resistance. As described earlier, enhanced impact strength is obtained by copolymerising the methacrylate with either butadiene or acrylonitrile or alternatively by the use of a poly(methyl methacrylate)-rubber blend. Such improvements in toughness are gained with a commensurate loss in clarity, water-whiteness and weathering resistance. Copolymerising with a second acrylic monomer such as butyl acrylate gives products which are softer, and sheet made from the copolymer may be formed without difficulty. A material of this

Table 15.5 Vicat softening of methacrylate polymers from monomers of type $\text{CH}_2 = \text{C}(\text{CH}_3)\text{COOR}(\text{°C})$

R =			
— CH_3	119	— $\text{C}\cdot(\text{CH}_3)_3$	104
— $\text{CH}_2\cdot\text{CH}_3$	81	— $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)_2$	46
— $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$	55	— $\text{CH}_2\cdot\text{C}\cdot(\text{CH}_3)_3$	115
— $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$	30	— $\text{CH}\cdot\text{C}(\text{CH}_3)_3$	119
— $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$	*		
— $\text{CH}\cdot(\text{CH}_3)_2$	88	CH_3	
— $\text{CH}_2\cdot\text{CH}\cdot(\text{CH}_3)_2$	67		

* Too rubbery for testing

type was available in the early 1960s (Asterite, ICI) but later withdrawn. Typical properties of such a copolymer are given in *Table 15.1*.

Latices of butadiene–methyl methacrylate copolymer have been used in paper and board finishes.

Terpolymers based on methyl methacrylate, butadiene and styrene (MBS) have been increasingly used in recent years both as tough transparent plastics materials in themselves and as additives for PVC (see also Chapters 12 and 16).

Mention may also be made here of a number of polyfunctional compounds such as allyl methacrylate and glycol dimethacrylates which have been used to produce a cross-linked sheet of enhanced heat resistance compared with conventional poly(methyl methacrylate). Some manufacturers supply the sheet in an incompletely cross-linked state which allows a limited amount of forming after which the sheet may be further heated to complete the cure.

Sheet from poly(methyl α -chloroacrylate) has also been available. This material has a higher softening point than poly(methyl methacrylate). It is, however, expensive, difficult to obtain in a water-white form and the monomer is most unpleasant to handle. It is because of these disadvantageous features that the polymer is believed to be no longer commercially available.

15.11 OTHER ACRYLIC POLYMERS

A number of acrylic polymers other than those already described have been produced but these are not generally of interest as plastics materials

Poly(acrylic acid) is insoluble in its monomer but soluble in water. It does not become thermoplastic when heated. The sodium and ammonium salts have been used as emulsion-thickening agents, in particular for rubber latex. The polymer of methacrylic acid (*Figure 15.13* (VI)) is similar in properties.

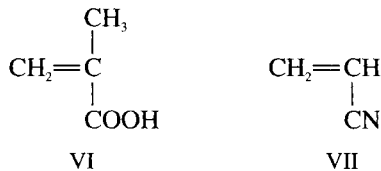


Figure 15.13

A large number of organic acrylic ester polymer have been prepared in the laboratory. Poly(methyl acrylate) is tough, leathery and flexible. With increase in chain length there is a drop in the brittle point but this reaches a minimum with poly(*n*-octyl acrylate) (see *Figure 15.12*). The increase in brittle point with the higher acrylates, which is similar to that observed with the poly- α -olefins and the poly(alkyl methacrylate)s, is due to side-chain crystallisation.

Poly(methyl acrylate) is water-sensitive and, unlike the corresponding methacrylate, is attacked by alkalis. This polymer and some of the lower acrylate polymers are used in leather finishing and as a textile size.

A number of thermosetting acrylic resins for use as surface coatings have appeared during recent years. These are generally complex copolymers and terpolymers such as a styrene–ethyl acrylate–alkoxy methyl acrylamide

polymer. Coating resins have also been produced by blending methyl methacrylate with a non-drying alkyd.

The ease with which acrylic monomers may polymerise with each other and with other monomers has led to a host of compositions, frequently of undisclosed nature, being offered for use as moulding materials, casting resins, coating resins, finishing agents and in other applications.

References

1. CASPARY, W., and TOLLENS, B., *Ann.* **167**, 241 (1873)
2. KAHLBAUM, G. W. A., *Ber.* **13**, 2348 (1880)
3. FITTIG, R., *Ber.* **12**, 1739 (1879)
4. FITTIG, R., and ENGELHORN, E., *Ann.* **200**, 65 (1880)
5. *U.S. Patent* 1,980,483; *British Patent* 395,687 (ICI)
6. *U.S. Patent* 2,042,458; *British Patent* 405,699 (ICI)
7. SALKIND, M. RIDDLE, E. H. and KEEFER, R. W., *Ind. Eng. Chem.*, **51**, 1232, 1328 (1959)
8. SWEDLOW INC., *Neth. Appl.*, **6**, 613,600 (1967); **6**, 613,601 (1967)
9. HORN, M. B. *Acrylic Resins*, Reinhold, New York (1960)
10. REHBERG, C. E., and FISHER, C. H., *Ind. Eng. Chem.*, **40**, 1431 (1948)
11. CRAWFORD, J. W. C. *Soc. Chem. Ind.*, **68**, 201 (1949)

Bibliography

- HORN, M. B. *Acrylic Resins*, Reinhold, New York (1960)
RIDDLE, E. H. *Monomeric Acrylic Esters*, Reinhold, New York (1954)
SCHILDKNECHT, C. E. *Vinyl and Related Polymers*, John Wiley, New York (1952)

Reviews

- BUCK, M. *Kunststoffe*, **77**, 1012-16 (1987)
BUCK, M. *Kunststoffe*, **80**, 1132-36 (1990)
GEISSLER, C., ALBRECHT, K., and WUNDERLICH, W., *Kunststoffe*, **86**, 1484-1488 (1996)

Plastics Based on Styrene

16.1 INTRODUCTION

It may well be argued that the history of polystyrene is more closely bound up with the history of the 20th century than is the case with any other plastics material.

In 1930 BASF, then part of IG Farben, installed a plant for producing 100 tonnes of polystyrene per annum and in 1933 the first injection moulded articles were produced. In the US semi-plant-scale work at the Dow Chemical Company showed promise of commercial success in 1934. As a consequence there became available shortly before World War II a material of particular interest because of its good electrical insulation characteristics but otherwise considerably inferior to the polystyrene available today. Because of these excellent electrical characteristics prices were paid of the order of several dollars per pound for these polymers.

In 1942 the Japanese overran Malaya and the then Dutch East Indies to cut off the main sources of natural rubber for the United States and the British Commonwealth. Because of this the US Government initiated a crash programme for the installation of plants for the manufacture of a rubber from butadiene and styrene. This product, then known as GR-S (Government Rubber-Styrene), provided at that time an inferior substitute for natural rubber but, with a renewed availability of natural rubber at the end of the war, the demand for GR-S slumped considerably. (Today the demand for SBR (as GR-S is now known) has increased with the great improvements in quality that have been made and SBR is today the principal synthetic rubber).

After the war, however, there was a large surplus capacity of plant for the manufacture of styrene and polystyrene together with a great deal of knowledge and experience that had been collected over the war years. It was therefore found possible to produce polystyrene, not as an expensive electrical insulator, but as a cheap general purpose thermoplastic.

Because of such desirable characteristics as low cost, good mouldability, excellent colour range, transparency, rigidity and low water absorption, polystyrene became rapidly developed. For many purposes, however, it was considered to be unacceptably brittle and this led to the development of the rubber-modified high-impact polystyrene (HIPS) and to the complex ABS, AMBS and

MBS materials. These developments, together with the considerable success of expanded polystyrene as both insulation and packaging materials, have led to the plastics materials based on styrene becoming a most important group of thermoplastics. In the late 1990s global capacity for polystyrene production, including high impact or toughened polystyrene was of the order of 10×10^6 tonnes which in tonnage terms rates it fourth after polyethylene, PVC and polypropylene among plastics materials. At this time production was of the order of 85% of capacity with consumption roughly equally divided between North America, Europe and the Rest of the World. It has also been estimated, in Western Europe at least, that high-impact polystyrene accounts for about 60% of the total. Global production of expanded polystyrene has been estimated at 1.85×10^6 t.p.a.

Whilst there is a large number of manufacturers, two companies, Dow and BASF, have a significant share of the market, with 16.2% and 11.4% respectively for their products Styron and Polystyrol.

In addition to polystyrene and high-impact polystyrene there are other important styrene-based plastics. Most important of these is ABS, with a global capacity of about 5×10^6 t.p.a. and production of about 3×10^6 t.p.a. The styrenic PPO materials reviewed in Chapter 21 have capacity and production figures about one-tenth those for ABS. Data for the more specialised styrene-acrylonitrile copolymers are difficult to obtain but consumption estimates for Western Europe in the early 1990s were a little over 60 000 t.p.a.

In the late 1990s a crystalline form of polystyrene, *syndiotactic polystyrene* became commercially available but unless otherwise stated references to polystyrene in this chapter will refer to the traditional amorphous polymer.

The rarely used systematic IUPAC name for polystyrene is poly-(1-phenylethylene).

16.2 PREPARATION OF THE MONOMER

In 1786 William Nicholson wrote *A Dictionary of Practical and Theoretical Chemistry*. In this work Nicholson mentions that a chemist named Neuman, on distillation of storax (a balsam derived from the tree *Liquambar orientalis*), had produced a fragrant 'empyreumatic oil'. In 1839 E. Simon¹ carried out some similar experiments, apparently quite independently, and again obtained this essential oil which he called styrol. In 1845 M. Glenard and R. Boudault² reported on the production of styrol (now known as styrene) by dry distillation of dragons blood, a resin obtained from the fruit of the Malayan rattan palm.

In 1869 Berthelot³ reported the production of styrene by dehydrogenation of ethylbenzene. This method is the basis of present day commercial methods. Over the year many other methods were developed, such as the decarboxylation of acids, dehydration of alcohols, pyrolysis of acetylene, pyrolysis of hydrocarbons and the chlorination and dehydrogenation of ethylbenzene.⁴

There are today two methods of interest, (a) the laboratory preparation, and (b) commercial preparation.

16.2.1 Laboratory Preparation

The principal constituent of storax is cinnamic acid and for laboratory purposes styrene is still most easily obtained in high purity but dry distillation of cinnamic acid and its salts under atmospheric pressure (*Figure 16.1*).

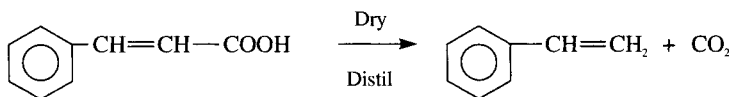


Figure 16.1

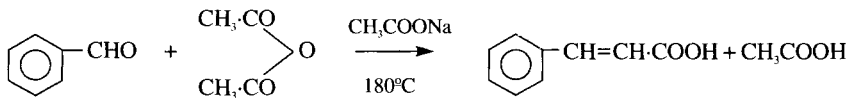


Figure 16.2

The cinnamic acid is readily prepared by heating benzaldehyde with acetic anhydride and sodium acetate (the Perkin Reaction) (Figure 16.2).

16.2.2 Commercial Preparation

The bulk of commercial styrene is prepared by the Dow process or some similar system. The method involves the reaction of benzene and ethylene to ethylbenzene, its dehydrogenation to styrene and a final finishing stage. It is therefore useful to consider this process in each of the three stages.

Preparation of ethylbenzene

Ethylbenzene is prepared by reaction of ethylene and benzene in the presence of a Friedel–Crafts catalyst such as aluminium chloride at about 95°C (Figure 16.3).

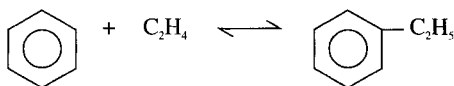


Figure 16.3

To improve the catalyst efficiency some ethyl chloride is added which produces hydrochloric acid at the reaction temperatures.

The purity of the ethylene is not critical providing that acetylene is not present. The normal purity of ethylene used is about 95%. The purity of the benzene is somewhat higher at about 99% and it is important here that sulphur, as impurity, should be below 0.10%.

In order that the amount of side reaction should be reduced and to minimise the production of polyethylbenzenes, the molar ratios of feedstock and products are approximately as indicated in the following equation (Figure 16.4).

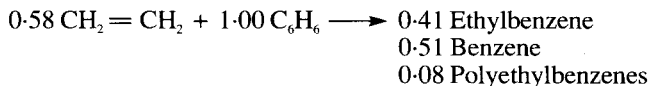


Figure 16.4

After passing through the reaction chamber the products are cooled and the aluminium chloride, which is in the form of a complex with the hydrocarbons, settles out. The ethylbenzene, benzene and polyethylbenzenes are separated by fractional distillation, the ethylbenzene having a purity of over 99%. The polyethylbenzenes are dealkylated by heating at 200°C in the presence of aluminium chloride and these products together with the unchanged benzene are recycled.

Plants have now been installed by some manufacturers to produce ethylbenzene via catalytic reforming processes. The reforming process is one which converts aliphatic hydrocarbons into a mixture of aromatic hydrocarbons. This may be subsequently fractionated to give benzene, toluene and a 'xylene fraction' from which ethylbenzene may be obtained.

Dehydrogenation

Styrene is produced from the ethylbenzene by a process of dehydrogenation (Figure 16.5).

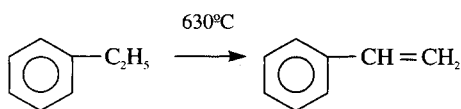


Figure 16.5

This is an endothermic reaction in which a volume increase accompanies dehydrogenation. The reaction is therefore favoured by operation at reduced pressure. In practice steam is passed through with the ethylbenzene in order to reduce the partial pressure of the latter rather than carrying out a high-temperature reaction under partial vacuum. By the use of selected catalysts such as magnesium oxide and iron oxide a conversion of 35–40% per pass with ultimate yields of 90–92% may be obtained.

Styrene purification

The dehydrogenation reaction produces 'crude styrene' which consists of approximately 37.0% styrene, 61% ethylbenzene and about 2% of aromatic hydrocarbon such as benzene and toluene with some tarry matter. The purification of the styrene is made rather difficult by the fact that the boiling point of styrene (145.2°C) is only 9°C higher than that of ethylbenzene and because of the strong tendency of styrene to polymerise at elevated temperatures. To achieve a successful distillation it is therefore necessary to provide suitable inhibitors for the styrene, to distil under a partial vacuum and to make use of specially designed distillation columns.

In one process the crude styrene is first passed through a pot containing elemental sulphur, enough of which dissolves to become a polymerisation inhibitor. The benzene and toluene are then removed by distillation. The ethylbenzene is then separated from the styrene and tar by passing this through two distillation columns, each with top temperatures of about 50°C and bottom temperatures of 90°C under a vacuum of about 35 mmHg. The tar and sulphur are

Table 16.1

Molecular weight	104.14
Density at 25°C	0.9010 g/cm ³
Refractive index at 25°C	1.5439
Boiling point	145.2°C
Vol. shrinkage on polymerisation	17%

removed by a final distillation column and the styrene is permanently inhibited by addition of 10 ppm of *t*-butylcatechol, which has less adverse effects on the final polymer than sulphur.

Styrene is a colourless mobile liquid with a pleasant smell when pure but with a disagreeable odour due to traces of aldehydes and ketones if allowed to oxidise by exposure to air. It is a solvent for polystyrene and many synthetic rubbers, including SBR, but has only a very limited mutual solubility in water. *Table 16.1* shows some of the principal properties of pure styrene.

Styrene takes part in a very large number of chemical reactions. In particular it has a strong tendency to polymerise on heating or on exposure to ultraviolet light.

16.3 POLYMERISATION

Polystyrene was first made by E. Simon in 1839 who at the time believed he had produced an oxidation product, which he called styrol oxide. Since that time the polymerisation of styrene has been extensively studied. In fact a great deal of the work which now enables us to understand the fundamentals of polymerisation was carried out on styrene.

The polymer may be prepared by mass, suspension, solution, and emulsion methods, the first two being the most important. Mass polymerisation has the advantage of apparent simplicity and gives a polymer of high clarity and very good electrical insulation characteristics. There are, however, severe problems due to the exothermic reaction and the product has a broad molecular weight distribution. Polymerisation in solution reduces the exotherm but may lead to problems of solvent recovery and solvent hazards. The solvent may also act as a chain transfer agent and cause a reduction in molecular weight. Suspension polymerisation avoids most of these problems but there is some contamination of the polymer by water and the suspension agent. Furthermore the polymer must be dried and aggregated before being sold as pellets suitable for injection moulding and extrusion. Emulsion polymerisation techniques are seldom used with polystyrene since the large quantities of soap used seriously affects clarity and electrical insulation characteristics. This process is therefore used only for the production of polystyrene latex.

16.3.1 Mass Polymerisation

Continuous mass polymerisation units are extensively used for making polystyrene. Great care is necessary to prevent the heat of reaction accelerating the polymerisation to such an extent that the reaction gets out of control. The problem is made particularly difficult by the fact that heat can only be taken away from the points of higher temperature by conduction because of the very high

viscosity of the reacting material, and also the low thermal conductivities of both styrene and polystyrene.

Most mass processes used today are a variation of that developed by Wolff in Germany before World War II. In this process the styrene is prepolymerised by heating (without initiators) in a prepolymerisation kettle at 80°C for two days until a 33–35% conversion to polymer is reached (see *Figure 16.6*). The monomer–polymer mixture is then run into a tower about 25 ft high. The tower is fitted with heating and cooling jackets and internally with a number of heating and cooling coils. The top of the tower is maintained at a temperature of about 100°C, the centre at about 150°C and the bottom of the tower at about 180°C. The high bottom temperature not only ensures a higher conversion but boils off the residual styrene from the polymer. The base of the tower forms the hopper of an extruder from which the melt emerges as filaments which are cooled, disintegrated and packed.

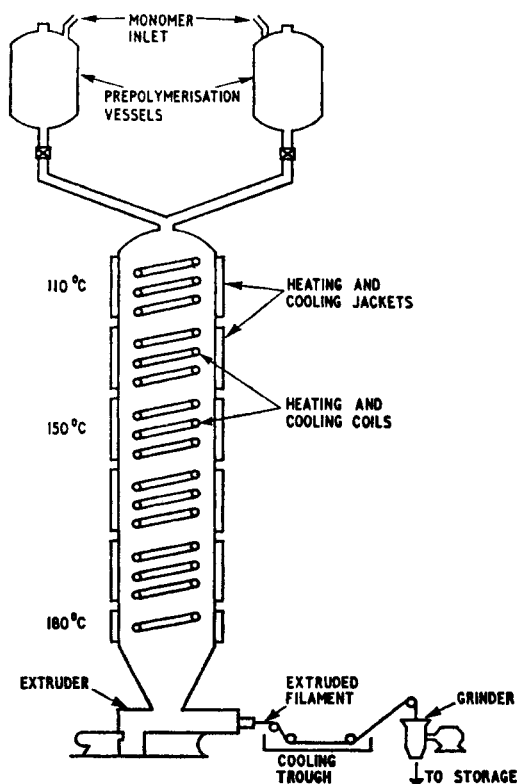


Figure 16.6. Tower process for mass polymerisation of styrene

That such a process is today commercially important is a measure of the success of chemical engineers in overcoming heat transfer problems involved with masses incapable of being stirred. An idea of the extent of the problem can be gauged from the fact that it takes six hours to cool a sample of polystyrene from 160°C using a cooling medium at 15°C when the heat transfer distance is two inches.

16.3.2 Solution Polymerisation

By polymerising styrene in solution many problems associated with heat transfer and the physical movement of viscous masses are reduced, these advantages being offset by problems of solvent recovery and the possibility of chain transfer reactions. In 1955 Distrene Ltd started a plant at Barry in South Wales for the production of styrene by such a solution polymerisation process and some details have been made available.^{5,6} The essential details of this process are indicated by Figure 16.7.

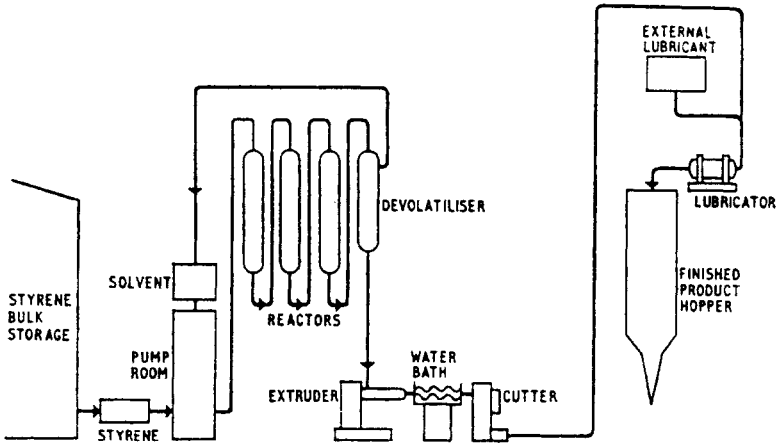


Figure 16.7. Flow diagram for commercial solution polymerisation of styrene

Styrene and solvent are blended together and then pumped to the top of the first reactor which is divided into three heating zones. In the first zone the solution is heated to start up the polymerisation reaction but because of the exothermic reaction in the second and third zones of the first reactor and the three zones of the second reactor Dowtherm cooling coils are used to take heat out of the system. By the time the reaction mixture reaches the third reactor the polymerisation reaction has started to slow down and so the reaction mixture is reheated.

From the third reactor the polymer is then run into a devolatilising ('stripping') vessel in the form of thin strands. At a temperature of 225°C the solvent, residual monomer and some very low molecular weight polymers are removed, condensed and recycled. The polymer is then fed to extruder units, extruded as filaments, granulated, lubricated and stored to await dispatch.

16.3.3 Suspension Polymerisation

Suspension polymerisation of styrene is widely practised commercially.⁷ In this process the monomer is suspended in droplets $\frac{1}{32}$ – $\frac{1}{64}$ in. in diameter in a fluid, usually water. The heat transfer distances for the dissipation of the exotherm are thus reduced to values in the range $\frac{1}{64}$ – $\frac{1}{128}$ in. Removal of heat from the low-viscosity fluid medium presents little problem. The reaction is initiated by monomer-soluble initiators such as benzoyl peroxide.

It is necessary to coat the droplets effectively with some suspension agent, e.g. poly(vinyl alcohol), talc etc., to prevent them cohering. Control of the type and quantity of suspension agent and of the agitation has a pronounced effect on the resulting particles. It is not unknown for the whole of the polymerising mass to aggregate and settle to the bottom of the reaction vessel because of such conditions being incorrect. Following polymerisation, unreacted monomer may be removed by steam distillation and the polymer is washed and dried.

The disadvantages of the suspension process are that about 70% of the volume of the kettle is taken up by water, the need for a drying stage which could cause discolouration by degradation and the need to convert the small spheres formed into a larger shape suitable for handling. Furthermore, the suspension method cannot easily be converted into a continuous process.

16.3.4 Emulsion Polymerisation

Because of the large quantities of soap left in the polymer, which adversely affects clarity, electrical insulation characteristics and problems in agitation and densification, this process is used only for making latices.

The techniques used are in many respects similar to those for emulsion polymerised PVC.

16.3.5 Grades Available

In addition to the high-impact (toughened) polystyrenes dealt with later in this chapter, polystyrene is available in a number of grades. These may conveniently be grouped as follows:

- (1) General purposes grades. In these grades a balance is attempted to obtain good heat resistance, reasonably high setting-up temperature, good flow properties and reasonable impact strength.
- (2) High molecular weight grades. Polystyrene has little strength if its molecular weight is below 50 000 but increase rapidly, with molecular weight up to 100 000 (*Figure 16.8*). An increase in molecular weight above 100 000 has little further effect on tensile strength but continues to have an adverse effect on the ease of flow. Such higher molecular weight grades are sometimes used where improved impact strength is required without the loss of clarity that occurs with the toughened polystyrenes.

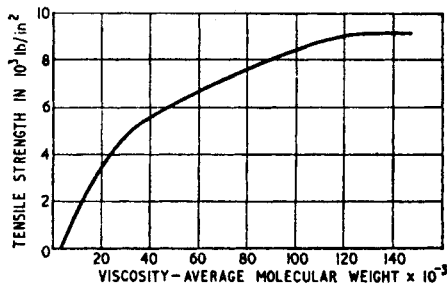


Figure 16.8. Influence of molecular weight on the tensile strength of polystyrene

- (3) Heat-resistant grades. By reducing the amount of volatile matter the softening point of the polystyrene can be raised. For example, by reducing the monomer content from 5% to 0% the softening point may be raised from 70°C to 100°C. Commercial heat-resisting grades usually have a softening point about 7°C above the softening point of general purpose polystyrene.
- (4) Easy flow grades. By incorporating an internal lubricant such as butyl stearate or liquid paraffin, by using a polymer of lower molecular weight, by careful control of granule shape and size and by lubrication of the granules with an external lubricant such as zinc stearate, the flow properties of polystyrene may be improved with little effect on other properties apart from reduction of up to 10°C in the softening point. These materials are very useful for thin-wall mouldings, for moulding with minimum frozen-in strains or other products where the moulding is rather intricate. They have not, however, replaced general purpose polystyrene because of their lower setting-up temperature, which causes a prolongation of the injection moulding cycle.

16.4 PROPERTIES AND STRUCTURE OF POLYSTYRENE

Polystyrene has the simple repeating structure shown in *Figure 16.9* and as might be expected from such a substantially linear polymer it is thermoplastic. As with polypropylene, PVC and other vinyl compounds there is the possibility of various stereo-regular forms. Because of its amorphous nature the commercial polymer has for long been regarded as atactic. As with poly(methyl methacrylate) subsequent work has, however, indicated that the syndiotactic segments are more frequent than atactic segments and it appears that this may be a common feature of most free-radical initiated vinyl polymers. The specific position of the benzene ring is, however, sufficiently random to inhibit crystallisation.

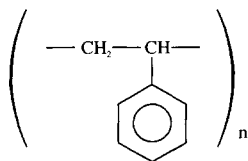


Figure 16.9

Because of the chain-stiffening effect of the benzene ring the T_g s of commercial materials are in the range 90–100°C and isotactic polymers have similar values (approx. 100°C). A consequence of this T_g value plus the amorphous nature of the polymer is that we have a material that is hard and transparent at room temperature. Isotactic polystyrenes have been known since 1955 but have not been of commercial importance. Syndiotactic polystyrene using metallocene catalysis has recently become of commercial interest. Both stereoregular polymers are crystalline with T_m values of 230°C and 270°C for the isotactic and syndiotactic materials respectively. They are also somewhat brittle (see Section 16.3).

Being a hydrocarbon with a solubility parameter of 18.6 MPa^{1/2} it is dissolved by a number of hydrocarbons with similar solubility parameters, such as benzene and toluene. The presence of a benzene ring results in polystyrene having greater reactivity than polyethylene. Characteristic reactions of a phenyl group such as chlorination, hydrogenation, nitration and sulphonation can all be performed with

polystyrene. Chain rupture and discolouration are frequently additional effects of such reactions.

The pure hydrocarbon nature of polystyrene gives it excellent electrical insulation characteristics, as a result of both the fundamentally good characteristics of the material and to the low water absorption of such a hydrocarbon polymer. The insulation characteristics are therefore well maintained in humid conditions.

16.5 GENERAL PROPERTIES

Polystyrene is a hard, rigid transparent thermoplastic which emits a characteristic metallic ring when dropped. It is free from odour and taste, burns with a sooty flame and has a low specific gravity of 1.054. Because of its low cost, good mouldability, low moisture absorption, good dimensional stability, good electric insulation properties, colourability and reasonable chemical resistance it is widely used as an injection moulding and vacuum forming material. Additionally the low thermal conductivity has been made use of in polystyrene foam used for thermal insulation. The principal limitations of the polymer are its brittleness, inability to withstand the temperature of boiling water and its mediocre oil resistance.

The mechanical properties of polystyrene depend to some extent on the nature of the polymer (e.g. its molecular weight), on the method of preparing the sample for testing and on the method of test, as is the case with all plastics materials.

Some typical mechanical properties of polystyrene are indicated in *Table 16.2*. It will be observed that there is little real difference in the mechanical properties of the four types of straight polystyrene considered in the table.

Table 16.2

Property	Test method	Grade of polystyrene			
		General purpose	High mol. wt	Heat resistant	Easy flow
Tensile strength (MPa) (10^3 lbf/in ²)	ASTM D. 638-58T	40-48	45-52	45-52	40-48
Elongation(%)	ASTM D. 638-58T	6-7	6.5-7.5	6.5-7.5	6-7
Modulus in tension (MPa) (10^5 lbf/in ²)	ASTM D.638-58T	1.0-2.5	1.0-2.5	1.0-2.5	1.0-2.5
Flexural strength (MPa) (10^3 lbf/in ²)	ASTM D. 790-58T	35	35	38	35
Impact strength (notched Izod ft lbf in ⁻¹ notch)	BSI493	5.0	5.0	5.5	5.0
		62-76	69-83	76-97	62-76
		9-11	10-12	11-14	9-11
		0.25-0.35	0.25-0.35	0.25-0.35	0.25-0.35

Amongst the optical properties of polystyrene of importance are its high transmission of all wavelengths of visible light and its high refractive index (1.592) which gives it a particularly high 'brilliance'. Certain factors may, however, mar the good optical characteristics such as haze and yellowing. Haze is believed to be due to the presence of dust and also to variations in the refractive index caused by localised molecular orientation. Yellowness may be due to coloured impurities in the monomer, or to impurities which cause reaction during

polymerisation to contribute to the yellowness, or to aging. Yellowing on aging has been shown to be an oxidation reaction, the rate of yellowing increasing with decrease in wavelength, monomer content and in the presence of traces of sulphur. In one example radiation from a 15W germicidal lamp (2537 Å) one foot from a polystyrene sample caused yellowing in a few hours. In another experiment it was found that the presence of 0.040% sulphur caused a seven-fold increase in the amount of yellowing after a given time in an artificial light aging cabinet. This has meant that sulphur cannot be tolerated as a polymerisation inhibitor during storage of the monomer. The incorporation of about 1% of saturated aliphatic amines, cyclic amines or aminoalcohols has been found to improve greatly the resistance to weathering. Example of materials quoted in the literature include diethylaminoethanol and piperazine. Many proprietary materials are now marketed.

The electrical insulation characteristics of polystyrene are extremely good. Typical figures are given in *Table 16.3*.

Table 16.3

<i>Property</i>	<i>Value</i>	<i>ASTM test</i>
Dielectric strength (kV/cm)	190–270	D.149–44
Volume resistivity (Ω m)	10^{19} – 10^{21}	D.257–46
Dielectric constant 60– 10^6 Hz	2.45–2.65	D.150–46T
Power factor 60– 10^6 Hz	$1-2 \times 10^{-4}$	D.150–46T

The negligible effect of frequency on dielectric constant and power factor from 60 to 10^6 Hz is particular interest. It should, however, be noted that at 10^7 Hz the power factor may increase about four-fold.

The chemical resistance of polystyrene is not generally as good as that of polyethylene. It is dissolved by a number of hydrocarbons such as benzene, toluene and ethylbenzene, by chlorinated hydrocarbons such as carbon tetrachloride, chloroform and *o*-dichlorobenzene, by a number of ketones (but not acetone), and esters and by a few oils (e.g. oil of verbena and ylang ylang oil). Many other materials, in particular acids, alcohols, oils, cosmetic creams and foodstuffs, will cause crazing and cracking and in some cases chemical decomposition. The extent of attack will also depend on such factors as the grade of polystyrene, internal stresses in the polystyrene product, external stresses to which the part is subjected, the time and temperature of exposure and the concentration of the reagent. Furthermore many materials do not attack polystyrene individually but do so in combination. Cosmetic cream and patent medicines provide many examples of this synergistic-type behaviour. Technical service bulletins supplied by the manufacturer provide useful information on the subject of chemical resistance.

Particular mention should be made of the influence of styrene monomer (*Figure 16.10*). An increase of the residual monomer from 0 to 5% can cause a 30°C reduction in softening point. On the other hand there is a marked increase in the ease of flow. It is not, however, good practice to change the flow properties in this way as the monomer will volatilise in the processing machine and the

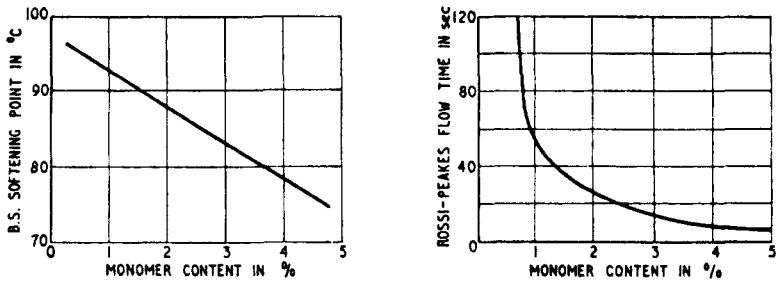


Figure 16.10. Influence of styrene monomer content of the softening point and flow characteristics of polystyrene, (After Haward and Crabtree)⁸

bubbles formed will be distorted to produce such faults as 'silver streaks' and 'mica marks' in the finished product.

The thermal properties are of interest to both the user of the end-product and to the processor. From the user's point of view the principal features are the very low thermal conductivity (approx. 0.13 W/mK) and the comparatively low softening point. Standard tests give softening points of about 90°C, that is below the boiling point of water. In addition many properties are affected by temperature (Figure 16.11).

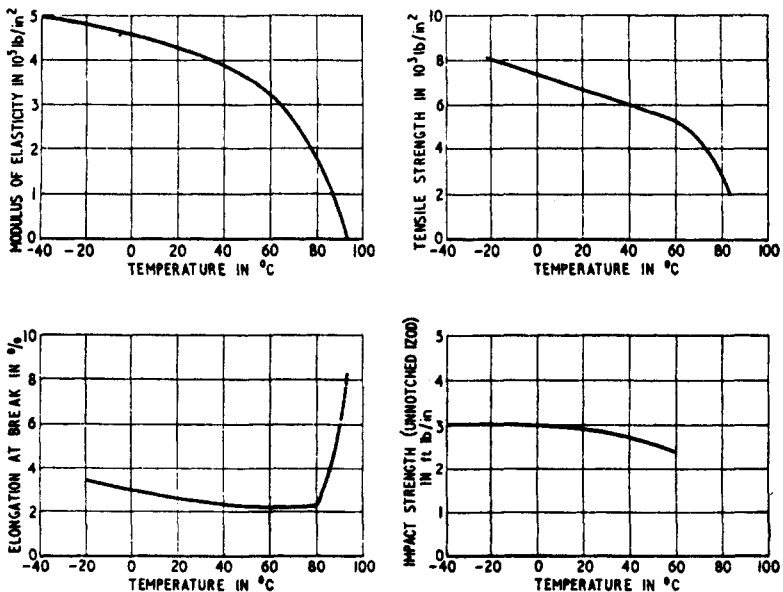


Figure 16.11. Influence of temperature on some mechanical properties of polystyrene. (After Boundy and Boyer)⁴

In common with other thermoplastic melts polystyrene exhibits pseudoplastic behaviour. At shearing stresses below $60/M_w$ MPa (where M_w = average molecular weight), the ratio of shear stress to shear rate is almost constant and the melt is substantially Newtonian. Above this shear stress non-Newtonian

Table 6.4 Effect of shear stress on melt viscosity⁹

Shearing stress	Apparent viscosity at 232°C (poise)	
	GP polystyrene	Polyethylene $D = 0.916$ $MFI = 2$
Zero shear	24 000	9500
7 kPa	1 500	5300

behaviour becomes pronounced. The much stronger dependence on shear rate of polystyrene compared with low-density polyethylene is shown in *Table 16.4*. The shear stress selected is considered as typical during injection moulding of polystyrene.

The melt viscosity is also strongly dependent on temperature and molecular weight. The equation

$$\log \mu_a = K + 3.4 \log_{10} \bar{M}_w$$

(μ_a = apparent viscosity at zero shear rate; \bar{M}_w = weight average molecular weight) has been found¹⁰ to be applicable to polystyrene (and also to other linear polymers—see Chapter 8). Although a wide range of viscosities are obtained by varying processing conditions and polymer molecular weight the numerical values generally lie between the high values experienced with unplasticised PVC and the low values observed with the nylons (see also *Figure 16.11*).

The specific heat of polystyrene is dependent on temperature and at 200°C the value is approximately double that at room temperature.⁴

16.6 HIGH-IMPACT POLYSTYRENE (HIPS) (TOUGHENED POLYSTYRENES (TPS))

For many applications polystyrene might be considered to be too brittle a polymer. Because of this, polystyrene manufacturers have made a number of attempts to modify their products.

The methods of approaching this problem include:

- (1) Use of higher molecular weight polymers.
- (2) Use of plasticisers.
- (3) Incorporation of fillers such as glass fibre, wood flour, etc.
- (4) Deliberate orientation of the polymer molecules.
- (5) Copolymerisation
- (6) The use of rubbery additives.

Of these methods the first gives only marginal improvements whilst the second approach has far too severe an effect on the softening point to be of any commercial value. The use of fillers has been practised to some extent in the United States but is not of importance in Europe. Deliberate orientation is limited to filament and sheet.

Very many copolymers with styrene as the principal constituent have been prepared and a number have been marketed. In some instances there is an appreciable increase in toughness but usually in such cases the softening point of the copolymer is much lower than that of the homopolymer. For example copolymers from 70 parts of styrene and 30 parts butadiene, although tough, are leather-like. Such materials have in the past been used primarily as stiffening resins in rubber compounds, it generally being considered that if sufficient butadiene were present in the polymer to raise toughness sufficiently then the softening point would be unacceptably low. One exception to this rule is the range of materials first marketed by Phillips as BDS K-resin. These are a special type of block copolymer dealt with later.

The materials now classified as high-impact polystyrenes, or with increasing frequency as toughened polystyrenes, are combinations of polystyrene with rubbery materials. The early grades that were first developed in the 1950s used hot polymerised SBR (see Chapter 11) but for technical reasons discussed later SBR has now been largely replaced by solution polymerised polybutadiene rubber (also see Chapter 11). More recently, there has been interest in the use of SBS triblock thermoplastic rubbers for this purpose. Because of the presence of main chain double bonds both rubbers are subject to oxidation, with the consequence that high-impact polystyrene polymers prepared using such diene rubbers become brittle on prolonged exposure to sunlight. Materials showing improved weathering resistance have been developed in Japan using EPDM rubbers and similar materials have now been developed elsewhere.

The polystyrene and the rubber may be blended in a number of ways. Originally the ingredients were compounded in a two-roll mill, in an internal mixer or in an extruder. The impact strength of the products was, however, little better than the unmodified polymer. Blending of SBR latex and polystyrene latex, which is then followed by co-coagulation and drying, has also been employed in the past but once again the improvement is only marginal.

Today the common practice is first to dissolve the rubber in the styrene monomer and then to polymerise the styrene in the usual way. By this process the resultant blend will contain not only rubber and polystyrene but also a graft polymer where short styrene side chains have been attached to the rubber molecules. This gives a marked improvement in the impact strengths that can be obtained.

It has been demonstrated that with SBR polystyrene blends the rubber should exist in discrete droplets, less than $50\mu\text{m}$ in diameter where a good finish is required, within the polystyrene matrix. It is believed that in such a form the rubber can reduce crack propagation and hence fracture in various ways.¹¹ The most favoured current explanations of this were discussed in Chapter 3. Suffice it to say here that the following features appear necessary for a suitable blend:

- (1) The rubber and the polystyrene should not be compatible. If they are there will be molecular mixing and no improvement in toughness.
- (2) The rubber should not be too incompatible if good rubber-polystyrene adhesion is to be obtained.

In effect this means that, to achieve reasonable toughness, semicompatible rubbers should be used. Semicompatibility may be achieved (*a*) by selecting mixtures of slightly different solubility parameter from the polystyrene, (*b*) by

judicious amounts of cross-linking or (c) by judicious use of selected graft polymers. In current commercial grades it is probable that all three features are involved.

In commercial SBR-based polymers there are three main variables to be considered:

- (1) The amount of SBR added, usually 5–20% (see Figure 16.12). An increase in the SBR will increase the toughness but there will be an attendant reduction in softening point.
- (2) The size of the rubber particles. In a typical blend these would be in the range 1–10 μm . Grades containing large particles (and which contain up to 10% acrylonitrile residues in the matrix polymer) are used where good stress cracking resistance is required. Small particles are used where high gloss, toughness and stiffness are priority requirements.
- (3) The gel content (toluene insoluble per cent) of the rubber and the swelling index of the gel (the ratio of the volume of a swollen gel to its unswollen volume). The former is a measure of the amount of cross-linked material and the second a measure of the intensity of cross-linking. It has been found¹¹ that a sample of medium gel content (5–20%) and a medium swelling index (10–20) gives the best impact strength in the blend.

A high-impact polystyrene (polystyrene SBR blend) may have seven times the impact strength of ordinary polystyrene, but about half the tensile strength, a lower hardness and a softening point some 15°C lower. Because of the rubber content there may be a reduction in light and heat stability and stabilisers are normally incorporated.

The use of stabilisers (antioxidants) may, however, have adverse effects in that they inhibit cross-linking of the rubber. The influence of phenolic antioxidants on polystyrene-SBR alloys blended in an internal mixer at 180°C has been studied. It was found that alloys containing 1% of certain phenolic antioxidants were gel-deficient in the rubber phase.¹² The gel-deficient blends were blotchy in appearance, and had lower flow rates compared with the normal materials, and mouldings were somewhat brittle. Substantial improvements in the impact properties were achieved when the antioxidant was added later in the mixing cycle after the rubber had reached a moderate degree of cross-linking.

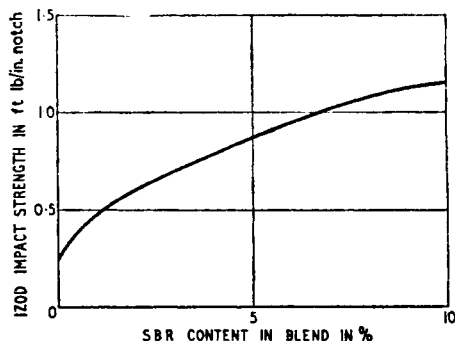


Figure 16.12. Effect of adding SBR on the impact strength of polystyrene

SBR has now been superseded by high *cis*-1,4-polybutadiene because of the greater effectiveness of the latter.^{13,14} Reasons given for this greater effectiveness include a better balance of the compatibility–incompatibility factors, the lower glass transition temperature of the rubber (-100°C instead of -55°C for SBR), greater resilience than SBR and the higher reactivity towards grafting. In addition the polybutadiene is not contaminated with the large amounts of soap associated with emulsion polymerised SBR and so leads to better gloss and lower moisture pick-up. For the best results a typical poly-1,4-butadiene would have a high *cis* content (for minimum T_g), low gel ($<0.05\%$ for maximum gloss) and low molecular weight (Mooney Viscosity of approx. 38) to facilitate dissolution and would be water-white and free of residual traces of catalyst fragments such as titanium which may cause severe discolouration. High-impact materials with a degree of transparency have been prepared from 1:2-polybutadiene. In this case the double bond is present in a pendant vinyl group rather than in the main chain. It is thus more reactive and unless the grafting process is carried out at temperatures below 100°C and under carefully controlled conditions excess cross-linking may occur.

Transparent toughened polystyrene polymers are produced by blending polystyrene with SBS block copolymers (see Section 11.8). During the 1970s and 1980s most development was with block copolymers with a radial (or star) shape. Two types were developed: block copolymers with a central butadiene block, and block copolymers with a central polystyrene block.

More recently Fina Chemicals have introduced linear SBS materials (Finaclear) in which the butadiene is present both in block form and in a mixed butadiene–styrene block. Thus comparing typical materials with a total styrene content of about 75% by weight, the amount of rubbery segment in the total molecule is somewhat higher. As a result it is claimed that when blended with polystyrene the linear block copolymers give polymers with a higher impact strength but without loss of clarity.

Tough transparent sheet may be produced by blending standard polystyrene with block copolymer in an extruder in the ratios 80:20 to 20:80, depending on the application of the products subsequently thermoformed from the sheet. For example, sheet for thermoforming an egg tray will not require the same level of impact strength as that required for jam jars.

Optical properties of the blends are somewhat dependent on the molecular weight of the polystyrene, presence of additives such as lubricant in the polystyrene, ratio of polystyrene to SBS, processing conditions and mixing effectiveness of the extruder. It is stated that the optical properties of the sheets are similar whether linear or radial type stereoblock polymers are used.

A number of polyisoprenes¹⁵ have also been investigated as potential toughening agents. By careful control of grafting conditions high-impact blends have been made from 3:4-polyisoprenes. Neither natural rubber (essentially *cis*-1,4-polyisoprene) nor the other synthetic polyisoprenes give a significant reinforcing effect. Ethylene–propylene rubbers which have been peroxidised by bubbling oxygen through a solution of the polymer whilst irradiating with ultraviolet light may also toughen polystyrene. The peroxidised rubber is dissolved in styrene monomer in the concentration range of 5–20% and the solution reacted at above 70°C . The peroxide or hydroperoxide groups present then decompose with the formation of free radicals which initiate growth of a polystyrene branch on the chain of the rubber molecule.

16.7 STYRENE-ACRYLONITRILE COPOLYMERS

Styrene-acrylonitrile copolymers (~20–30% acrylonitrile content) have been commercially available for a number of years. Initially, however, the price of these materials was too high for them to find more than a few specialised outlets. Because of the polar nature of the acrylonitrile molecule these copolymers have better resistance to hydrocarbons, oils and greases than polystyrene. They also have a higher softening point, a much better resistance to stress cracking and crazing and an enhanced impact strength and yet retain the transparency of the homopolymer. The higher the acrylonitrile content the greater the toughness and chemical resistance but the greater the difficulty in moulding and the greater the yellowness of the resin. Typical resins have a water absorption about that of poly(methyl methacrylate), i.e. about ten times that of polystyrene but about one-tenth that of cellulose acetate.

Some typical properties of styrene-acrylonitrile plastics, referred to in many countries as SAN, are compared with those of other styrene-based plastics in *Table 16.7*.

The market for SAN has remained small relative to that for polystyrene and ABS (discussed in the next section) and is probably only about 5% that of the latter. Major producers are BASF, Dow, Monsanto and Montedison.

The important features of rigidity and transparency make the material competitive with polystyrene, cellulose acetate and poly(methyl methacrylate) for a number of applications. In general the copolymer is cheaper than poly(methyl methacrylate) and cellulose acetate, tougher than poly(methyl methacrylate) and polystyrene and superior in chemical and most physical properties to polystyrene and cellulose acetate. It does not have such a high transparency or such food weathering properties as poly(methyl methacrylate). As a result of these considerations the styrene-acrylonitrile copolymers have found applications for dials, knobs and covers for domestic appliances, electrical equipment and car equipment, for picnicware and housewares, and a number of other industrial and domestic applications with requirements somewhat more stringent than can be met by polystyrene.

SAN is also used for pharmaceutical and cosmetic packaging. Usage breakdown for Western Europe in the early 1990s has been estimated at 28% for household products, 21% for domestic electrical applications, 8% for battery casings, 12% for pharmaceutical/cosmetic packaging and a large figure of 31% for other applications.

Glass-reinforced grades of SAN exhibit a modulus several times that of the unfilled polymer and, as with other glass-filled polymers, a reduced coefficient of thermal expansion and lower moulding shrinkage. The materials are thus of interest on account of their high stiffness and dimensional stability.

One unusual but nevertheless important application of SAN has been in the manufacture of polymer polyols used in the manufacture of flexible polyurethane foams. Proportions of up to 40% of the polyol may be used to increase stiffness as foam bulk densities are lowered (see Section 27.5.4).

16.8 ABS PLASTICS

Although tough enough for many uses, styrene-acrylonitrile copolymers are inadequate in this respect for other purposes. As a consequence, a range of

materials popularly referred to as ABS polymers first became available in the early 1950s. Since that time the ABS polymers have become well established, with production now of the order of 3×10^6 tonnes per annum and thus in tonnage terms only surpassed by the 'big four'; polyethylene, polypropylene, PVC and polystyrene. In particular, the material has become of considerable importance for quality equipment housings. The reasons for its widespread acceptance are:

- (1) High impact resistance.
- (2) Good stiffness.
- (3) Excellent surface quality.
- (4) High dimensional stability at elevated temperatures.
- (5) Good chemical resistance.
- (6) Good stress cracking resistance.

Its main disadvantages are:

- (1) Lack of transparency.
- (2) Poor weathering resistance.
- (3) Poor flame resistance.

16.8.1 Production of ABS materials

The term ABS was originally used as a general term to describe various blends and copolymers containing acrylonitrile, butadiene and styrene. Prominent among the earliest materials were physical blends of acrylonitrile-styrene copolymers (SAN) (which are glassy) and acrylonitrile-butadiene copolymers (which are rubbery). Such materials are now obsolete but are referred to briefly below, as Type 1 materials, since they do illustrate some basic principles. Today the term ABS usually refers to a product consisting of discrete cross-linked polybutadiene rubber particles that are grafted with SAN and embedded in a SAN matrix.

The Type 1 materials may be produced by blending on a two-roll mill or in an internal mixer or blending the lattices followed by coagulation or spray drying. In these circumstances the two materials are compatible and there is little improvement in the impact strength. If, however, the rubber is lightly cross-linked by the use of small quantities of peroxide the resultant reduction in compatibility leads to considerable improvements in impact strength (see *Figures 16.14* and *16.15*). A wide range of polymers may be made according to the nature of each copolymer and the proportion of each employed.¹¹ A typical blend would consist of:

- 70 parts (70:30 styrene-acrylonitrile copolymer)
- 40 parts (63:35 butadiene-acrylonitrile rubber).

By altering these variables, blends may be produced to give products varying in processability, toughness, low-temperature toughness and heat resistance.

Although the nitrile rubbers employed normally contain about 35% acrylonitrile the inclusion of nitrile rubber with a higher butadiene content will increase the toughness at low temperatures. For example, whereas the typical blend cited above has an impact strength of only $0.9 \text{ ft lbf in}^{-1}$ notch at 0°F , a blend of 70 parts styrene-acrylonitrile, 30 parts of nitrile rubber (35% acrylonitrile) and 10 parts nitrile rubber (26% acrylonitrile) will have an impact value of $4.5 \text{ ft lbf in}^{-1}$ notch at that temperature.¹¹

From *Figure 16.13* it will be seen that a minimum of about 20% cross-linked nitrile rubber is required in order to obtain tough products. For high-impact

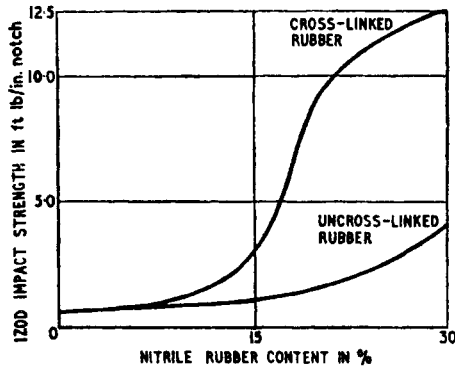


Figure 16.13. Variation in impact strength against concentration of rubber in ABS Type 1 blends¹¹

material the acrylonitrile–styrene copolymers should have a high molecular weight. The commercial copolymers containing 20–30% acrylonitrile are suitable for the preparation of Type 1 ABS polymers. The amount of gelled rubber also has a profound effect on the strength, as shown in *Figure 16.14*. The samples used were prepared by milling the rubber and peroxide for 15 minutes, the styrene–acrylonitrile resin then being added and blended for a further 15 minutes. The physical nature of the blend is more complex than with the SBR-modified polystyrene, as it appears that rubber molecule networks may exist in the resin phase.

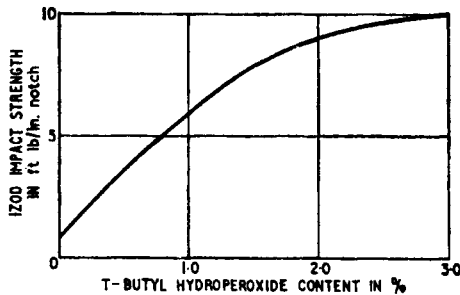


Figure 16.14. Effect of cross-linking agent on impact strength of 75/25 styrene–acrylonitrile/nitrile rubber blend.

To produce the Type 2 polymers, styrene and acrylonitrile are added to polybutadiene latex and the mixture warmed to about 50°C to allow absorption of the monomers. A water-soluble initiator such as potassium persulphate is then added to polymerise the styrene and acrylonitrile. The resultant materials will be a mixture of polybutadiene, polybutadiene grafted with acrylonitrile and styrene, and styrene–acrylonitrile copolymer. The presence of graft polymer is essential since straightforward mixtures of polybutadiene and styrene–acrylonitrile copolymers are weak. In addition to emulsion processes such as those described above, mass and mass/suspension processes are also of importance.

The resulting polymers may vary in the following respects:

- (a) SAN-rubber ratio;
- (b) the styrene to acrylonitrile ratio in the SAN component;
- (c) the amount of grafted SAN;
- (d) rubber particle size and particle size distribution;
- (e) cross-link density of the rubber;
- (f) use of modified styrenes such as α -methyl styrene to increase heat deflection temperatures;
- (g) use of saturated rubbers instead of polybutadiene to improve weatherability.

It is obvious that the range of possible ABS-type polymers is very large. Not only may the ratios of the three monomers be varied but the way in which they can be assembled into the final polymer can also be the subject of considerable modifications. Neither is it necessary to be restricted to the use of acrylonitrile, butadiene, and styrene. Because of the wide range of products available and because the chemical nature of these materials is rarely divulged it is not possible to give detailed properties of these materials unless one resorts to lists of properties of named proprietary materials. In general, however, these materials have a high impact strength, have softening points as high as, and sometimes higher than, general purpose polystyrene, and moulded specimens generally have a very good surface appearance. Some typical properties of ABS polymers compared with other styrene-containing polymers are given in *Table 16.5*.

In recent years there has been an increased demand for a variety of special ABS grades, for example products with improved flame retardancy.

Improvements in flame retardancy have been met in two ways:

- (1) By the use of fire-retardant additives.
- (2) By blending ABS with PVC.

Bromine compounds are often used as flame retardant additives but 15–20 pts phr may be required. This is not only expensive but such large levels lead to a serious loss of toughness. Of the bromine compounds, octabromodiphenyl ether has been particularly widely used. However, recent concern about the possibility of toxic decomposition products and the difficulty of finding alternative flame retarders for ABS has led to the loss of ABS in some markets where fire retardance is important. Some of this market has been taken up by ABS/PVC and ASA/PVC blends and some by systems based on ABS or ASA (see Section 16.9) with polycarbonates. Better levels of toughness may be achieved by the use of ABS/PVC blends but the presence of the PVC lowers the processing stability.

There is also a demand for glass-clear forms of ABS since standard forms are opaque. This can be achieved by matching the refractive indices (μ) of the rubber particle, graft and matrix phases and eliminating any additives or polymerisation ingredients that may cause opacity. A variety of approaches have been used including the use of SBR or carboxy-terminated NBR to modify the refractive index of the rubber phase and to use terpolymers of methyl methacrylate, styrene and acrylonitrile instead of the normal SAN. In such applications it is important that the refractive index match should be over the operating temperature range.

Table 16.5 Typical mechanical properties of compression-moulded polystyrene plastics as measured by appropriate ASTM tests

<i>Property</i>	<i>Units</i>	<i>G.P. polystyrene</i>	<i>Medium-impact PS-SBR blend</i>	<i>Very high impact PS-SBR blend</i>	<i>Styrene acrylonitrile</i>	<i>Medium impact ABS</i>	<i>High impact ABS</i>	<i>MBS</i>
Specific gravity	–	1.05	1.05	1.02	1.06	1.04–1.07	1.01–1.04	1.07–1.10
Tensile strength	lbf/in ² MPa	7500 52	5000 35	2000 14	6000–10 000 40–70	5500–7000 38–48	3500–6000 24–40	6000–7800 40–55
Tensile modulus	10 ⁵ lbf/in ² MPa	5.7 3900	4.7 3250	2.5 1750	5.4 3700	3.0–4.2 2000–3000	2.0–3.0 1500–2000	2.5–3.5 1700–2500
Impact strength	ft lbf in ⁻¹ notch	0.25	0.6	4.5	0.3–0.6	1.0–6.8	7.0	–
Vicat softening point	°C	100	94	94	106	100–108	104	96–99

There has also been a demand in recent years for an ABS-type material with an enhanced heat distortion temperature. In ABS polymers this is largely controlled by the T_g of the resin or glassy component. Consequently three approaches to raising the distortion temperature have been developed. They are:

- (1) Replacement, in full or in part, of the styrene by a monomer whose homopolymer has a higher T_g than polystyrene. In the case of partial replacement it is also important that the copolymers have T_g s intermediate to the two homopolymers. Fortunately this is usually the case.
- (2) The addition of third monomers that enhance T_g .
- (3) Blending the glassy phase polymer with another polymer of higher T_g such as a polycarbonate.

The first approach has been important commercially. The monomer most commonly used is α -methylstyrene (see Section 16.11), whose polymer has a T_g of about 120°C. The heat distortion temperature of the resultant-ABS type polymer will depend on the level of replacement of styrene by the α -methylstyrene. (It may be noted in passing that α -methylstyrene-acrylonitrile binary copolymers have been available as alternatives to styrene-acrylonitrile materials but have not achieved commercial significance.)

The second approach is typified by maleic anhydride. This material does not homopolymerise but will polymerise with styrene or styrene and acrylonitrile, in the latter case to give terpolymers with T_g above 122°C.

Blends of ABS with polycarbonates have been available for several years (e.g. Bayblend by Bayer and Cycoloy by Borg-Warner). In many respects these polymers have properties intermediate to the parent plastics materials with heat distortion temperatures up to 130°C. They also show good impact strength, particularly at low temperatures. Self-extinguishing and flame retarding grades have been made available. The materials thus provide possible alternatives to modified poly(phenylene oxides) of the Noryl type described in Chapter 21. (See also sections 16.16 and 20.8.)

The process of blending with another glassy polymer to raise the heat distortion temperature is not restricted to polycarbonate, and the polysulphones are obvious candidates because of their higher T_g . One blend has been offered (Arylon T by USS Chemicals) which has a higher softening point than the ABS-polycarbonates.

Blending of ABS with other polymers is not restricted to the aim of raising the distortion temperature. Blends with PVC are made for various purposes. For example, 80:20 ABS/PVC blends are used to produce fire-retarding ABS-type materials, as already mentioned, while 10:90 blends are considered as impact-modified forms of unplasticised PVC. ABS materials have also been blended with plasticised PVC to give a crashpad sheet material.

Blending of ABS with an acrylic material such as poly(methyl methacrylate) can in some cases allow a matching of the refractive indices of the rubbery and glassy phases and providing that there is a low level of contaminating material such as soap and an absence of insoluble additives a reasonable transparent ABS-type polymer may be obtained. More sophisticated are the complex terpolymers and blends of the MBS type considered below. Seldom used on their own, they are primarily of use as impact modifiers for unplasticised PVC.

16.8.2 Processing of ABS Materials

The processing behaviour of ABS plastics is largely predictable from their chemical nature, in particular their amorphous nature and the somewhat unpleasant degradation products. The main points to bear in mind are:

- (1) ABS is more hygroscopic than polystyrene. (It will absorb up to 0.3% moisture in 24 hours.) It must therefore be dried carefully before moulding or extrusion.
- (2) The heat resistance in the melt is not so good as that of polystyrene and unpleasant fumes may occur if the melt is overheated. This can occur at the higher end of the processing range (250–260°C) and when high screw speeds and high back pressures are used when injection moulding. Volatile decomposition products can also lead to bubbles, mica marks (splay marks), and other moulding defects. The problem is often worse with flame-retarding grades. It is usual to purge the material at the end of a run.
- (3) The flow properties vary considerably between grades but some grades are not free flowing. Flow path ratios in the range 80 to 150:1 are usually quoted, generally being lower with the heat-resistant grades.
- (4) Being amorphous, the materials have a low moulding shrinkage (0.044–0.008 cm/cm).

One particular feature of the material is the facility with which it may be electroplated. In order to obtain a good bond the ABS polymer is first treated by an acid etching process which dissolves out some of the rubber particles at or near the polymer surface. After sensitisation and activation electroless metal deposition processes are carried out. Much of the strength between the ABS and the plating depends on a mechanical press-stud type of effect. It is commonly observed that low peel strength usually arises not through failure at the interface but in the moulding just below the surface. It would seem that the greater the molecular orientation in such regions the lower the interlayer forces and hence the lower the peel strength.

16.8.3 Properties and Applications of ABS Plastics

Because of the range of ABS polymers that may be produced, a wide range of properties is exhibited by these materials. Properties of particular importance are toughness and impact resistance, dimensional stability, good heat distortion resistance (relative to the major tonnage thermoplastics), good low-temperature properties and their capability of being electroplated without great difficulty.

Several classes of ABS which show the above general characteristics but with specific attributes are recognised. One supplier for example classifies ABS materials into the following categories:

- general purpose grades
- fire retardant grades
- improved heat resistance grades
- enhanced chemically resistant grades
- static dissipation grades
- extrusion grades
- fire retardant extrusion grades

transparent grades
electroplating grades
blow moulding grades.

Over the years there has been some difference in the balance of use between UPVC and ABS in the United States compared with Western Europe. This was due largely to the earlier development in Western Europe of UPVC and in the United States of ABS. Thus, for example, whilst ABS consolidated its use for pipes and fittings in the United States, UPVC was finding similar uses in Europe. Whilst some of these traditional differences remain, ABS is now well established in both Europe and the United States.

As well as unplasticised PVC, ABS also finds competition from polypropylene. In recent years polypropylene has been the cheaper material on a tonnage basis and even more economic on the more relevant volume basis. On the other hand the properties listed above, in particular the extreme toughness and superior heat distortion resistance, lead to ABS being preferred in many instances. Because ABS, typically, has a higher flexural modulus than polypropylene, mouldings of the latter will have to a wall thickness some 15–25% greater in order to show an equal stiffness. It is also interesting to note that because of its higher specific heat as well as possessing a latent heat of fusion, polypropylene requires longer cooling times when processing (see Section 8.2.3). Applications of ABS are considered in more detail in Section 16.16.

16.9 MISCELLANEOUS RUBBER-MODIFIED STYRENE-ACRYLONITRILE AND RELATED COPOLYMERS

The commercial success of ABS polymers has led to the investigation of many other polyblend materials. In some cases properties are exhibited which are superior to those of ABS and some of the materials are commercially available. For example, the opacity of ABS has led to the development of blends in which the glassy phase is modified to give transparent polymers whilst the limited light aging has been countered by the use of rubbers other than polybutadiene.

Notable among the alternative materials are the MBS polymers, in which methyl methacrylate and styrene are grafted on to the polybutadiene backbone. This has resulted in two clear-cut advantages over ABS. The polymers could be made with high clarity and they had better resistance to discolouration in the presence of ultraviolet light. Disadvantages of MBS systems are that they have lower tensile strength and heat deflection temperature under load.

The MBS polymers are two-phase materials, with the components being only partially compatible. It is, however, possible to match the refractive indices providing the copolymerisation is homogeneous, i.e. copolymers produced at the beginning of the reaction have the same composition as copolymers produced at the end. Such homogeneity of polymerisation appears to be achieved without great difficulty. The poor aging of ABS appears to be due largely to oxidative attack at the double bonds in the polybutadiene backbone. Methyl methacrylate appears to inhibit or at least retard this process whereas acrylonitrile does not.

Besides the MBS materials, related terpolymers have been prepared. These include materials prepared by terpolymerising methyl methacrylate, acrylonitrile and styrene in the presence of polybutadiene (Toyolac, Hamano 500); methyl methacrylate, acrylonitrile and styrene in the presence of a butadiene–methyl methacrylate copolymer (XT Resin), and methylacrylate, styrene and acrylonitrile on to a butadiene–styrene copolymer.

Because the polybutadiene component is liable to oxidation, ABS materials are embrittled on prolonged exposure to sunlight. By replacing polybutadiene rubber with other elastomers that contain no main chain double bonds it has been possible to produce blends generally similar to ABS but with improved weathering resistance. Three particular types that have achieved commercial status are:

- (1) ASA polymers which utilise an acrylic ester rubber (see Chapter 15).
- (2) AES polymers which use an ethylene–propylene termonomer rubber (see Chapter 11).
- (3) ACS polymers based on elastomeric chlorinated polyethylene.

The ASA materials were introduced by BASF about 1970 as Luran S. Similar to ABS, they show improved light resistance and heat resistance (both during processing and in service). Because of their generally very good weatherability these materials have become best known for automotive grilles and mirror housings and have also been successfully used in garden equipment including pumps, marine equipment and satellite dishes. Other applications reported include chain covers and guards for agricultural machines, moped guards, housings for street lighting, road signs and mileage indicators. Where greater toughness is required alloys of ASA and polycarbonate resins (see also Section 20.8) are available from BASF (Luran SC). The extension of ABS-type materials into such exterior applications means that these products have to be considered alongside other plastics that show good weathering behaviour such as poly(methyl methacrylate), cellulose acetate–butyrate and several fluorine-containing polymers.

Whilst the ASA materials are of European origin, the AES polymers have been developed in Japan and the US. The rubber used is an ethylene–propylene terpolymer rubber of the EPDM type (see Chapter 11) which has a small amount of a diene monomer in the polymerisation recipe. The residual double bonds that exist in the polymer are important in enabling grafting with styrene and acrylonitrile. The blends are claimed to exhibit very good weathering resistance but to be otherwise similar to ABS.

ACS polymers, developed primarily in Japan, are grafts of acrylonitrile and styrene onto elastomeric chlorinated polyethylene. Although the polymer has good weathering properties it is somewhat susceptible to thermal degradation during processing and to date these polymers have been of limited interest.

Blends have also been produced containing neither acrylonitrile and styrene in the glassy phase nor polybutadiene in the rubbery phase.

One such system involved grafting 70 parts of methyl methacrylate on to 30 parts of an 81–19 2-ethylhexyl acrylate–styrene copolymer. Such a grafted material was claimed to have very good weathering properties as well as exhibiting high optical transmission.

Perhaps the greatest resistance to development with these materials is the strong competition offered by the clear impact-modified grades of unplasticised PVC which are generally less expensive.

16.10 STYRENE–MALEIC ANHYDRIDE COPOLYMERS

There has been some interest in random copolymers of styrene with small amounts of maleic anhydride. Manufacturers included Monsanto (Cadon), Dow (Resin XP5272) and Dainippon (Ryurex X-15). However, the only current manufacturer of high molecular weight materials appears to be Arco, which markets its products under the trade name Dylarc. The abbreviation SMA is commonly used for these materials.

The unmodified copolymers are transparent and have a T_g and deflection temperature under load in excess of 125°C. Toughened grades may be obtained by incorporating a graftable rubber during the polymerisation stage. Glass-fibre reinforcement of the copolymer is also common. Long glass-fibre grades have recently become available in addition to the more common grades obtained by melt blending of polymers with glass fibre.

The processing of SMA materials is largely predictable from a consideration of the structure. The polymer is easy flowing but setting temperatures are somewhat higher than for polystyrene and thus facilitate short cycle times. The low shrinkage, typical of an amorphous polymer, does, however, require that excessive pressures and pressure holding times during injection moulding should not occur since this could hinder mould release.

Styrene–maleic anhydride copolymers have achieved a good market penetration in the USA for auto instrument panels, where factors such as good heat resistance, rigidity, predictable impact properties and dimensional stability are important. Commercial blends of SMA with polycarbonate resin have been marketed. Such blends have deflection temperatures about 15°C above those for straight SMA copolymers and are also attractive for their ductility, toughness and ease of mouldability. A composite material consisting of an SMA foamed core sandwiched between an elastomer-modified SMA compound has been of interest as a car roof lining. This interest arose from the ability to expose components to the elevated temperatures that occur in hot paint drying equipment and in metallising baths. Other applications include car heating and ventilating systems and transparent microwave packaging material.

In addition to the above SMA materials, low molecular weight (1660–2500) copolymers with 25–50% maleic anhydride content have been made available (SMA Resins—Elf Atochem). These find use in such diverse applications as levelling agents in floor polishes, embrittling/anti-resoil agents in rug shampoos, and pigment dispersants in inks, paints and plastics. They are also used in paper sizing and metal coating. The suppliers of these materials lay emphasis on the reactivity of such materials. For example, the maleic anhydride groups may be esterified with alcohols, enabling a wide spectrum of chemical structures to be grafted onto the chain, neutralised with ammonia, or imidised by reaction with an amine. As with all styrene polymers, the benzene ring may also be subject to a number of chemical reactions such as sulphonation.

Production of SMA materials is of the order of 25 000 t.p.a. and recent reports refer to an annual growth rate of the order of 10–15%.

16.11 BUTADIENE–STYRENE BLOCK COPOLYMERS

Random copolymers of butadiene and styrene have been known for over half a century and such polymers containing about 25% of styrene units are well known

as SBR (see Section 11.7.4). Styrene–butadiene–styrene triblock copolymers have also been known since 1965 as commercial thermoplastic elastomers (Section 11.8).

Closely related to these but thermoplastic rather than rubber-like in character are the K-resins developed by Phillips. These resins comprise star-shaped butadiene–styrene block copolymers containing about 75% styrene and, like SBS thermoplastic elastomers, are produced by sequential anionic polymerisation (see Chapter 2).

An interesting feature of these polymers is that they have a tetramodal molecular mass distribution which has been deliberately built in and which is claimed to improve processability. This is achieved by the following procedure:

- (1) Initiating polymerisation of styrene with *sec*-butyl-lithium.
- (2) When the styrene has been consumed, to give living polymers of narrow molecular mass distribution, more styrene *and* more catalyst is added. The styrene adds to the existing chains and also forms new polymer molecules initiated by the additional *sec*-butyl-lithium.
- (3) When the replenishing styrene had also been consumed butadiene is added to give a living diblock and when the monomer has been consumed the diblocks will have two modal molecular weights.
- (4) The linear diblocks are then coupled by a polyfunctional coupling agent such as epoxidised linseed oil to give a star-shaped polymer. As already mentioned, commercial materials of this type have a tetramodal distribution.

Polymers of this sort possess an interesting combination of properties. They are clear and tough (although notch sensitive) and exhibit a level of flexibility somewhat higher than that of polypropylene. Typical properties are given in Table 16.6.

The block copolymers are easy to process but in order to obtain maximum clarity and toughness attention has to be paid to melt and mould temperatures during injection moulding.

Polymers of this type find application in toys and housewares and are of interest for medical applications and a wide variety of miscellaneous industrial uses.

Table 16.6 Some typical properties of styrene–butadiene block copolymer thermoplastics (Phillips K-Resins)

<i>Property</i>	<i>Value</i>
Specific gravity	1.04
Tensile strength	27–30 MPa
Tensile modulus	1400 MPa
Hardness (Rockwell R)	72
Heat deflection temperature (at 1.81 MPa stress)	71°C
Vicat softening point	93°C
Water absorption (24 hours)	0.09%
Transparency	Transparent

16.12 MISCELLANEOUS POLYMERS AND COPOLYMERS

In addition to the polymers, copolymers and alloys already discussed, styrene and its derivatives have been used for the polymerisation of a wide range of polymers and copolymers. Two of the more important applications of styrene, in SBR and in polyester laminating resins, are dealt with in Chapters 11 and 25 respectively.

The influence of nuclear substituents on the properties of a homopolymer depends on the nature, size and shape of the substituent, the number of the substituents and the position of entry into the benzene ring.

Table 16.7 shows how some of these factors influence the softening point of the polymers of the lower *p*-alkylstyrenes.

Table 16.7

<i>Polymer</i>	<i>BS1524 softening point</i>
Poly-(<i>p</i> -methylstyrene)	88°C
Poly-(<i>p</i> - <i>n</i> -propylstyrene)	R.T.
Poly-(<i>p</i> -isopropylstyrene)	87°C
Poly-(<i>p</i> - <i>n</i> -butylstyrene)	rubber
Poly-(<i>p</i> - <i>sec</i> -butylstyrene)	86°C
Poly-(<i>p</i> - <i>tert</i> -butylstyrene)	130°C

It will be seen that increasing the length of the *n*-alkyl side group will cause a reduction in the interchain forces and a consequent reduction in the transition temperature, and hence the softening point. Branched alkyl groups impede free rotation and may more than offset the chain separation effect to give higher softening points. Analogous effects have already been noted with the polyolefins and polyacrylates.

Polar substituents such as chlorine increase the interchain forces and hinder free rotation of the polymer chain. Hence polydichlorostyrenes have softening points above 100°C. One polydichlorostyrene has been marketed commercially as Styramic HT. Such polymers are essentially self-extinguishing, have heat distortion temperatures of about 120°C and a specific gravity of about 1.40.

A poly(tribromostyrene) with the bromine atoms attached to the benzene ring is marketed by the Ferro corporation as Pyro-Chek 68 PB as a heat-resisting fire retardant used in conjunction with antimony oxide. The polymer has an exceptionally high specific gravity, reputedly of 2.8, and a softening point of 220°C.

The nuclear substituted methyl styrenes have been the subject of much study and of these poly(vinyl toluene) (i.e. polymers of *m*- and *p*-methylstyrenes) has found use in surface coatings. The Vicat softening point of some nuclear substituted methyl styrenes is given in *Table 16.8*.

In 1981 Mobil marketed *p*-methylstyrene monomer as a result of pressure on the chemical industry to replace benzene with toluene, which was less expensive.

Table 16.8

Polymer	VSP (°C)
Poly-(<i>m</i> -methylstyrene)	92
Poly-(<i>o</i> -methylstyrene)	128
Poly-(<i>p</i> -methylstyrene)	105
Poly-(2,4-dimethylstyrene)	135
Poly-(2,5-dimethylstyrene)	139
Poly-(3,4-dimethylstyrene)	99
Poly-(2,4,5-trimethylstyrene)	147
Poly-(2,4,6-trimethylstyrene)	164
Poly-(2,3,5,6,-tetramethylstyrene)	150

Whilst the homopolymer is similar to polystyrene, it does exhibit certain distinct differences, including:

- (1) Lower specific gravity (1.01 compared to 1.05).
- (2) Higher softening point (Vicat temperatures of 110–117°C compared to 89–107°C).
- (3) Increased hardness.
- (4) Easier flow.

Copolymers based on *p*-methylstyrene analogous to SAN (PMSAN) and to ABS (ABPMS) have also been developed by Mobil. The differences in properties reported are very similar to the differences between the homopolymers.

Catalytic dehydrogenation of cumene, obtained by alkylation of benzene with propylene, will give α -methylstyrene (Figure 16.15).

Both the alkylation and dehydrogenation may be carried out using equipment designed for the production of styrene.

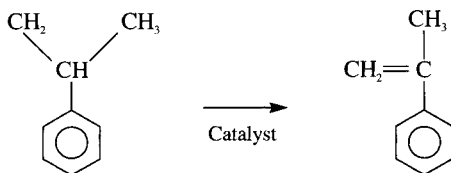


Figure 16.15

It has not been found possible to prepare high polymers from α -methylstyrene by free-radical methods and ionic catalysts are used. The reaction may be carried out at about -60°C in solution.

Polymers of α -methylstyrene have been marketed for various purposes but have not become of importance for mouldings and extrusions. On the other hand copolymers containing α -methylstyrene are currently marketed. Styrene- α -methylstyrene polymers are transparent, water-white materials with BS softening points of $104\text{--}106^{\circ}\text{C}$ (c.f. 100°C for normal polystyrenes). These materials have melt viscosities slightly higher than that of heat-resistant polystyrene homopolymer.

Many other copolymers are mentioned in the literature and some of these have reached commercial status in the plastics or some related industry. The reason for the activity usually lies in the hope of finding a polymer which is of low cost, water white and rigid but which has a greater heat resistance and toughness than polystyrene. This hope has yet to be fulfilled.

16.13 STEREOREGULAR POLYSTYRENE

Polystyrene produced by free-radical polymerisation techniques is part syndiotactic and part atactic in structure and therefore amorphous. In 1955 Natta¹⁶ and his co-workers reported the preparation of substantially isotactic polystyrene using aluminium alkyl–titanium halide catalyst complexes. Similar systems were also patented by Ziegler¹⁷ at about the same time. The use of *n*-butyl-lithium as a catalyst has been described.¹⁸ Whereas at room temperature atactic polymers are produced, polymerisation at -30°C leads to isotactic polymer, with a narrow molecular weight distribution.

In the crystalline region isotactic polystyrene molecules take a helical form with three monomer residues per turn and an identity period of 6.65 Å. One hundred percent crystalline polymer has a density of 1.12 compared with 1.05 for amorphous polymer and is also translucent. The melting point of the polymer is as high as 230°C . Below the glass transition temperature of 97°C the polymer is rather brittle.

Because of the high melting point and high molecular weight it is difficult to process isotactic polystyrenes. Various techniques have been suggested for injection moulding in the literature but whatever method is employed it is necessary that the moulding be heated to about 180°C , either within or outside of the mould, to allow the material to develop a stable degree of crystallinity.

The brittleness of isotactic polystyrenes has hindered their commercial development. Quoted Izod impact strengths are only 20% that of conventional amorphous polymer. Impact strength double that of the amorphous material has, however, been claimed when isotactic polymer is blended with a synthetic rubber or a polyolefin.

16.13.1 Syndiotactic Polystyrene

The first production of syndiotactic polystyrene has been credited to research workers at Idemitsu Kosan in 1985 who used *cyclopentadienyl* titanium compounds with methyl aluminoxane as catalyst.

Whereas the isotactic polymer has not been commercialised Dow were scheduled to bring on stream plant with a nameplate capacity of 37 000 t.p.a. in 1999 to produce a syndiotactic polystyrene under the trade name Questra. The particular features of this material are:

- (a) T_g of about 100°C (similar to that of amorphous polystyrene) and T_m of 270°C .
- (b) Low density with crystalline and amorphous zones both having densities of about 1.05 g/cm^3 . This is similar to that occurring with poly-4-methyl pentene-1, discussed in Chapter 11 and with both polymers a consequence of the spatial requirements in the crystal structure of the substantial side groups.

An advantage of the matching densities of the two zones or phases is that there is little warping and generally good dimensional stability.

- (c) While the unfilled polymer is somewhat brittle, impact strength is substantially increased by the use of glass fibres and/or impact modifiers.
- (d) While the heat deflection temperatures of unfilled materials are similar to T_g , that of glass-filled grades approaches T_m . This is in line with observation made with other crystalline thermoplastics as discussed in Chapter 9.
- (e) Electrical, chemical and thermal properties and dimensional stability are similar to those of general purpose ('atactic') polystyrene and thus has some advantages over more polar crystalline, so-called, engineering plastics such as the polyamides and linear polyesters.

Some typical properties are given in *Table 16.9*.

Table 16.9 Some properties of syndiotactic polystyrene

Property	ASTM method	Units	Unfilled	30% glass filled	30% glass filled and impact modified
Tensile strength	D638	MPa	42	121	105
Tensile modulus	D638	MPa	3500	10000	7580
Elongation @ break	D638	%	1	1.5	3.4
Notched Izod 23°C D256	J/m		10	96	117
Deflection temp. under load @ 1.82 MPa	D648	°C	100	249	232
Specific gravity	D792		1.05	1.25	1.21
Dielectric constant	D150		2.6	3.1	3.1
Dissipation factor	D150		0.0002	0.001	0.001
Moulding shrinkage	D955	in/in		0.0027	0.003
				-0.0037	0.004

Potential applications for glass-filled grades include electronic/electrical connectors, coil bobbins, relays; automotive lighting and cooling system components and pump housings and impellers. Unfilled grades are of interest as capacitor film with a heat resistance that can withstand infra-red reflow soldering combined with excellent electrical insulation properties little affected by temperature and frequency. Non-woven fabrics with good heat, moisture and chemical resistance are of interest for filter media.

There has also been some interest in melt blending with polyamides to increase the toughness but at some sacrifice to dimensional stability and moisture resistance.

16.14 PROCESSING OF POLYSTYRENE

Polystyrene and closely related thermoplastics such as the ABS polymers may be processed by such techniques as injection moulding, extrusion and blow moulding. Of less importance is the processing in latex and solution form and the

process of polymerisation casting. The main factors to be borne in mind when considering polystyrene processing are:

- (1) The negligible water absorption avoids the need for predrying granules.
- (2) The low specific heat (compared with polyethylene) enables the polymer to be rapidly heated in injection cylinders, which therefore have a higher plasticising capacity with polystyrene than with polyethylene. The setting-up rates in the injection moulds are also faster than with the polyolefins so that faster cycles are also possible.
- (3) The strong dependence of apparent viscosity on shear rate. This necessitates particular care in the design of complex extrusion dies.
- (4) The absence of crystallisation gives polymers with low mould shrinkage.
- (5) Molecular orientation.

Although it is not difficult to make injection mouldings from polystyrene which appear to be satisfactory on visual examination it is another matter to produce mouldings free from internal stresses. This problem is common to injection mouldings of all polymers but is particularly serious with such rigid amorphous thermoplastics as polystyrene.

Internal stresses occur because when the melt is sheared as it enters the mould cavity the molecules tend to be distorted from the favoured coiled state. If such molecules are allowed to freeze before they can re-coil ('relax') then they will set up a stress in the mass of the polymer as they attempt to regain the coiled form. Stressed mouldings will be more brittle than unstressed mouldings and are liable to crack and craze, particularly in media such as white spirit. They also show a characteristic pattern when viewed through crossed Polaroids. It is because compression mouldings exhibit less frozen-in stresses that they are preferred for comparative testing.

To produce mouldings from polystyrene with minimum strain it is desirable to inject a melt, homogeneous in its melt viscosity, at a high rate into a hot mould at an injection pressure such that the cavity pressure drops to zero as the melt solidifies. Limitations in the machines available or economic factors may, however, lead to less ideal conditions being employed.

A further source of stress may arise from incorrect mould design. For example, if the ejector pins are designed in such a way to cause distortion of the mouldings, internal stresses may develop. This will happen if the mould is distorted while the centre is still molten, but cooling, since some molecules will freeze in the distorted position. On recovery by the moulding of its natural shape these molecules will be under stress.

A measure of the degree of frozen-in stresses may be obtained comparing the properties of mouldings with known, preferably unstressed, samples, by immersion in white spirit and noting the degree of crazing, by alternately plunging samples in hot and cold water and noting the number of cycles to failure or by examination under polarised light. Annealing at temperatures just below the heat distortion temperature followed by slow cooling will in many cases give a useful reduction in the frozen-in stresses.

The main reason for extruding polystyrene is to prepare high-impact polystyrene sheet. Such sheet can be formed without difficulty by vacuum forming techniques. In principle the process consists of clamping the sheet above the mould, heating it so that it softens and becomes rubbery and then applying a vacuum to draw out the air between the mould and the sheet so that the sheet takes up the contours of the mould.

16.15 EXPANDED POLYSTYRENE¹⁹⁻²¹

Polystyrene is now available in certain forms in which the properties of the product are distinctly different from those of the parent polymer. Of these by far the most important is expanded polystyrene, an extremely valuable insulating material now available in densities as low as 1 lb/ft³ (16 kg/m³). A number of processes have been described in the literature for the manufacture of the cellular product of which four are of particular interest in the manufacture of large slabs.

- (1) Polymerisation in bulk of styrene with azodi-isobutyronitrile as initiator. This initiator evolves nitrogen as it decomposes so that expansion and polymerisation occur simultaneously. This method was amongst the earliest suggested but has not been of commercial importance. There has, however, been recent resurgence of interest in this process.
- (2) The Dow 'Log' Process. Polystyrene is blended with a low boiling chlorinated hydrocarbon and extruded. The solvent volatilises as the blend emerges from the die and the mass expands. This process is still used to some extent.
- (3) The BASF Process. Styrene is blended with a low boiling hydrocarbon and then polymerised. The product is chipped. The chips are then converted into expanded polymer as in method (4) described in detail below.
- (4) Bead Processes. As these processes have generally replaced the above techniques. The styrene is polymerised by bead (suspension) polymerisation techniques. The blowing agent, typically 6% of low boiling petroleum ether fraction such as n-pentane, may be incorporated before polymerisation or used to impregnate the bead under heat and pressure in a post-polymerisation operation.

The impregnated beads may then be processed by two basically different techniques: (a) the steam moulding process, the most important industrially and (b) direct injection moulding or extrusion. In the steam moulding process the beads are first 'prefoamed' by heating them in a steam bath. This causes the beads to expand to about 40 times their previous size. At this stage the beads should not fuse or stick together in any way. It has been shown that expansion is due not only to volatilisation of the low boiling liquid (sometimes known as a pneumatogen) but also to an osmotic-type effect in which steam diffuses into the cells with the bead as they are formed by the expanding pneumatogen. The entry of steam into the cells causes a further increase in the internal pressure and causes further expansion. It has been estimated¹⁹ that about half of the expansion is due to the effect of steam, which can diffuse into the cells at a much greater rate than the pneumatogen can diffuse out. The expansion of the beads is critically dependent on both temperature and time of heating. At low steaming pressures the temperature obtained is about that of the softening point of polystyrene and it is important to balance the influences of polymer modulus, volatilisation rates and diffusion rates of steam and pneumatogen. In practice prefoaming temperatures of about 100°C are used. Initially the amount of bead expansion increases with the time of prefoaming. If, however, the beads are heated for too long the pneumatogen diffuses out of the cells and the residual gas cannot withstand the natural tendency of the bead to collapse. (This natural tendency is due to beads consisting largely of membranes of highly oriented polymers in a

rubbery state at prefoaming temperatures. The natural tendency of molecules to disorient above the glass transition temperature, the reason why rubbers are elastic, was discussed in the early chapters of this book.)

The second stage of the process is to condition the beads, necessary because on cooling after prefoaming pneumatogen and steam within the cells condense and cause a partial vacuum within the cell. By allowing the beads to stand in air for at least 24 hours air can diffuse into the cells in order that at room temperature the pressure within the cell equilibrates with that outside.

The third stage of the process is the steam moulding operation itself. Here the prefoamed beads are charged into a chest or mould with perforated top, bottom and sides through which steam can be blown. Steam is blown through the preform to sweep air away and the pressure then allowed to increase to about 15 lbf/in² (approx. 0.11 MPa). The beads soften, air in the cells expands on heating, pneumatogen volatilises and steam once again permeates into the cells. In consequence the beads expand and, being enclosed in the fixed volume of the mould, consolidate into a solid block, the density of which is largely decided by the amount of expansion in the initial prefoaming process. Heating and cooling cycles are selected to give the best balance of economic operation, homogeneity in density through the block, good granule consolidation, good block external appearance and freedom from warping. This process may be used to give slabs which may be subsequently sliced to the appropriate size or alternatively to produce directly such objects as containers and flower pots. The steam moulding process, although lengthy, has the advantages of being able to make very large low-density blocks and being very economic in the use of polymer.

Whilst it is possible to purchase standard equipment for the steam moulding process, attempts continue to be made to make sweeping modifications to the process. These include the use of dielectric and microwave heating and the development of semicontinuous and continuous processes.

The outstanding features of steam moulded polystyrene foam are its low density and low thermal conductivity. These are compared with other important insulating materials in *Table 16.10*.

One alternative approach to the two-stage steam moulding process is that in which impregnated beads are fed directly to an injection moulding machine or extruder so that expansion and consolidation occur simultaneously. This approach has been used to produce expanded polystyrene sheet and paper by a tubular process reminiscent of that used with polyethylene. Bubble nucleating

Table 16.10

	Density		Thermal conductivity	
	(lb/ft ³)	(g/cm ³)	(Btu in ft ² h ⁻¹ °F ⁻¹)	(W/mK)
Expanded polystyrene	1.0	0.016	0.22	0.031
Polyurethane foam (with chloro-fluorocarbon gas)	2.0	0.032	0.16	0.022
Expanded ebonite	3.75	0.06	0.21	0.030
Cork (expanded)	6.25	0.10	0.27	0.038
Wood	25.0	0.40	0.65	0.094
Glass wool	4.0	0.064	0.26	0.036
Expanded PVC	2.5	0.040	0.22	0.031

agents such as sodium bicarbonate and citric acid which evolve carbon dioxide during processing are often incorporated to prevent the formation of a coarse pore structure. Typical film has a density of about 3 lb/ft^3 (0.05 g/cm^3). Injection moulding of impregnated beads gives an expanded product with densities of about $12\text{--}13 \text{ lb/ft}^3$ ($0.22\text{--}0.24 \text{ g/cm}^3$). This cannot compare economically with steam moulding and the product is best considered as a low-cost polystyrene (in terms of volume) in which air and pneumatogen act as a filler. Such products generally have an inferior appearance to normal polystyrene mouldings. Nevertheless, there has been considerable interest recently in higher density cellular polymers (sometimes known as structural foams) (see Section 16.4.1). In some processes it is possible to produce mouldings with a non-cellular skin. The dependence of the properties of such cellular polymers on structure has been studied.

It is important to note that the thermal conductivity is dependent on the mean temperature involved in the test. The relationship may be illustrated by quoting results obtained from a commercial material of density 1 lb/ft^3 (0.016 g/cm^3) (Table 16.11).

Table 16.11

Mean temperature (°F)	Thermal conductivity	
	(Btu in $\text{ft}^{-2} \text{h}^{-1} \text{°F}^{-1}$)	(W/mk)
50	0.24	0.034
0	0.21	0.030
-27	0.19	0.028
-40	0.18	0.026
-126	0.14	0.020

Other typical properties for a 1 lb/ft^3 (0.016 g/cm^3) expanded polystyrene material are

Tensile strength	$15\text{--}20 \text{ lbf/in}^2$ ($0.11\text{--}0.14 \text{ MPa}$)
Flexural strength	$20\text{--}30 \text{ lbf/in}^2$ ($0.14\text{--}0.21 \text{ MPa}$)
Compression strength	$10\text{--}15 \text{ lbf/in}^2$ ($0.07\text{--}0.11 \text{ MPa}$)
Water absorption	2 g/100 cm^3 (max)

16.15.1 Structural Foams

The term *structural foam* was originally coined by Union Carbide to describe an injection moulded thermoplastic cellular material with a core of relatively low density and a high-density skin. The term has also been used to describe rigid 'foams' that are load bearing. Today it is commonly taken to imply both of the above requirements, i.e. it should be load bearing and with a core of lower density than the skin. In this section the broader load-bearing definition will be used. Whilst structural foams are frequently made from polymers other than polystyrene, this polymer is strongly associated with such products and it is convenient to deal with the topic here.

Cellular thermoplastics can be made by feeding a blend of polymer and chemical blowing agent to an injection moulding machine. The agent decomposes in the heated barrel but because of the high pressures in the melt in the barrel gases do not form until the material is injected into the mould. In order for the process to work satisfactorily the machine should have a cylinder shut-off nozzle to prevent egress of material during the plasticating stage, a non-return valve on the screw tip, a capability of operating at high injection speeds and good control over screw back pressure. As an alternative to chemical blowing agents, volatile blowing agents or, more commonly, nitrogen may be introduced into the polymer melt shortly before mould filling.

Moulding systems are usually divided into low-pressure and high-pressure systems.

In the low-pressure systems a shot of material is injected into the mould which, if it did not expand, would give a short shot. However, the expanding gas causes the polymer to fill the mould cavity. One important form of the low-pressure process is the Union Carbide process in which the polymer is fed to and melted in an extruder. It is blended with nitrogen which is fed directly into the extruder. The extruder then feeds the polymer melt into an accumulator which holds it under pressure (14–35 MPa) to prevent premature expansion until a pre-determined shot builds up. When this has been obtained a valve opens and the accumulator plunger rams the melt into the mould. At this point the mould is only partially filled but the pressurised gas within the melt allows it to expand.

Although such products do not have a high-quality finish they do exhibit two typical characteristics of structural foams:

- (1) The internal pressures can prevent the formation of sink marks, particularly on faces opposite to reinforcing ribs.
- (2) Thick mouldings may be produced, again without distortion such as sink marks.

Perhaps, however, the greatest virtue of structural foams is the ability to increase the ratio of part rigidity/weight. A foam of half the density of a solid material only requires a 25% increase in wall thickness to maintain the rigidity.

High-pressure processes generally involve partial mould opening after mould filling. In several cases these processes may also be described as counter-pressure processes. The principle involved in such processes is to fill the mould cavity with a gas such as air or nitrogen under pressure before injection of the polymer/blowing agent melt. This pressure prevents bubbles at or near the surface of the advancing front from breaking through the surface and subsequently marring the appearance of the moulding.

One such process is the TAF process, the basic patent being held by Dow. It was developed in Japan by Asahi in conjunction with Toshiba. Foam expansion after mould filling is made possible by use of retractable mould cores. Because of the difficulty of allowing expansion in more than one direction this process has been largely limited to the production of flat products. Efficient gas sealing systems are also vital and the process needs close control. For this reason it has not been widely used in either Europe or North America.

A counter-pressure process was also used by Buhler-Miag, details of which were only disclosed to licensees. It has been stated that expansion does not involve mould movement or egression back through the sprue but that the key to success is in the venting. This suggests that egress of melt through mould vents

allows the expansion. This process has been used in England for furniture, computer housings and sailing boat rudders.

A high-pressure process not involving counter-pressure is the sandwich moulding process developed by ICI in the United Kingdom and by Billion in France. The principle of the process is to inject two polymer formulations from separate injection units one after the other into a mould through the same sprue. If a foamed core is desired the mould is partially opened just after filling to allow the foamable polymer in the core to expand. To seal off the core the injection stage is completed by a brief injection through the sprue of the first (skin) material injected. A modification of the sandwich process involves co-injection simultaneously through two concentric nozzles, a process generally credited to Siemag and developed by Battenfield.

16.16 ORIENTED POLYSTYRENE

Deliberately oriented polystyrene is available in two forms; filament (moniaxially oriented) and film (biaxially oriented). In both cases the increase in tensile strength in the direction of stretching is offset by a reduction in softening point because of the inherent instability of oriented molecules.

Filament is prepared by extrusion followed by hot stretching. It may be used for brush bristles or for decorative purposes such as in the manufacture of 'woven' lampshades.

Biaxially stretched film has proved of value as a packaging material. Specific uses include blister packaging, snap-on lids, overwrapping, 'envelope windows' and de luxe packaging.

It may be produced by extrusion either by a tubular process or by a flat film extrusion.²³ The latter process appears to be preferred commercially as it allows greater flexibility of operation. The polystyrene is first extruded through a slit die at about 190°C and cooled to about 120°C by passing between rolls, The moving sheet then passes above a heater and is rewarmed to 130°C, the optimum stretching temperature. The sheet is then stretched laterally by means of driven edge rollers and longitudinally by using a haul-off rate greater than the extrusion rate. Lateral and longitudinal stretching is thus independently variable. In commercial processes stretch ratios of 3:1–4:1 in both directions are commonly employed (see *Figure 16.16*).

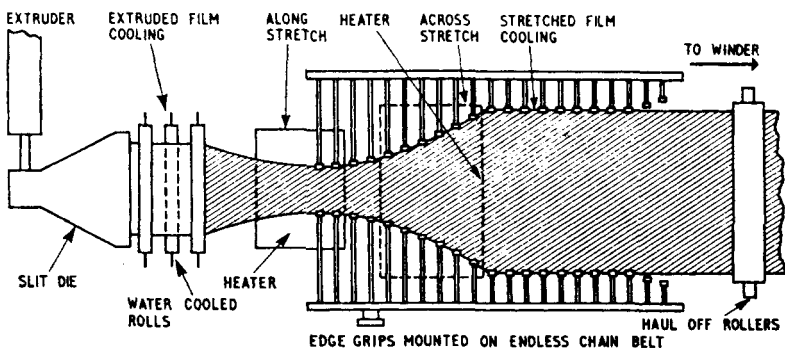


Figure 16.16. Plax process for manufacture of biaxially stretched polystyrene film

Commercial oriented film has a tensile strength of 10 000–12 000 lbf/in² (70–83 MPa; c.f. 41–55 MPa for unstretched material) and an elongation of break of 10–20% (c.f. 2–5%). The impact strength of bars laminated from biaxially stretched film have impact strengths of the order of 15 times greater than the basic polymer. The heat distortion temperature is negligibly affected. Whereas toughness and clarity are the principal desirable features of oriented polystyrene film the main disadvantages are the high moisture vapour transmission rate compared with polyethylene and the somewhat poor abrasion resistance.

Although it is possible to vacuum form these films the material has such a high modulus at its shaping temperatures that an exceptionally good vacuum is required for shaping. As a consequence of this the pressure forming technique has been developed. In this process the sheet is clamped between the mould and a heated plate. Air is blown through the mould, pressing the sheet against the hot plate. After a very short heating period the air supply is switched so that compressed air passes through holes in the heater plate and blows the sheet into the mould.

16.17 APPLICATIONS

As mentioned earlier, unmodified polystyrene first found application where rigidity and low cost were important prerequisites. Other useful properties were the transparency and high refractive index, freedom from taste, odour and toxicity, good electrical insulation characteristics, low water absorption and comparatively easy processability. Carefully designed and well-made articles from polystyrene were often found to be perfectly suitable for the end-use intended. On the other hand the extensive use of the polymers in badly designed and badly made products which broke only too easily caused a reaction away from the homopolymer. This resulted, first of all, in the development of the high-impact polystyrene and today this is more important than the unmodified polymer (60% of Western European market).

At the beginning of the 1980s, world capacity for polystyrene manufacture was about 6 000 000 tonnes, with Western Europe and North America each having a capacity of about 2 225 000 tonnes. Over the next decade both capacity and production increased by about 66%, with extensive market growth particularly in the late 1980s. Some indication of the application breakdown of GPPS and HIPS together with data for ABS and SAN is given in *Table 16.12*.

In recent years general purpose polystyrene and high-impact polystyrenes have had to face intensive competition from other materials, particularly polypropylene, which has been available in recent years at what may best be described as an abnormally low price. Whilst polystyrene has lost some of its markets it has generally enjoyed increasing consumption and the more pessimistic predictions of a decline have as yet failed to materialise. Today about 75% of these materials are injection moulded whilst the rest is extruded and/or thermoformed.

The largest outlet for polystyrene is in packaging applications. Specific uses include bottle caps, small jars and other injection moulded containers, blown containers (a somewhat recent development but which has found rapid acceptance for talcum powder), vacuum formed toughened polystyrene as liners for boxed goods and oriented polystyrene film for foodstuffs such as creamed

Table 16.12 Production and consumption breakdown for main types of styrene-based plastics in the late 1990s

	<i>GPPS and HIPS</i>	<i>XPS</i>	<i>ABS</i>	<i>SAN</i>
Global production (10 ⁶ t)	8.0	1.85	3.0	–
Application breakdown (%)				
Packaging	40	29	–	12
Insulation (including refrigerator parts)	5	68	–	–
Electrical/electronics	25	–	24	29
Domestic appliances	10	–	24	28
Automotive	–	–	23	–
Other	20	3	29	31

Note: The application breakdown for ABS and XPS is based on data for Western Europe for 1997. The data for SAN is based on data available in the early 1990s but still believed approximately correct.

cheese. Vacuum formed cigarette packets were introduced in the United States in the early 1960s and were claimed to be as economical to produce as those from cardboard.

A second important outlet is in refrigeration equipment, where the low thermal conductivity and improved impact properties of polystyrene at low temperatures are an asset. Specific uses in this area include door liners and inner liners made from toughened polystyrene sheet, mouldings for flip lids, trays and other refrigerator ‘furnishings’ and expanded polystyrene for insulation. Although in the past most liners have been fabricated from sheet there is a current interest in injection moulding these parts since these will give greater design flexibility. It is also claimed that with sufficiently high production rates the injection process will be cheaper.

Polystyrene and high-impact polystyrene mouldings are widely used for housewares, for example storage containers, for toys, games and sports equipment, radio and electrical equipment (largely as housings, knobs and switches), for bathroom and toilet fittings (such as cistern ball-cock floats) and for shoe heels. Light-stabilised polymer is used for light fittings but because of the tendency of polystyrene to yellow, poly(methyl methacrylate) is preferred. Polystyrene monofilament finds limited use for brushes and for handicraft work. Both in North America and in Western Europe about two-thirds of the expanded polystyrene produced is used for thermal insulation. Most of this is used in building construction. It is also used to some extent in refrigeration insulation. In this field it meets intensive competition from polyurethane foams. The expanded polystyrene has a low density, a low weight cost, is less brittle and can be made fire retarding. On the other hand polyurethane foams produced by systems using auxiliary blowing agents (see Chapter 27) have a lower thermal conductivity and can be formed *in situ*. This latter property makes the polyurethane foam self-sealing, thus aiding the overall insulation characteristics of the whole construction rather than just that of the foam.

Nearly all the expanded polystyrene that is not used for thermal insulation is used for packaging. Uses range from individually designed box interiors for packing delicate equipment such as cameras and electronic equipment, thermoformed egg-boxes to individual beads (which may be up to 5 cm long and about 1 cm in diameter) for use as a loose fill material. There is also some use of thin-wall containers for short-term packaging and conveying of hot food from

take-away service areas. A small amount is used for buoyancy applications and as decorative flower pots and *jardinières*.

Expanded polystyrene accounts for over 20% of the weight consumption of polystyrene and high-impact polystyrene. The volume of expanded material produced annually exceeds even the volume production of the aliphatic polyolefins.

Because of their toughness and good appearance ABS polymers have become regarded as a de luxe form of polystyrene, their biggest drawbacks being their limited weathering resistance and relatively high cost. It is one of the few major polymers where there is different pattern of use in North America compared with Europe.

In Western Europe the largest user is the vehicle construction industry where ABS has been used for fascia panels, door covers, door handles, radiator grilles, ventilation system components, heater housings, seat belt fastenings, console panels, loudspeaker housings, interior trim and other uses. For some years there was extensive use of electroplated ABS. Whilst this continues to be used for nameplates, reflectors and other parts where a bright reflecting surface is a requirement, it has tended to fall out of favour simply for decoration.

The use of ABS has in recent years met considerable competition on two fronts, particularly in automotive applications. For lower cost applications, where demands of finish and heat resistance are not too severe, blends of polypropylene and ethylene-propylene rubbers have found application (see Chapters 11 and 31). On the other hand, where enhanced heat resistance and surface hardness are required in conjunction with excellent impact properties, polycarbonate-ABS alloys (see Section 20.8) have found many applications. These materials have also replaced ABS in a number of electrical fittings and housings for business and domestic applications. Where improved heat distortion temperature and good electrical insulation properties (including tracking resistance) are important, then ABS may be replaced by poly(butylene terephthalate).

In the US the largest single application area is for pipes and fittings whereas in Western Europe the corresponding market is largely dominated by unplasticised PVC. This is largely a reflection of the earlier development of methods of handling unplasticised PVC in Europe than was generally the case in the USA.

Other important application areas in both regions are household appliances, consumer electronic equipment, refrigerator sheeting, toys, telephones, office equipment, recreational equipment, luggage and as a modifier for PVC.

Styrene-acrylonitrile plastics are used on a smaller scale in a variety of areas as may be seen from *Table 16.11*. Individual applications were discussed in Section 16.7.

The uses of blends of polystyrene with the so-called polyphenylene oxide polymers are discussed in Chapter 21.

References

1. SIMON, E., *Ann.*, **31**, 265 (1839)
2. GLENARD, M., and BOUDALT, R., *Ann.*, **53**, 325 (1845)
3. BERTHELOT, M., *Ann. Chim. Phys.*, (4), **16**, 153 (1869)
4. BOUNDY, R. H., and BOYER, R. F. *Styrene, its Polymers, Copolymers and Derivatives*, Reinhold, New York (1952)
5. *Brit. Plastics*, **30**, 26 (1957)
6. *Plastics (London)*, **22**, 3 (1957)

7. SAMARAS, N. N. T., and PARRY, E., *J. Appl. Chem. (London)*, **1**, 243 (1951)
8. HAWARD, R. N., and CRABTREE, D. R., *Trans. Plastics Inst.*, **23**, 61 (1955)
9. GOGGIN, W. C., CHENEY, G. W., and THAYER, G. B., *Plastics Technol.*, **2**, 85 (1956)
10. FOX, T. G., and FLORY, P. J., *J. Am. Chem. Soc.*, **70**, 2384 (1948)
11. DAVENPORT, N. E., HUBBARD, L. W., and PETTIT, M. R., *Brit Plastics*, **32**, 549 (1959)
12. BUCKNALL, C. B., *Trans. Instn Rubber Ind.*, **39**, 221 (1963)
13. *British Patent*, 892, 910
14. *British Patent*, 897, 625
15. *British Patent*, 880, 928
16. NATTA, G., *J. Polymer Sci.*, **16**, 143 (1955)
17. *Belgian Patent*, 533, 362
18. CUBBAN, R. C. P., and MARGERISON, D., *Proc. Chem. Soc.*, 146 (1960)
19. SKINNER, S. J., BAXTER, S., and GREY, P. J., *Trans. Plastics Inst.*, **32**, 180 (1964)
20. SKINNER, S. J., *Trans. Plastics Inst.*, **32**, 212 (1964)
21. FERRIGNO, T. H., *Rigid Plastics Foams*, Reinhold, New York, 2nd Edn (1967)
22. BAXTER, S., and JONES, T. T., *Plastics & Polymers*, **40**, 69 (1972)
23. JACK, J., *Brit. Plastics*, **34**, 312, 391 (1961)

Bibliography

- BRIGHTON, C. A., PRITCHARD, G., and SKINNER, G. A., *Styrene Polymers: Technology and Environmental Aspects*, Applied Science, London (1979)
- BOUNDY, R. H., and BOYER, R. F., *Styrene, its Polymers, Copolymers and Derivatives*, Reinhold, New York (1952)
- FERRIGNO, T. H., *Rigid Plastics Foams*, Reinhold, New York, 2nd Edn (1967)
- GIBELLO, H., *Le Styrene et ses Polymères*, Dunod, Paris (1956)
- GOLDIE, W., *Metallic Coating of Plastics, Vol. 1*. Electrochemical Publications, London (1968)

Reviews

- ADAMS, M. E., BUCKLEY, D. J., COLBORN R. E., ENGLAND, W. P. and SCHISSEL, D. N. *Acrylonitrile-Butadiene-Styrene Polymers* A Review Report published by RAPRA Technology Ltd, Shawbury, England (1993)
- BACK, W. D., *Kunststoffe*, **86**, 1471-1472 (1996)
- THROWE, J. L., *J. Cellular Plastics* 264-83 (1976)
- GELLERT, R., *Kunststoffe*, **77**, 977-81 (1987)
- ELIAS, H.-G. and VOHWINKEL, F., *New Commercial Polymers-2*, Gordon and Breach, New York and London (1986)
- HILTON, G. B. and JOHNSON, C. A., Chapter 14 in *Engineering Thermoplastics* (Ed. MARGOLIS, J. M.), Marcel Dekker, New York and Basel (1985)
- JENNE, H., *Kunststoffe*, **77**, 972-6 (1987)
- LINDENSCHMIDT, G. and THEYSON, R., *Kunststoffe*, **77**, 982-8 (1987)
- REICHERT, U., *Kunststoffe*, **80** (10), 1092-6 (1990)
- SCHEIDEL, I. C., and FROBERE, E. *Kunststoffe*, **80** (10), 1099-106 (1990)
- WAGNER, D., *Kunststoffe*, **86**, 1466-1468 (1996)

Miscellaneous Vinyl Thermoplastics

17.1 INTRODUCTION

In addition to the various vinyl polymers discussed in the preceding seven chapters a large number of other polymers of this type have been described in the literature.¹ Some of these have achieved commercial significance and those which have interest as plastics or closely related materials are the subject of this chapter.

17.2 VINYLIDENE CHLORIDE POLYMERS AND COPOLYMERS

Vinylidene chloride polymerises spontaneously into poly(vinylidene chloride), a polymer sufficiently thermally unstable to be unable to withstand melt processing (*Figure 17.1*).

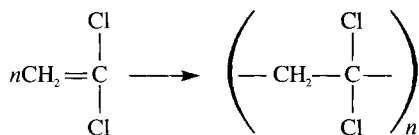


Figure 17.1

By copolymerising the vinylidene chloride with about 10–15% of vinyl chloride, processable polymers may be obtained which are used in the manufacture of filaments and films. These copolymers have been marketed by the Dow Company since 1940 under the trade name Saran. Vinylidene chloride–acrylonitrile copolymers for use as coatings of low moisture permeability are also marketed (Saran, Viclan). Vinylidene chloride–vinyl chloride copolymers in which the vinylidene chloride is the minor component (2–20%) were mentioned in Chapter 12.

The monomer is produced from trichloroethane by dehydrochlorination (Figure 17.2). This may be effected by pyrolysis at 400°C, by heating with lime or treatment with caustic soda. The trichloroethane itself may be obtained from ethylene, vinyl chloride or acetylene.

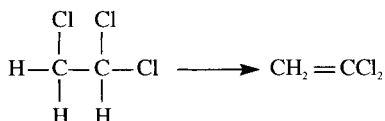


Figure 17.2

Vinylidene chloride is a clear mobile liquid which is highly inflammable and with the following physical properties:

Boiling point	31.9°C at 760 mmHg
Specific gravity	1.233 at 15.5°C
Refractive index	1.4246 at 20°C
Specific heat	1.13 J g ⁻¹ °C ⁻¹
Heat of polymerisation	60.6 kJ/mole

Although miscible with many organic solvents it has a very low solubility in water (0.04%).

The handling of the monomer presents a number of problems. The monomer will polymerise on storage even under an inert gas. Polymer deposition may be observed after standing for less than a day. Exposure to air, to water or to light will accelerate polymerisation. A number of phenolic materials are effective inhibitors, a typical example being 0.02% *p*-methoxyphenol. Exposure to light, air and water must, however, still be avoided. The monomer has an anaesthetic action and chronic toxic properties and care must therefore be taken in its handling.

The polymer may be prepared readily in bulk, emulsion and suspension, the latter technique apparently being preferred on an industrial scale. The monomer must be free from oxygen and metallic impurities. Peroxide such as benzoyl peroxide are used in suspension polymerisations which may be carried out at room temperature or at slightly elevated temperatures. Persulphate initiators and the conventional emulsifying soaps may be used in emulsion polymerisation. The polymerisation rate for vinylidene chloride–vinyl chloride copolymers is markedly less than for either monomer polymerised alone.

Consideration of the structure of poly(vinylidene chloride) (Figure 17.3) enables certain predictions to be made about its properties.

It will be seen that the molecule has an extremely regular structure and that questions of tacticity do not arise. The polymer is thus capable of crystallisation.

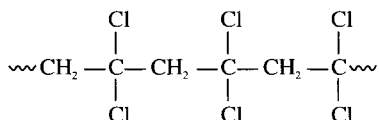


Figure 17.3

The resultant close packing and the heavy chlorine atom result in the polymer having a high specific gravity (1.875) and a low permeability to vapours and gases.

The solubility parameter is calculated at $20 \text{ MPa}^{1/2}$ and therefore the polymer is swollen by liquids of similar cohesive forces. Since crystallisation is thermodynamically favoured even in the presence of liquids of similar solubility parameter and since there is little scope of specific interaction between polymer and liquid there are no effective solvents at room temperature for the homopolymer.

The chlorine present results in a self-extinguishing polymer. It also leads to a polymer which has a high rate of decomposition at the temperatures required for processing.

Copolymerisation, with for example vinyl chloride will reduce the regularity and increase the molecular flexibility. The copolymers may thus be processed at temperatures where the decomposition rates are less catastrophic.

Vinylidene chloride–vinyl chloride polymers are also self-extinguishing and possess very good resistance to a wide range of chemicals, including acids and alkalis. They are dissolved by some cyclic ethers and ketones.

Because of the extensive crystallisation, even in the copolymers, high strengths are achieved even though the molecular weights are quite low ($\sim 20\,000$ – $50\,000$). A typical 85:15 copolymer plasticised with diphenyl ethyl ether has a melting point of about 170°C , a glass temperature of about -17°C and a maximum rate of crystallisation at approximately 90°C .²

17.2.1 Properties and Applications of Vinylidene Chloride–Vinyl Chloride Copolymers³

Since some properties of the vinylidene chloride–vinyl chloride copolymers are greatly dependent on crystallisation and orientation it is convenient to consider the applications of these copolymers and then to discuss the properties of the products.

The copolymers have been used in the manufacture of extruded pipe, moulded fittings and for other items of chemical plant. They are, however, rarely used in Europe for this purpose because of cost and the low maximum service temperature. Processing conditions are adjusted to give a high amount of crystallinity, for example by the use of moulds at about 90°C . Heated parts of injection cylinders and extruder barrels which come into contact with the molten polymer should be made of special materials which do not cause decomposition of the polymer. Iron, steel and copper must be avoided. The danger of thermal decomposition may be reduced by streamlining the interior of the cylinder or barrel to avoid dead-spots and by careful temperature control. Steam heating is frequently employed.

Additives used include plasticisers such as diphenyl diethyl ether, ultraviolet light absorbers such as 5-chloro-2-hydroxybenzophenone (1–2% on the polymer) and stabilisers such as phenoxy propylene oxide.

The copolymers are used in the manufacture of filaments.⁴ These may be extruded from steam-heated extruders with a screw compression ratio of 5:1 and a length/diameter of 10:1. The filaments are extruded downwards (about 40 at a time) into a quench bath and then round drawing rollers which cause a three- to four-fold extension of the filaments and an increase in strength from about 10 000 to 36 000 lbf/in² (70–250 MPa). The filaments are used for deck chair fabrics, car

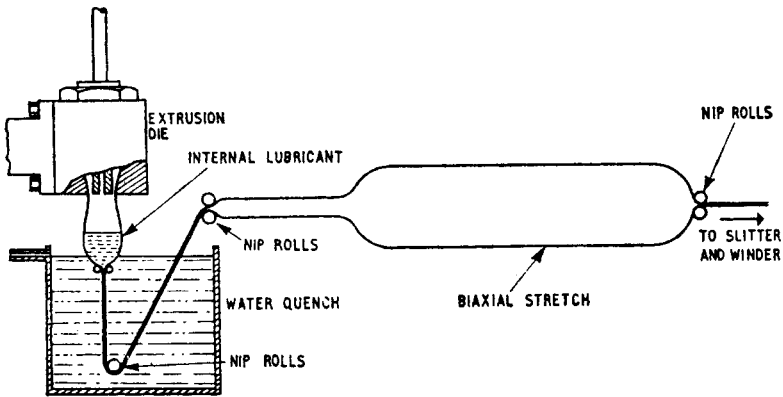


Figure 17.4. Extrusion process for the manufacture of biaxially oriented Saran film²

upholstery, decorative radio grilles, dolls' hair, filter presses and for sundry other applications where their toughness, flexibility, durability and chemical resistance are of importance.

Biaxially stretched copolymer film is a useful though expensive packaging material (Saran Wrap-Dow) possessing exceptional clarity, brilliance, toughness and water and gas impermeability. A number of grades are available differing in transparency, surface composition and shrinkage characteristics. It is produced by water quenching a molten tubular extrudate at 20°C and then stretching by air inflation at 20–50°C. Machine direction orientation of 2–4:1 and transverse orientation of 3–5:1 occurs and crystallisation is induced during orientation.² The process is shown schematically in Figure 17.4. Some general properties of vinylidene chloride–vinyl chloride copolymers containing about 85% vinylidene chloride are given in Table 17.1. Gas transmission date of typical films is given in Table 17.2. The water vapour transmission is about 0.05–0.15 g/100 in²/24 h at 70°F for 0.001 in thick film. The large variations in gas transmission values

Table 17.1 General properties of vinylidene chloride–vinyl chloride (85:15) copolymer

Specific gravity	1.67–1.7
Refractive index	1.60–1.61
Specific heat	1.34 J g ⁻¹ °C ⁻¹
Max. service temperature	60°C (continuous)
Dielectric constant 10 ² Hz	4.9–5.3 (ASTM D.150)
10 ⁵ Hz	3.4–4.0 (ASTM D.150)
Power factor 10 ² Hz	0.03–0.05 (ASTM D.150)
10 ⁵ Hz	0.04–0.05 (ASTM D.150)
Volume resistivity	10 ¹² –10 ¹⁶ Ω cm (ASTM D.257)
Tensile strength (unoriented)	8000 lbf/in ² (55 MPa)
Tensile strength (filaments)	20 000–40 000 lbf/in ² (140–280 MPa)
Tensile strength (film)	8000–20 000 lbf/in ² (55–140 MPa)

Table 17.2 Gas transmission ($\text{cm}^3/100 \text{ in}^2/24 \text{ H atm}$) at 73.4°F (tabulated to a 1 mil thickness)
ASTM D.1434-56T

O ₂	1.0-5.9
CO ₂	3.8-45.7
N ₂	0.16-1.6
Air	0.21-2.6
Freon 12	<0.03-4.0

Source: Dow Co. Literature

quoted are due to differences in formulation, films having the higher transmission having a softer feel.

17.2.2 Vinylidene Chloride-Acrylonitrile Copolymers

Copolymers of vinylidene chloride with 5-50% acrylonitrile were investigated by IG Farben during World War II and found to be promising for cast films. Early patents by ICI⁵ and Dow⁶ indicated that the copolymers were rigid, transparent and with a high impact strength.

The principal commercial outlet for these copolymers (Saran, Viclan) has, however, been as coatings for cellophane, polyethylene, paper and other materials and as barrier layers in multi-layer extruded films. Such coatings are of value because of their high moisture and gas impermeability, chemical resistance, clarity, toughness and heat sealability. The percentage of acrylonitrile used is normally in the range 5-15%. Higher quantities facilitate solubility in ketone solvents whereas lower amounts, i.e. higher vinylidene chloride contents, increase the barrier properties. The barrier properties of these copolymers are of the same order as those of the vinylidene chloride-vinyl chloride copolymers, and they are claimed in the trade literature to be between 100 and 1000 times more impermeable than low-density polyethylene in respect of CO₂, nitrogen and oxygen transmission. The development of multi-layer packaging films has led to widespread use of vinylidene chloride-based polymers as barrier layers. For example, a multi-layer system polystyrene-vinylidene chloride polymer-polystyrene exhibits low permeability to gases, water vapours and odours and is used for packaging dairy produce. The system polystyrene-vinylidene chloride polymer-polyethylene additionally exhibits good chemical resistance, stress cracking resistance and heat sealability (on the polyethylene surface) and is used for dairy produce, fruit juices, mayonnaise, coffee and pharmaceuticals.

Of commercial barrier polymers, only the ethylene-vinyl alcohol (EVOH) copolymers (see Chapter 14) show greater resistance to gas permeability. However, the EVOH materials exhibit much higher levels of moisture absorption.

In 1962 Courtaulds announced a flame-resisting fibre BHS said to be a 50:50 vinylidene chloride-acrylonitrile copolymer. This product has subsequently been renamed 'Teklan'.

A number of other copolymers with vinylidene chloride as the major component have been marketed. Prominent in the patent literature are methyl methacrylate, methyl acrylate and ethyl acrylate.

17.3. COUMARONE-INDENE RESINS

Fractionation of coal tar naphtha (b.p. 150–200°C) yields a portion boiling at 168–172°C consisting mainly of coumarone (benzofuran) and indene (*Figure 17.5*).

The products bear a strong formal resemblance to styrene and may be polymerised. For commercial purposes the monomers are not separated but are polymerised *in situ* in the crude naphtha, sulphuric acid acting as an ionic catalyst to give polymers with a degree of polymerisation of 20–25.

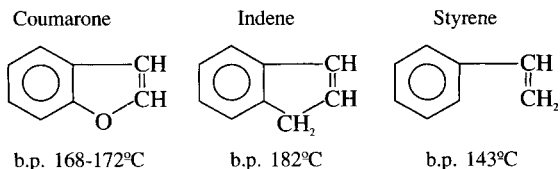


Figure 17.5

In one process the naphtha fraction boiling between 160 and 180°C is washed with caustic soda to remove the acids and then with sulphuric acid to remove basic constituents such as pyridine and quinoline. The naphtha is then frozen to remove naphthalene, and agitated with sulphuric acid, then with caustic soda and finally with water. Concentrated sulphuric acid is then run into the purified naphtha at a temperature below 0°C. The reaction is stopped by addition of water after 5–10 minutes, any sediment is removed, and the solution is neutralised and then washed with water. Residual naphtha is distilled off under vacuum, leaving behind the resin, which is run into trays for cooling.

By varying the coumarone/indene ratio and also the polymerisation conditions it is possible to obtain a range of products varying from hard and brittle to soft and sticky resins.

Being either brittle or soft, these resins do not have the properties for moulding or extrusion compounds. These are, however, a number of properties which lead to these resins being used in large quantities. The resins are chemically inert and have good electrical insulation properties. They are compatible with a wide range of other plastics, rubbers, waxes, drying oils and bitumens and are soluble in hydrocarbons, ketones and esters.

The resins tend to be dark in colour and it has been suggested that this is due to a fulvenation process involving the unsaturated end group of a polymer molecule. Hydrogenation of the polymer molecule, thus eliminating unsaturation, helps to reduce discolouration.

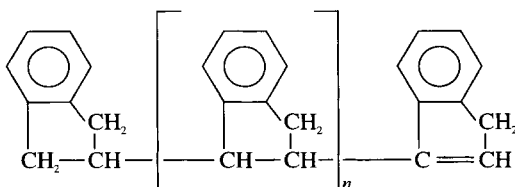


Figure 17.6. Structure of polyindene

Because of their wide compatibility and solubility, coumarone resins are used considerably in the paint and varnish industry. The resins also find application as softeners for plastics and rubbers such as PVC, bitumens and natural rubber.

Soon after World War II the hard thermoplastic floor tile was developed. These tiles use coumarone resins as a binder for the other ingredients, which may contain fibrous fillers such as asbestos, inert fillers such as china clay and softeners such as paraffin wax.

The initial mixing of these compounds is carried out in an internal mixer; the resin melts and forms a hot dough on admixture with the fillers. The dough is then pigmented and banded out on a hot mill. Marbling effects are produced by adding chips of another colour to the mill nip. The rough sheet is then cut off and calendered and the product cut into tiles. These tiles may easily be cut when warmed, thus making laying a simple operation. Because of the low cost of the raw materials and the relatively simple method of manufacture, coumarone tiles were cheaper than the vinyl tile based on vinyl chloride–vinyl acetate copolymers and have been extensively used for both industrial and domestic flooring.

17.4 POLY(VINYL CARBAZOLE)^{7,8,9}

Early in World War II there was a shortage of mica in Germany and in the United States. A need therefore arose for a material with good electrical insulation characteristics coupled with good heat resistance. In an attempt to meet this need poly(vinyl varbazole) was produced in both Germany (Luvican–IG Farben) and the United States (Poelectron–General Aniline & Film Corporation). In addition to the homopolymer (Luvican M.150) the IG Farben complex also produced styrene copolymers (Luvicans M.125 and M.100—the numerical term corresponding to the value of the Martens Softening point) and at one time production of vinyl carbazole polymers reached a level of five tons a month. Because of its brittleness and its tendency to cause an eczema-type of rash on people handling the material, production of these polymers became very small.

However, the discovery that exposure to light could increase substantially the electrical conductivity of this polymer, i.e. it is said to be *photoconductive*, has led to important new applications, particularly in xerography.

Vinyl carbazole is obtained by reacting carbazole, readily available as a by-product of coal tar distillation, with acetylene in the presence of a catalyst and solvent under pressure (*Figure 17.7*).

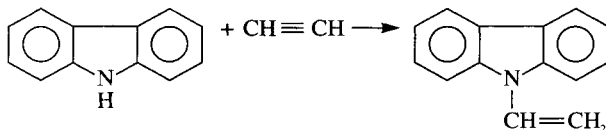


Figure 17.7

Typically, the reaction would be carried out at 140°C in white spirit with potassium carbazole as a catalyst. Davidge¹⁰ has reported problems in polymerisation of *N*-vinyl carbazole prepared from carbazole obtained from coal tar, attributing this to the presence of sulphur. To overcome these problems carbazole has been prepared synthetically by reactions of cyclohexanone with

phenylhydrazine to give tetrahydrocarbazole, which is then dehydrogenated with Raney nickel. *N*-Vinyl carbazole is a solid with a melting point of 64–67°C.

High molecular weight polymers are produced by an adiabatic bulk polymerisation process^{10,11} using di-*tert*-butyl peroxide (0.02%) and 2,2'-azo-bisdi-isobutyronitrile (0.01%) as initiators and pressurised with N₂. Heating to 80–90°C causes an onset of polymerisation and a rapid increase in temperature. After the maximum temperature has been reached the mass is allowed to cool under pressure. A typical current commercial material (Luvican M.170) has a *K*-value of about 70 (as assessed in a 1% tetrahydrofuran solution).

The polymerisation *in situ* of monomer impregnated into rolled and stacked condensers was at one time of commercial importance.¹²

The most important properties of poly(vinyl carbazole) are:

- (1) Its good photoconductivity.
- (2) A high softening point.
- (3) Excellent electrical insulating properties.
- (4) An exceptionally high refractive index ($n_{20}^D = 1.696$).
- (5) A brittleness associated with a tendency to crystallise and fibrillate during mechanical stressing.

Some numerical values of significant properties are given in *Table 17.3*.

The polymers are, however, more brittle than polystyrene and not suitable for applications which are to be subject to mechanical shock.

Table 17.3 Some properties of poly(*N*-vinyl carbazole)

<i>Property</i>	<i>Units</i>	<i>Value</i>	<i>ISO method</i>
Density	g/cm ³	1.19	R1183
Tensile strength	MPa	10	DIS527
Elongation at break	%	0.5	DIS527
Tension modulus	MPa	3700	DIS527
Impact resistance	KJ/mm ²	5–10	R179
Vicat softening point	°C	~195	306
Volume resistivity	ohm cm	10 ¹⁶	IEC93
Dielectric constant (1 kHz–100 MHz)		2.9–3	
Power factor (1 kHz–300 MHz)		0.0004–0.001	
Dielectric strength	kV/mm ¹	~50	IEC243
Moisture absorption	%	<0.1	DIS62
Specific heat	J g ⁻¹ K ⁻¹	1.26	

Poly(vinyl carbazole) is insoluble in alcohols, esters, ethers, ketones, carbon tetrachloride, aliphatic hydrocarbons and castor oil. It is swollen or dissolved by such agents as aromatic and chlorinated hydrocarbons and tetrahydrofuran.

The polymer is not easy to process and in injection moulding melt temperatures of 300°C are employed. In order to prevent excess embrittlement by shock cooling of the melt, mould temperatures as high as 150°C may be used. The polymer may also be compression moulded at temperatures of 250–260°C.

The main application today for poly(vinyl carbazole) arises out of its photoconductivity⁹ and is in electrostatic dry copying machines. The polymer is applied from solution in thin film (10–15 μm) layers onto a conductive substrate.

In order to obtain the desired photoconductive characteristics, toughness and adherence to the substrate it is usual to incorporate additives such as electron acceptors, plasticisers and primers. A typical electron acceptor is 2,4,7-trinitrofluoronone, plasticisers include benzyltetraline and phenanthrene whilst as primers styrene-butadiene block copolymers (30–35% styrene) and styrene-maleic anhydride copolymers (5–30% maleic anhydride) are of use.

When an electrostatic charge is applied to a coating in the dark it is observed to discharge to an equilibrium value. When the light source is switched on, the conductivity is increased and discharging occurs, leading to a negligible charge. In xerography this phenomenon is used as a means of forming a latent electrostatic image which is then developed by a dry method by transferring the charge onto a powder known as the toner.

The polymer may be regarded in these applications as a form of photoresistor (see Chapter 14) and is now finding other applications in this area. It has been used in holography and in the manufacture of printing plates whilst it has also been suggested for use in solar cells and for measuring photoelectric resistance.

Earlier applications as a capacitor dielectric and other electrical applications such as switch parts, cable connectors and co-axial cable spacers are now very limited.

17.5 POLY(VINYL PYRROLIDONE)¹³

Poly(vinyl pyrrolidone) (PVP) was introduced by the Germans in World War II as a blood plasma substitute.¹⁴ A water-soluble polymer, its main value is due to its ability to form loose addition compounds with many substances.

The monomer is prepared from acetylene, formaldehyde and ammonia via but-2-yne-1,4-diol, butane-1,4-diol, γ -butyrolactone and γ -pyrrolidone (*Figure 17.8*).

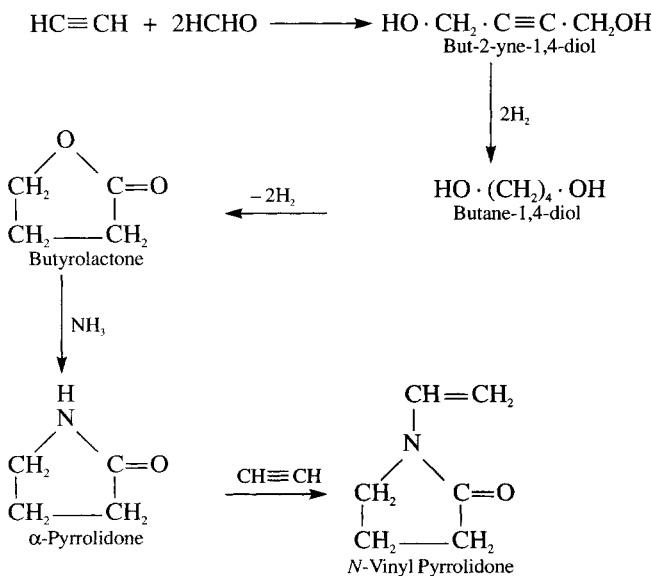


Figure 17.8

Polymerisation is carried out in aqueous solution to produce a solution containing 30% polymer. The material may be marketed in this form or spray dried to give a fine powder. Polymers may be produced with molecular weights in the range 10 000–100 000 (K values 20–100) of which products with a K value of 30–35 are the most important.^{15, 16}

In addition to its water solubility poly(vinyl pyrrolidone) is soluble in a very wide range of materials, including aliphatic halogenated hydrocarbons (methylene dichloride, chloroform), many monohydric and polyhydric alcohols (methanol, ethanol, ethylene glycol), some ketones (acetyl acetone) and lactones (α -butyrolactone), lower aliphatic acids (glacial acetic acid) and the nitro-paraffins. The polymer is also compatible with a wide range of other synthetic polymers, with gums and with plasticisers.

PVP has found several applications in the textile industry because of its affinity for dyestuffs. Uses include dye stripping, removal of identification tints, in the formulation of sizes and finishes and to assist in dye-levelling operations. In the field of cosmetics PVP is used because of its unique property of forming loose addition compounds with skin and hair. Hair lacquers may be formulated based on 4–6% PVP in ethyl alcohol, whilst wave sets use about 1–2% of polymer. The polymer is also said to reduce the sting of after-shave lotion and is used in hand cream, lotions and liquid make-up. On the continent of Europe PVP is still used as a blood plasma substitute, the original application, and is stockpiled for emergency use in the United States. It is not used for this purpose in Britain. Because of its complexing action it finds miscellaneous uses in the pharmaceutical, brewing, soap and paper industries.

Copolymers of vinyl pyrrolidone with vinyl acetate, styrene and ethyl acrylate have been marketed by the General Aniline and Film Corporation. See also section 18.

17.6 POLY(VINYL ETHERS)^{1, 17}

It is not possible to polymerise vinyl ethers by free-radical-initiated methods but, as with isobutylene polymers, it is possible to make polymers using Friedel-Crafts type catalysts.

The poly(vinyl ethers), which were first made available in Germany before 1940, are not of importance in the plastics industry but have applications in adhesives, surface coatings and rubber technology. Of the many vinyl ether polymers prepared, only those from the vinyl alkyl ethers and some halogenated variants are of interest. Two methods of monomer preparations may be used.

- (1) The direct vinylation of alcohols by acetylene diluted with nitrogen or methane (Reppe method) (*Figure 17.9*).

High pressure autoclaves may be used fitted with remote control behind safety barricades, which are necessary because of the danger of explosions. In a typical process the autoclave is half-filled with alcohol containing 15%

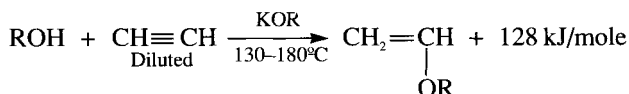


Figure 17.9

potassium hydroxide or potassium alcoholate. The free space is then thoroughly purged with oxygen-free nitrogen and the temperature raised to 140°C. Acetylene and nitrogen are run in under pressures of about 100 lbf/in² (0.69 MPa). Conversions are usually taken to 70–80%.

(2) Preparation via acetals (Carbide and Chemicals Corporation) (*Figure 17.10*).

A typical catalyst for the final stage would be 10% palladium deposited on finely divided asbestos.

The vinyl alkyl ethers polymerise violently in the presence of small quantities of inorganic acids.

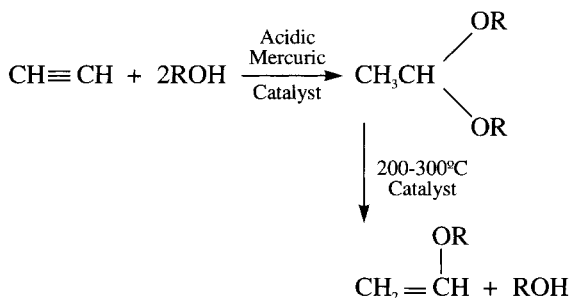


Figure 17.10

The following details for the commercial manufacture of poly(vinyl methyl ether) have been made available.¹ Agitated vinyl methyl ether at 5°C is treated over a period of 30 minutes with 0.2% of catalyst solution consisting of 3% BF₃•2H₂O in dioxane. When the reaction rises to 12°C the reaction is moderated by brine cooling. Over the next 3–4 hours further monomer and catalyst is added. The autoclave is then closed and the temperature allowed to rise slowly to 100°C.

The end of the reaction is indicated by the pressure and temperature observations. The total reaction time is of the order of 16–18 hours.

The polymer is a water-soluble viscous liquid which has found application in the adhesive and rubber industries. One particular use has been a heat sensitizer used in the manufacture of rubber latex dipped goods.

A number of higher poly(vinyl ether)s, in particular the ethyl and butyl polymers, have found use as adhesives. When antioxidants are incorporated, pressure-sensitive adhesive tapes from poly(vinyl ethyl ether) are said to have twice the shelf life of similar tapes from natural rubber. Copolymers of vinyl isobutyl ether with methyl acrylate and ethyl acrylate (Acronal series) and with vinyl chloride have been commercially marketed. The first two products have been used as adhesives and impregnating agents for textile, paper and leather whilst the latter (Vinoflex MP 400) has found use in surface coatings.

17.7 OTHER VINYL POLYMERS¹

In addition to the vinyl polymers reviewed in this and the previous seven chapters many others have been prepared. Few have, however, reached the pilot plant stage of manufacture and none appear, at present, to be of interest as plastics.

Typical of these materials are the poly(vinyl thioethers), the poly(vinyl isocyanates), the poly(vinyl ureas) and the poly(alkyl vinyl ketones). Methyl isopropenyl ketone and certain vinylpyridine derivatives have been copolymerised with butadiene to give special purpose rubbers.

References

1. SCHILDKNECHT, C. E., *Vinyl and Related Polymers*, John Wiley, New York (1952)

Vinylidene chloride polymers and copolymers

2. JACK, J., *Brit. Plastics*, **34**, 312 (1961)
3. GOGGIN, W. C., and LOWRY, R. D., *Ind. Eng. Chem.*, **34**, 327 (1942)
4. JACK, J., and HORSLEY, R. A., *J. Appl. Chem.*, **4**, 178 (1954)
5. *British Patent*, 570,711 (ICI)
6. *U. S. Patent*, 2,238,020 (Dow)

Poly(vinyl carbazole)

7. KLINE, G. M., *Mod. Plastics*, **24**, 157 (1946)
8. CORNISH, E. H., *Plastics*, **28** (305), 61, March (1963)
9. KÖNIG, W. and STEPHNEK, V., *Kunststoffe*, **69**, 223 (1979)
10. DAVIDGE, H., *J. Appl. Chem.*, **9**, 241, 553 (1959)
11. *German Patent*, 931,731; *Brit. Patent*, 739, 438 (BASF)
12. SHINE, W. M., *Mod. Plastics*, **25**, 130 (1947)

Poly(vinyl pyrrolidone)

13. DAVIDSON, R. L., and SITTIG, M. (Eds.), *Water-soluble Resins*, Reinhold, New York (1962)
14. B.I.O.S. Report 354, Item 22
15. *Ind. Chemist*, **29**, 122 (1953)
16. GREENFIELD, I., *Ind. Chemist*, **32**, 11 (1956)

Poly(vinyl ethers)

17. FIAT 856: BIOS 742: BIOS 1292

Bibliography

- LEONARD, E. C. (Ed), *Vinyl and Diene Monomers* (High Polymer Series Vol. 24), Wiley-Interscience, New York (1971)
- SCHILDKNECHT, C. E., *Vinyl and Related Polymers*, John Wiley, New York (1952)
- WESSLING, R. A., *Polyvinylidene Chloride*, Gordon and Breach, New York, London, Paris (1977)

Polyamides and Polyimides

18.1 POLYAMIDES: INTRODUCTION

Whilst by far the bulk of polyamide materials are used in the form of fibres, they have also become of some importance as speciality thermoplastics of particular use in engineering applications. The fibre-forming polyamides and their immediate chemical derivatives and copolymers are often referred to as *nylons*. There are also available polyamides of more complex composition which are not fibre-forming and are structurally quite different. These are not normally considered as nylons (see Section 18.10).

The early development of the nylons is largely due to the work of W. H. Carothers and his colleagues, who first synthesised nylon 66 in 1935 after extensive and classical researches into condensation polymerisation. Commercial production of this polymer for subsequent conversion into fibres was commenced by the Du Pont Company in December 1939. The first nylon mouldings were produced in 1941 but the polymer did not become well known in this form until about 1950.

In an attempt to circumvent the Du Pont patents, German chemists investigated a wide range of synthetic fibre-forming polymers in the late 1930s. This work resulted in the successful introduction of nylon 6 (and incidentally in the evolution of the polyurethanes) and today nylons 66 and 6 account for nearly all of the polyamides produced for fibre applications. Mention may, however, be made of nylons 7 (Enanth) and 9 (Pelargone) which have been investigated as fibres in the Soviet Union. Very many other aliphatic polyamides have been prepared in the laboratory and a few have become of specialised interest as plastics materials including nylons 11, 12, 46, 69, 612, 66/610 and 66/610/6.

For a variety of reasons the aromatic polyamides were slow in their development. A glassy aromatic polymer, poly(trimethylhexamethylene terephthalamide) became available in the early 1960s as Trogamid T, and this was followed by a series of other glassy aromatic polyamides in the 1970s and 1980s. During the same period several aromatic polyamides of more regular structure than the glassy polymers became important as fibres because of their exceptional strength in some cases or because of their fire-retarding properties in others. In

the latter part of the period polyamides became available which might be classified as thermoplastic rubbers.

There thus exists a very wide range of materials—fibres, crystalline plastics, amorphous plastics, adhesives and rubbers—which are classified as polyamides. They have the common feature that the amide (—CONH—) group occurs repeatedly in the polymer. Such an amide group can increase resistance to swelling and dissolution in hydrocarbons, increase interchain attraction and hence stiffness and heat deformation resistance, reduce electrical insulation resistance, particularly at high frequencies, and increase water absorption. However, as with other condensation polymers which are classified by the group formed during the condensation reaction, the amide groups form only a small proportion of the molecule, and other chemical groups may also have an important influence on the properties.

Of the many possible methods for preparing linear polyamides five are of commercial importance:

- (1) The reaction of diamines with dicarboxylic acids, via a 'nylon salt' (*Figure 18.1*).

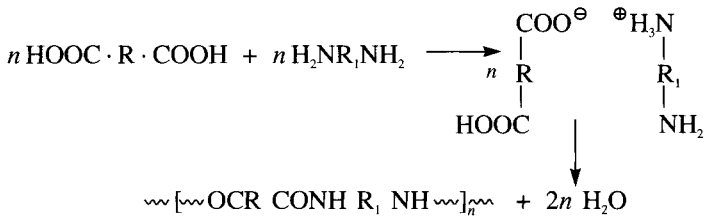


Figure 18.1

- (2) Self-condensation of an ω -amino acid (*Figure 18.2*).

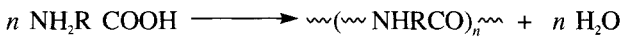


Figure 18.2

- (3) Opening of a lactam ring (*Figure 18.3*).

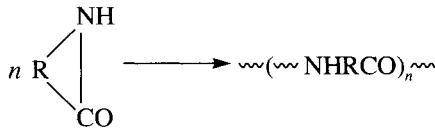
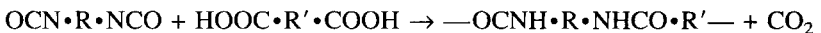


Figure 18.3

- (4) The reaction of diamines with diacid chlorides (see Sections 18.12 and 18.14).
 (5) The reaction of di-isocyanates with dicarboxylic acids.



This route has only been developed during the 1980s and has proved of particular interest in the manufacture of thermoplastic polyamide rubbers.

An example of the first route is given in the preparation of nylon 66, which is made by reaction of hexamethylenediamine with adipic acid. The first '6' indicates the number of carbon atoms in the diamine and the second the number of carbon atoms in the acid. Thus, as a further example, nylon 6.10 is made by reacting hexamethylenediamine with sebacic acid ($\text{HOOC}\cdot(\text{CH}_2)_8\cdot\text{COOH}$). (In this context the numbers 10,11 and 12 are considered as single numbers: the need to use two digits results simply from the limitations of the decimal system.)

Where the material is denoted by a single number, viz nylon 6 and nylon 11, preparation from either an ω -amino acid or a lactam is indicated. The polymer nylon 66/6.10 (60:40) indicates a copolymer using 60 parts of nylon 6.6 salt with 40 parts of nylon 6.10 salt.

Closely related to the polyamides are the *polyimides* and derivatives such as polyamide-imides and polyether-imides. These are discussed in Sections 18.13 and 18.14.

18.2 INTERMEDIATES FOR ALIPHATIC POLYAMIDES

18.2.1 Adipic Acid

It is possible to produce adipic acid by a variety of methods from such diverse starting points as benzene, acetylene and waste agricultural products. In practice, however, benzene is the favoured starting point and some of the more important routes for this material are illustrated in *Figure 18.4*

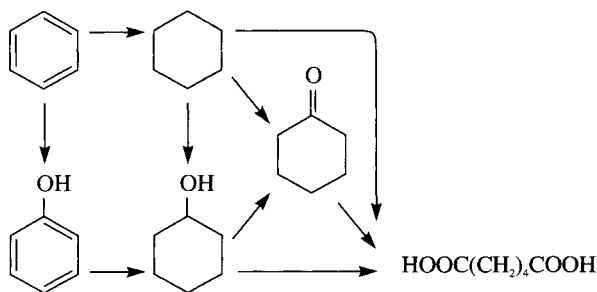
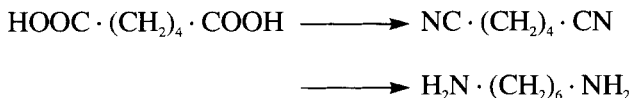


Figure 18.4

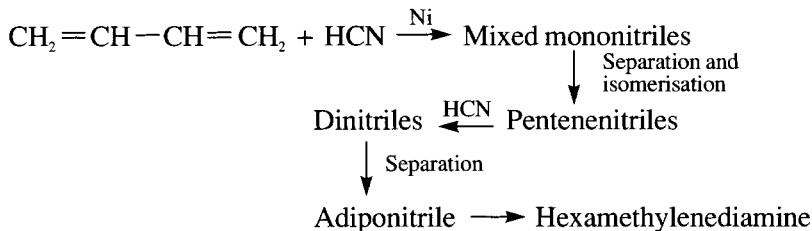
A typical route is that via cyclohexane, and cyclohexanol. To produce cyclohexane, benzene is subjected to continuous liquid phase hydrogenation at 340 lbf/in^2 pressure and a temperature of 210°C using a Raney nickel catalyst. After cooling and separation of the catalyst the produce is fed to the cyclohexane store. In the next stage of the operation for cyclohexane is preheated and continuously oxidised in the liquid phase by air using a trace of cobalt naphthenate as catalyst. This gives an approximately 70% yield of a mixture of cyclohexanol and cyclohexanone with a small quantity of adipic acid. The cyclohexanol–cyclohexanone mixture is converted into adipic acid by continuous oxidation with 50% HNO_3 at about 75°C using a copper-ammonium vanadate catalyst. The adipic acid is carefully purified by subjection to such processes as steam distillation and crystallisation. The pure material has a melting point of 151°C .

18.2.2 Hexamethylenediamine

Hexamethylenediamine may be conveniently prepared from adipic acid via adiponitrile



In a typical process adiponitrile is formed by the interaction of adipic acid and gaseous ammonia in the presence of a boron phosphate catalyst at 305–350°C. The adiponitrile is purified and then subjected to continuous hydrogenation at 130°C and 4000 lbf/in² (28 MPa) pressure in the presence of excess ammonia and a cobalt catalyst. By-products such as hexamethyleneimine are formed but the quantity produced is minimized by the use of excess ammonia. Pure hexamethylenediamine (boiling point 90–92°C at 14 mmHg pressure, melting point 39°C) is obtained by distillation. Hexamethylenediamine is also prepared commercially from butadiene. The butadiene feedstock is of relatively low cost but it does use substantial quantities of hydrogen cyanide. The process developed by Du Pont may be given schematically as:



Another process using butadiene as the starting material was developed by Esso. This involved the reaction of butadiene with iodine and cuprous cyanide to give the cuprous iodide complex of dehydroadiponitrile. This is further reacted with HCN to give a high yield of dehydroadiponitrile and regeneration of the iodine and cuprous iodide.

Commercial routes from acrylonitrile and from caprolactam have also been developed. This diamine may also be prepared from furfural and from butadiene.

18.2.3 Sebacic Acid and Azelaic Acid

Sebacic acid is normally made from castor oil, which is essentially glyceryl ricinoleate. The castor oil is treated with caustic soda at high temperature, e.g. 250°C, so that saponification, leading to the formation of ricinoleic acid; is followed by a reaction giving sebacic acid and octan-2-ol *Figure 18.5*.

Because of the by-products formed, the yield of sebacic acid is necessarily low and in practice yields of 50–55% (based on the castor oil) are considered to be good.

In a process said to be operated in Britain¹ castor oil is subjected to alkaline fusion under critically controlled conditions to produce a mixture of methyl hexyl ketone and ω-hydroxydecanoic acid. Interaction of these two materials at higher

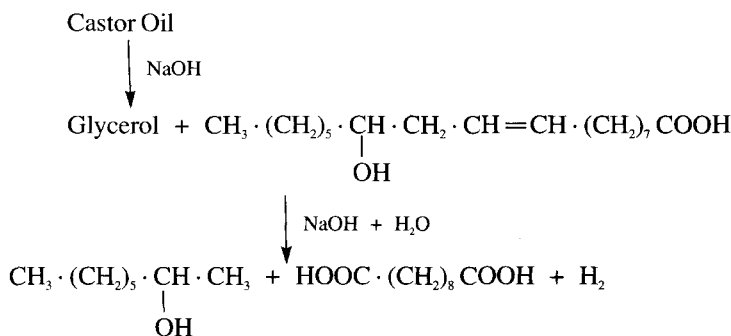
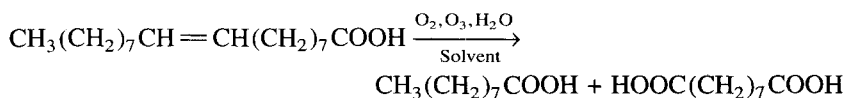


Figure 18.5

temperatures leads to the formation of sebacic acid, as the sodium salt, and capryl alcohol. Heating must be rapid and even and any tendency to preheating must be avoided. The sebacic acid is formed from the sodium salt by precipitation with sulphuric acid.

Azelaic acid is made by the ozonolysis of another natural product, oleic acid:



Sebacic acid is used for nylon 610 and azelaic acid for nylon 69.

18.2.4 Caprolactam

Caprolactam is preferred to ω -aminocaproic acid for the manufacture of nylon 6 because it is easier to make and to purify. Over the years many routes for the manufacture of caprolactam itself have been developed and major commercial routes are summarised in Figure 18.6. Of these routes the bulk of manufacture is via cyclohexanone and cyclohexanone oxime.

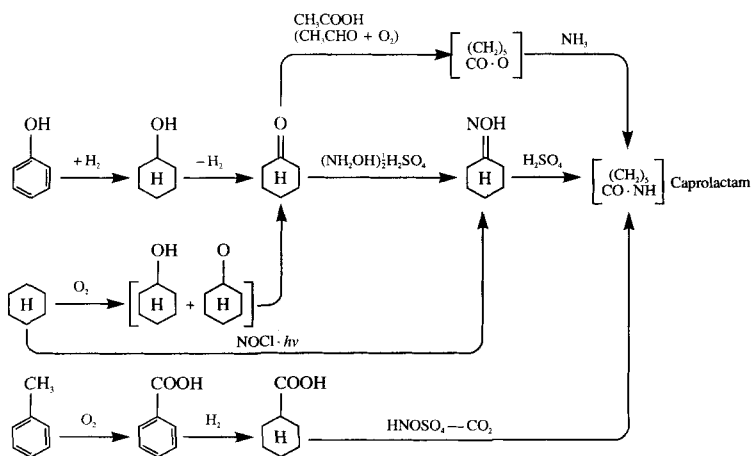


Figure 18.6

Cyclohexanone is normally prepared either from phenol or from cyclohexane. The phenol route is a two-stage process. In the first stage phenol and hydrogen are reacted in the presence of a nickel catalyst at about 180°C to form cyclohexanol. This hydrogenation stage is followed by a dehydrogenation stage in which the cyclohexanol is reacted in the gaseous phase at about 400°C in the presence of a copper catalyst to yield the cyclohexanone.

The alternative route involves the air oxidation of cyclohexane and proceeds via the production of a mixture of cyclohexanol and cyclohexanone often known as KA oil. It was in the cyclohexane oxidation section of the caprolactam plant of Nypro Ltd that the huge explosion occurred at Flixborough, England in 1974.

The conversion of cyclohexanone to cyclohexanone oxime is brought about by the use of hydroxylamine sulphate. The sulphuric acid is neutralised with ammonia to ammonium sulphate and this is separated from the oxime. In the presence of oleum the oxime undergoes the process known as the Beckmann rearrangement to yield the crude caprolactam. After further neutralisation with ammonia the caprolactam and further ammonium sulphate are separated by solvent extraction (*Figure 18.7*).

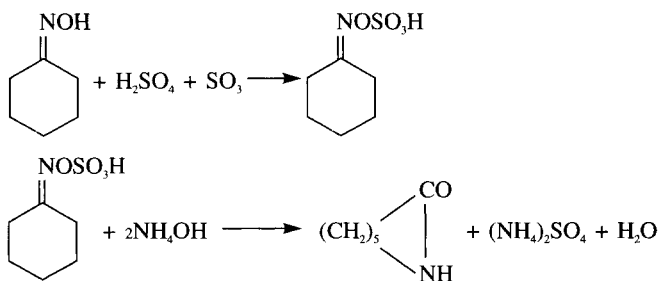


Figure 18.7

In one process the resulting solution is continuously withdrawn and cooled rapidly to below 75°C to prevent hydrolysis and then further cooled before being neutralised with ammonia. After phase separation, the oil phase is then treated with trichlorethylene to extract the caprolactam, which is then steam distilled. Pure caprolactam has a boiling point of 120°C at 10 mmHg pressure. In the above process 5.1 tons of ammonium sulphate are produced as a by-product per ton of caprolactam.

Of the other routes the photonitrosation process involving nitrosyl chloride is in use in Japan. This avoids, at the expense of complicated purification processes, the high yields of ammonium sulphate unavoidably produced in the route involving the Beckmann rearrangement.

18.2.5 ω -Aminoundecanoic Acid

The starting point for this amino acid, from which nylon 11 is obtained, is the vegetable product castor oil, composed largely of the triglyceride of ricinoleic acid. This is first subjected to treatment with methanol or ethanol to form the appropriate ricinoleic acid ester.

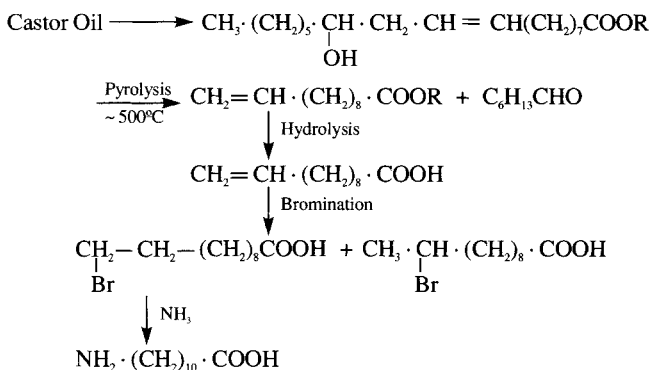


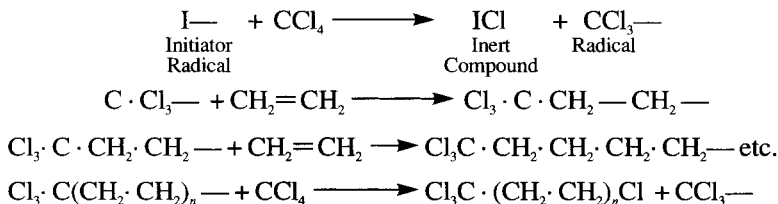
Figure 18.8

Cracking of the ester at about 500°C leads to the formation of the undecylenic acid ester together with such products as heptyl alcohol, heptanoic acid and heptaldehyde. Undecylenic acid may then be obtained by hydrolysis of the ester. Treatment of the acid by HBr in the presence of a peroxide leads to ω -bromoundecanoic acid together with the 10-isomer, which is removed. Treatment of the ω -bromo derivative with ammonia leads to ω -aminoundecanoic acid, which has a melting point of 50°C (Figure 18.8).

This amino acid may also be produced via telomerisation reactions (see below).

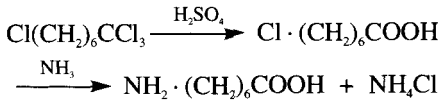
18.2.6 ω -Aminoanthic Acid

Interest in this material as an intermediate for nylon 7 arises largely from the development by Russian scientists of the process of *telomerisation*,² a process yielding low molecular weight polymers of simple unsaturated compounds, the polymers possessing useful reactive end-groups. Of greatest interest to date is the reaction of ethylene with carbon tetrachloride initiated by a peroxide such as benzoyl peroxide. The reaction proceeds by the following stages.



Because of the random nature of the occurrence of the chain transfer reaction which terminates molecular growth, polymers varying in molecular weight will be formed. For reaction at about 100°C , 100 atmospheres pressure and with an ethylene-carbon tetrachloride ratio of about 4:1, about 60% of the telomers have 7, 9 or 11 carbon atoms in the molecule. The individual telomers may be fractionated at reduced pressures. ω -Amino acid may be obtained from the isolated telomers by hydrolysing the ---CCl_3 group on heating the telomer with concentrated sulphuric acid for one hour at $90\text{--}100^\circ\text{C}$ and then treating the

product with an aqueous solution of ammonia under pressure. As an example, for ω -aminoenanthic acid the following reactions occur



The amino acid and the ammonium chloride may conveniently be separated by passing through a column of ion-exchange resins. The amino acid melts at 195°C .

ω -Aminopelargonic acid (for nylon 9) and ω -aminoundecanoic acid may also be prepared by this route.

18.2.7 Dodecanelactam

Nylon 12 first became available on a semicommercial scale in 1963. The monomer, dodecanelactam, is prepared from butadiene by a multistaged reaction. In one process butadiene is treated with a Ziegler-type catalyst system to yield the cyclic trimer, cyclododeca-1, 5, 9-triene. This may then be hydrogenated to give cyclododecane, which is then subjected to direct air oxidation to give a mixture of cyclododecanol and cyclododecanone. Treatment of the mixture with

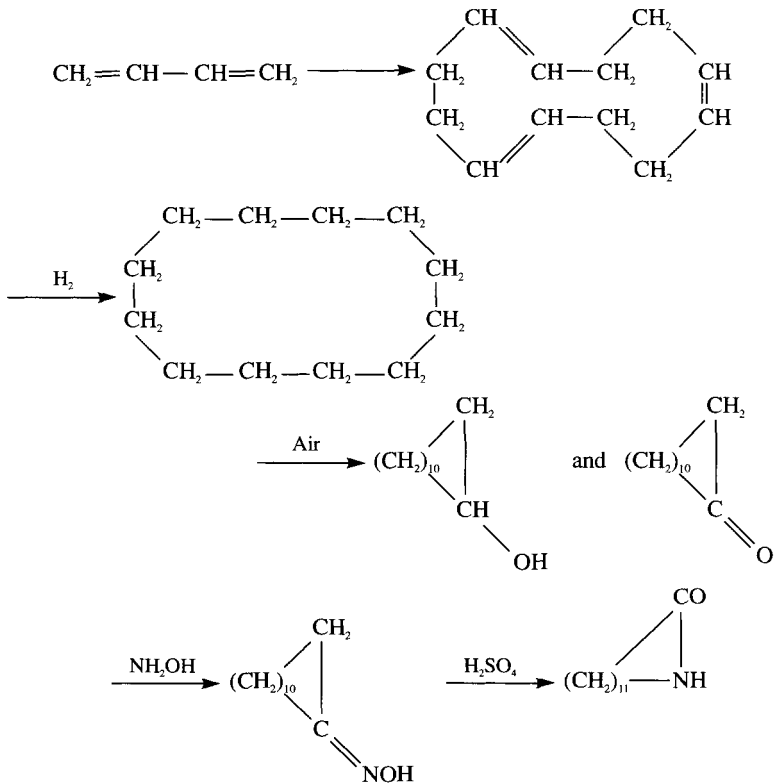


Figure 18.9

hydroxylamine yields the corresponding oxime, which on treatment with sulphuric acid rearranges to form the lactam (*Figure 18.9*).

A number of variations in the process are also being investigated, including the direct photo-oximation of cyclododecane.

18.3 POLYMERISATION OF ALIPHATIC POLYAMIDES

As already indicated, the fibre-forming polyamides are produced commercially by reacting diamines with dibasic acids, by self-condensation of an amino acid or by opening of a lactam ring. Whatever method is chosen it is important that there should be an equivalence in the number of amine and acid groups for polymers of the highest molecular weight to be obtained. In the case of the amino acids and lactams this is ensured by the use of pure monomer but when diamines and dibasic acids are used it is necessary to form a salt to ensure such an equivalence. Small quantities of monofunctional compounds are often used to regulate molecular weight.

18.3.1. Nylons 46, 66, 69, 610 and 612

The nylon 66 salt is prepared by reacting the hexamethylenediamine and adipic acid in boiling methanol, the comparatively insoluble salt (melting point 190–191°C) precipitating out.

A 60% aqueous solution of the salt is then run into a stainless steel autoclave together with a trace of acetic acid to limit the molecular weight (9000–15000). The vessel is sealed and purged with oxygen-free nitrogen and the temperature raised to about 220°C. A pressure of 250 lbf/in² (1.7 MPa) is developed. After 1–2 hours the temperature is raised to 270–280°C and steam bled off to maintain the pressure at 250 lbf/in² (1.7 MPa). The pressure is then reduced to atmospheric for one hour, after which the polymer is extruded by oxygen-free nitrogen on to a water-cooled casting wheel, to form a ribbon which is subsequently disintegrated. Nylon 610 is prepared from the appropriate salt (melting point 170°C) by a similar technique. Nylon 612 uses decane-1, 10-dicarboxylic acid. Azelaic acid is used for nylon 69. Nylon 46, introduced in the late 1970s as Stanyl by DSM, is prepared by reacting 1,4-diaminobutane with adipic acid.

18.3.2 Nylon 6

Both batch and continuous processes have been used for the manufacture of nylon 6. In a typical batch process the caprolactam, water (which acts as a catalyst) and a molecular weight regulator, e.g. acetic acid, are charged into the vessel and reacted under a nitrogen blanket at 250°C for about 12 hours. The product consists of about 90% high polymer and 10% low molecular weight material such as the monomer. In order to achieve the best physical properties the low molecular weight materials may be removed by leaching and/or vacuum distillation. In the continuous process the reactants are maintained in reservoirs which continuously feed reaction columns kept at a temperature of about 250°C.

The polymerisation casting of nylon 6 *in situ* in the mould has been developed in recent years. Anionic polymerisation is normally employed; a typical system³ uses as a catalyst 0.1–1 mol.% of acetic caprolactam and 0.15–0.50 mol.% of the

sodium salt of caprolactam. The reaction temperature initially is normally between 140 and 180°C but during polymerisation this rises by about 50°C. Mouldings up to one ton in weight are claimed to have been produced by these casting techniques.

Reaction injection moulding techniques, developed primarily for polyurethanes (see Chapter 27), have also been adapted for nylon 6 in what must be considered as a variation of the polymerisation casting technique.

18.3.3 Nylon 11

This polymer may be prepared by stirring the molten ω -aminoundecanoic acid at about 220°C. The reaction may be followed by measurements of the electrical conductivity of the melt and the intrinsic viscosity of solutions in *m*-cresol.⁴ During condensation 0.4–0.6% of a 12-membered ring lactam may be formed by intramolecular condensation but this is not normally removed since its presence has little effect on the properties of the polymer.

18.3.4 Nylon 12

The opening of the caprolactam ring for nylon 6 involves an equilibrium reaction which is easily catalysed by water. In the case of nylon 12 from dodecanolactam, higher temperatures, i.e. above 260°C, are necessary for opening the ring structures but since in this case the condensation is not an equilibrium reaction the process will yield almost 100% of high polymer.⁵

18.3.5 Nylon 7

The ω -aminoenanthic acid is polymerised in an aqueous solution under nitrogen at 14–15 atm pressure at 250–260°C. The process takes several hours.²

18.4 STRUCTURE AND PROPERTIES OF ALIPHATIC POLYAMIDES

Aliphatic polyamides such as nylons 46, 66, 6, 610 and 11 are linear polymers and thus thermoplastic. They contain polar —CONH— groups spaced out at regular intervals so that the polymers crystallise with a high intermolecular attraction. These polymer chains also have aliphatic chain segments which give a measure of flexibility in the amorphous region. Thus the combination of high interchain attraction in the crystalline zones and flexibility in the amorphous zones leads to polymers which are tough above their apparent glass transition temperatures.

The high intermolecular attraction leads to polymers of high melting point. However, above the melting point the melt viscosity is low because of the polymer flexibility at such high temperatures, which are usually more than 200°C above the T_g , and the relatively low molecular weight.

Because of the high cohesive energy density and their crystalline state the polymers are soluble only in a few liquids of similar high solubility parameter and which are capable of specific interaction with the polymers.

The electrical insulation properties are quite good at room temperature in dry conditions and at low frequencies. Because of the polar structure they are not good insulators for high-frequency work and since they absorb water they are

also generally unsuitable under humid conditions (see Section 18.8 for exceptions).

There are a number of structural variables which can considerably affect the properties of the aliphatic polyamides:

- (1) The distance between the repeating —CONH— group. It is the presence of the —CONH— groups which causes the aliphatic polyamides to differ from polyethylene, and the higher their concentration the greater the difference. As a rule, the higher the amide group concentration, i.e. the shorter the distance between —CONH— groups, the higher the: (a) density; (b) forces required to mechanically separate the polymer molecules and hence the higher the tensile strength, rigidity, hardness and resistance to creep; (c) the T_m and heat deflection temperature; (d) resistance to hydrocarbons; (e) water absorption. Nylon 11 has twice the distance between amide groups of that in nylon 6, and consequently is intermediate in properties between nylon 6 and polyethylene.
- (2) The number of methylene groups in the intermediates. It has been observed that polymers from intermediates with an even number of methylene groups have higher melting points than similar polymers with an odd number of methylene groups. This is seen clearly in *Figure 18.10*⁶, where it is seen that

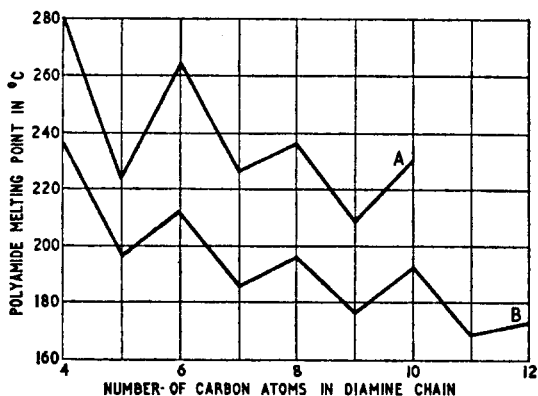


Figure 18.10. Melting points of polyamides from aliphatic diamines: A, with adipic acid, B, with sebacic acid. (After Coffmann et al⁶)

nylon 66 has a higher melting point than either nylon 56 or nylon 76. With polymers from amino acids or lactams the same rule applies, nylon 7 having a higher melting point (~227°C) than either nylon 6 (~215°C) or nylon 8 (~180°C) (see also *Figure 4.11*). These differences are due to the differences in the crystal structure of polymers with odd and even methylene groups which develop in order that oxygen atoms in one molecule are adjacent to amino groups of a second molecule. Hydrogen bonds with an NH—O distance of 2.8 Å are produced and are the reason for the high strength and the high melting points of polyamides such as nylon 6, 66 and 7. The crystal structures of the polyamides differ according to the type of polymer and in some cases, such as with nylon 66, two crystal forms co-exist in the same mass of polymer. These structures have been discussed in detail elsewhere.⁷⁻¹⁰

- (3) The molecular weight. Specific types of nylon, e.g. 66, are frequently available in forms differing in molecular weight. The main difference between such grades is in melt viscosity, the more viscous grades being more suitable for processing by extrusion techniques.
- (4) *N*-Substitution. Replacement of the hydrogen atom in the —CONH— group by such groups as $\sim\text{CH}_3$ and $\sim\text{CH}_2\text{OCH}_3$ will cause a reduction in the interchain attraction and a consequent decrease in softening point. Rubbery products may be obtained from methoxymethyl nylons. These materials are considered in more detail in Section 18.9.
- (5) Copolymerisation. Except in those rare cases where monomer segments are isomorphous (see *Figure 4.11*), copolymerisation, as usual, leads to less crystalline and frequently amorphous materials. As might be expected, these materials are tough, leather-like, flexible and, when unfilled, reasonably transparent.

The properties of the nylons are considerably affected by the amount of crystallisation. Whereas in some polymers, e.g. the polyacetals and PCTFE, processing conditions have only a minor influence on crystallinity, in the case of the nylons the crystallinity of a given polymer may vary by as much as 40%. Thus a moulding of nylon 6, slowly cooled and subsequently annealed, may be 50–60% crystalline, while rapidly cooled thin-wall mouldings may be only 10% crystalline.

As with other crystalline polymers, properties are dependent not only on total percentage crystallinity but also on the size of morphological structures such as spherulites. According to the method of processing, different morphological structures will be produced.¹¹ Slowly cooled melts may form spherulites, rapidly cooled polymers may form only fine aggregates. It follows that in an injection moulding the morphological form of rapidly cooled surface layers may be quite different from that of the slower cooled centres. Smaller spherulites can be obtained by the use of nucleating agents as was described in Chapter 3 and this can give a more uniform structure in an injection moulding. Several years ago it was found that seeding the polymer with about 0.1% of a fine silica gave a polymer of greater tensile strength, hardness and abrasion resistance but with some reduction in impact strength and elongation at break. Subsequent developments using phosphorus compounds as nucleating agents were found to give profoundly shortened moulding cycles, in a typical instance down from 30 to 4 seconds. It was also found that overnucleation tended to give a crystalline surface layer with some undesirable properties and the current aim is to produce a polymer which on moulding is of a two-phase structure, the bulk consisting of a union crystal structure with a very thin near-amorphous surface layer.

The suppliers of nylon 46 have laid particular emphasis on the fact that this polymer, with its highly symmetrical chain structure, leads to both a high level of crystallinity and a high rate of nucleation. In turn the high nucleation rate leads to a fine crystalline structure which in this case is claimed to lead to a higher impact strength (dry as moulded) than with nylons 6 and 66.

As is commonly the case with crystalline polymers the glass transition temperature is of only secondary significance with the aliphatic polyamide homopolymers. There is even considerable uncertainty as to the numerical values. Rigorously dried polymers appear to have T_g s of about 50°C, these figures dropping towards 0°C as water is absorbed. At room temperature nylon 66 containing the usual amounts of absorbed water appears to be slightly above the T_g

and crystallisation may occur only very slowly. This can lead to after-shrinkage effects which may occur for periods up to two years. With nylon 6 the effect is less marked. The after-shrinkage process may be accelerated by annealing the samples at an elevated temperature, typically that which corresponds to the maximum crystallisation rate for that polymer (see also Section 18.7).

The greater the degree of crystallinity the less the water absorption and hence the less will be the effect of humidity on the properties of the polymer. The degree of crystallinity also has an effect on electrical and mechanical properties. In particular high crystallinity leads to high abrasion resistance.

18.5 GENERAL PROPERTIES OF THE NYLONS

Typical mechanical properties of some commercial grades of nylon are given in *Table 18.1*.

The figures given in the table are obtained on mouldings relatively free from orientation and tested under closely controlled conditions of temperature, testing rate, and humidity. Changes in these conditions or the use of additives may profoundly affect these properties. Details of the influence of these factors on mechanical properties have been published in the trade literature but *Figures 18.11–18.14* have been included to illustrate some salient features.

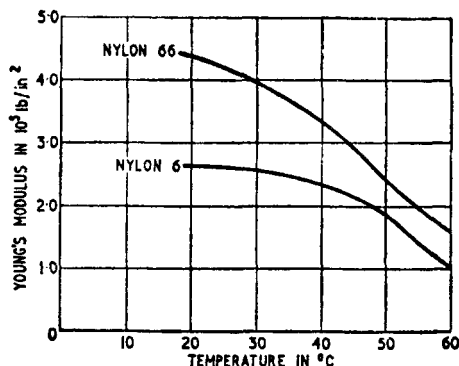


Figure 18.11. Effect of temperature on the Young's modulus of nylon 66 and nylon 6

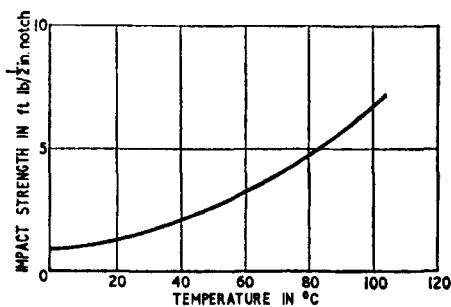


Figure 18.12. Effect of temperature on the impact strength of nylon 66. (Reproduced by permission of ICI)

Table 18.1 Mechanical properties of typical polyamides

<i>Property</i>	<i>Unit</i>	<i>ASTM test</i>	<i>46 (dry)</i>	<i>66</i>	<i>6</i>	<i>610</i>	<i>612</i>	<i>11</i>	<i>12</i>	<i>66/610 (35:65)</i>	<i>66/610/6 40:30:30</i>
Tensile stress at yield	lbf/in ² (MPa)	D.638	14 700 (100)	11 500 (80)	11000 (76)	8500 (55)	8800 (60)	5500 (38)	6600 (45)	5500 (38)	— —
At break	lbf/in ² (MPa)	D.638	11 500 (80)	— —	— —	— —	8800 (60)	7600 (52)	7800 (54)	— —	7500 (51)
Elongation at break	%	D.638	30	80–100	100–200	100–150	100–250	30–300	200	>200	300
Tension modulus	lbf/in ² (MPa)	— —	4.3×10^5 (3000)	4.3×10^5 (3000)	4×10^5 (2800)	3×10^5 (2100)	— —	2×10^5 (1400)	2×10^5 (1400)	2×10^5 (1400)	2×10^5 (1400)
Impact strength (dry) (IZOD) 73°F	ft lbf in ⁻¹	(BS 2712) D.256	— —	1.3 —	1.0 —	1.1 —	— 0.65–0.85	— —	— —	— —	— —
Rockwell hardness		D.785	R 123	R 118	R 112	R 111	R 114	R 108	R 107	—	R 83
Specific gravity		D.792	1.18	1.14	1.13	1.09	1.07	1.04	1.02	1.08	1.09

Figure 18.11 shows the influence of temperature on the tension modulus of nylons 66 and 6 and Figure 18.12 the effect of temperature on impact strength of nylon 66. Figure 18.13 shows the profound plasticising influence of moisture on the modulus of nylons 6 and 66, while Figure 18.14 illustrates the influence of moisture content on impact strength.

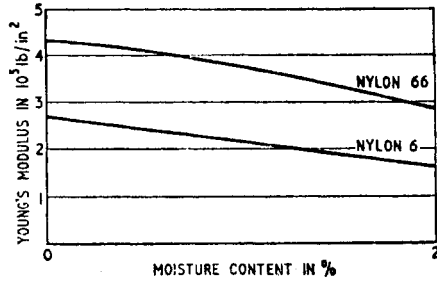


Figure 18.13. Effect of moisture content on the Young's modulus of nylon 66 and nylon 6

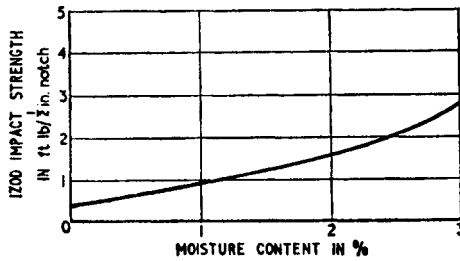


Figure 18.14. Effect of moisture content on the impact strength of nylon 66. (After Riley¹²)

Laboratory tests and experience during use have demonstrated that the nylons have extremely good abrasion resistance. This may be further improved by addition of external lubricants and by processing under conditions which develop a highly crystalline hard surface e.g. by use of hot injection moulds and by annealing in a non-oxidising fluid at an elevated temperature (150–200°C for nylon 66).

The coefficients of friction of the nylons are somewhat higher than the acetal resins (Chapter 19). Results obtainable will depend on the method of measurement but typical properties are given in Table 18.2.¹²

Table 18.2 Kinetic coefficient of friction of nylon 66¹²

Moving surface	Stationary surface		
	Nylon (moulded)	Nylon (machined surface)	Mild steel
Nylon (moulded)	0.63	0.52	0.31
Nylon (machined surface)	0.45	0.46	0.33
Mild steel	0.41	0.41	0.6–1.0

The effect of lubricants on the kinetic coefficient of friction of nylon 66 (like surfaces) is shown in *Table 18.3*.¹²

For bearing applications the upper working limits are determined by frictional heat built-up, this being related to the coefficient of friction under working conditions. A measure of the upper working limits of a material for this application is the maximum *PV* value (the product of load in lbf/in² on the projected bearing area and the peripheral speed in ft/min) which can be tolerated. Maximum *PV* values of 500–1000 are suggested for continuous operation of unlubricated nylon 66 bearings whilst initially oiled nylon bearings can be used intermittently at *PV* values of 8000. Higher maximum *PV* values can be employed with continuously lubricated bearings (see also Chapter 19 for data on polyacetals).

Table 18.3 Effect of lubricants on the kinetic coefficient of friction of nylon 66 (like surfaces)¹²

<i>Lubricant</i>	<i>Coefficient of friction</i>
None	0.46
Water	0.24
Liquid paraffin	0.13
Graphite	0.28

The glass transition temperatures of the nylons appear to be below room temperature so that the materials have a measure of flexibility in spite of their high crystallinity under general conditions of service. The polymers have fairly sharply defined melting points and above this temperature the homopolymers have low melt viscosities. Some thermal properties of the nylons are given in *Table 18.4*.

Table 18.4 Thermal properties of unfilled nylons

<i>Property</i>	<i>Units</i>	46 (dry)	66	6	610	612	11	12	66/610/6 (40:30:30)
Melting point	°C	295	264	215	215	210	185	175	160
Deflection temp. (heat distortion temp.) (264 lbf/in ²) (66 lb/in ²)	°C	150–170	75	60	55	65	55	51	30
Coefficient of linear expansion	10 ⁻⁵ cm/cm °C	9.2	10	9.5	15	9	15	12	—

The high figure for the deflection temperature of nylon 46 is in part due to the high *T_m* consequent upon the small and even number of methylene groups between the —CONH— groups but also to the high levels of crystallinity, which have a high stiffening effect. The lower figure of 150°C quoted is where a mould temperature of 80°C has been used. If a mould temperature of 120°C is used,

facilitating faster nucleation and crystallisation, the deflection temperature is raised to 170°C. All figures quoted are for unfilled nylons. Incorporation of glass fibre as a filler will considerably narrow the gap between the values for deflection temperature obtained at the two loadings.

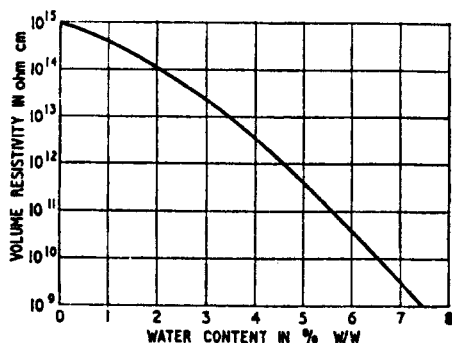


Figure 18.15. Effect of moisture content on the volume resistivity of nylon 66

The nylons are reasonably good electrical insulators at low temperatures and under conditions of low humidity but the insulation properties deteriorate as humidity and temperature increase. The effects of the amount of absorbed water on the volume resistivity of nylon 66 is shown in *Figure 18.15*. This effect is even greater with nylon 6 but markedly less with nylon 11. Some typical electrical properties of the nylons are given in *Table 18.5*.

Table 18.5 Electrical properties of the nylons*

Property	Units	Nylon 66	Nylon 6	Nylon 11	Nylon 610	Nylon 66/610/6 (40:30:30)	Nylon 66/610 (35:65)
Volume resistivity	Ω m (dry)	$>10^{17}$	$>10^{17}$	—	$>10^{17}$	—	—
	Ω m 50% RH	10^{15}	—	—	10^{16}	10^{15}	10^{15}
	Ω m 65% RH	10^{14}	—	10^{13} – 10^{14}	—	—	—
Dielectric constant	10^3 Hz dry	3.6–6.0	3.6–6.0	—	3.7	—	—
	10^3 Hz 65% RH	—	—	3.7	—	—	—
	10^6 Hz 50% RH	3.4	—	—	—	—	—
Power factor	10^3 Hz dry	0.04	0.02–0.06	—	0.02	—	—
	10^6 Hz 65% RH	—	—	0.06	—	—	—
Dielectric strength	kV/cm 50% RH 25°C	>100	>100	—	>100	—	—

* The data on nylon 11 are from trade literature on Rilsan, those on the other polymers from information supplied by ICI

Nylons 46, 6, 66, 610, 11 and 12 are polar crystalline materials with exceptionally good resistance to hydrocarbons. Esters, alkyl halides, and glycols have little effect. Alcohols generally have some swelling action and may in fact dissolve some copolymers (e.g. nylon 66/610/6). There are few solvents for the nylons, of which the most common are formic acid, glacial acetic acid, phenols and cresols.

Mineral acids attack the nylons but the rate of attack depends on the type of nylon and the nature and concentration of the acid. Nitric acid is generally active at all concentrations. The nylons have very good resistance to alkalis at room temperature. Resistance to all chemicals is more limited at elevated temperatures.

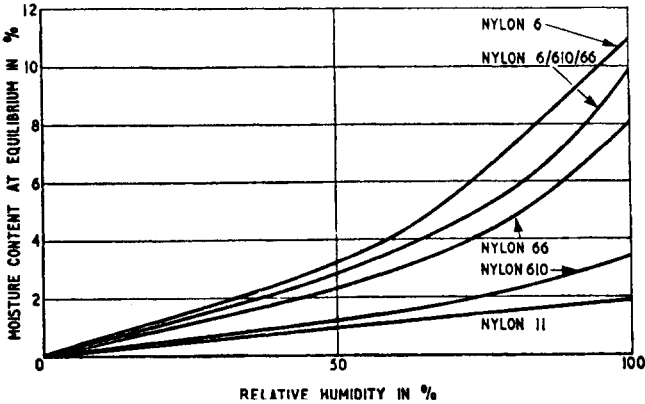


Figure 18.16. Effect of relative humidity on the water absorption of the nylons

The nylons are hygroscopic. Figure 18.16 shows how the equilibrium water absorption of different nylons varies with humidity at room temperature. Figure 18.17 shows how the rate of moisture absorption is affected by the environmental conditions.

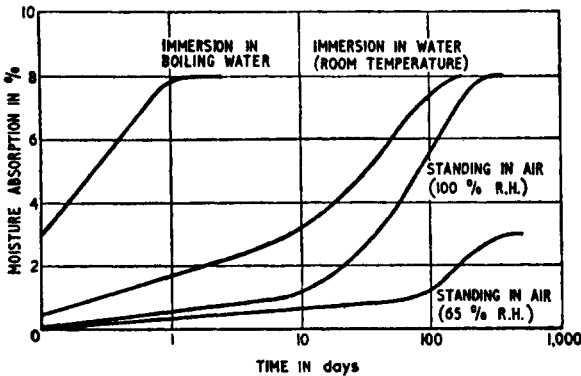


Figure 18.17. Effect of environmental conditions on rate of moisture absorption of nylon 66 ($\frac{1}{8}$ in thick specimens)

The absorbed water has a plasticising effect and thus will cause a reduction in tensile strength and modulus, and an increase in impact strength. As has already been mentioned the presence of absorbed water also results in a deterioration of electrical properties.

As may be expected from its structure, nylon 46 has a higher level of water absorption (about 14% in water at 23°C) than any of the other commercial nylons

discussed so far in this chapter. For this reason there can be large differences in properties of dry, as moulded, samples, compared to samples conditioned to more common atmospheric conditions. Some of these differences are emphasised in *Table 18.6*.

Table 18.6 Effect of conditioning on selected mechanical properties of nylon 46 (Conditioning according to ISO 1110 accelerated method; 70°C/62% RH. All measurements at 23°C)

<i>Property</i>	<i>ISO Test No.</i>	<i>Dry</i>	<i>Conditioned</i>
Impact strength (Izod Notched kJ/m ²)	R180	10	40
Tensile yield strength (MPa)	R527	100	40
Tensile strength (break) (MPa)	R527	80	65
Elongation at break (%)	R527	30	280
Tensile modulus (MPa)	R527	3000	1000
Flexural modulus (MPa)	178	3200	1000
Rockwell hardness	(ASTM D 785)	R123	R107

When in service indoors or otherwise protected from sunlight the nylons show no appreciable change of properties on aging at room temperature. Care should be taken in the use of the polymers when exposed to direct sunlight, particularly in film and filament applications, where embrittlement is liable to occur. Some improvement may be achieved if stabilised compounds are used (see Section 18.1). Continuous exposure to air at temperatures above 60°C will also cause surface discolouration and a lower impact strength of mouldings. The useful life of a moulding in service at 100°C will be of the order of only four to six weeks. If the moulding is immersed in oil, or otherwise shielded from oxygen, a considerably longer life-time may be expected. Heat-stabilised grades have markedly improved resistance.

18.6 ADDITIVES

The major nylon moulding materials are each available in a number of grades. These may differ in molecular weight but they may also differ in the nature of additives which may be present.

Additives used in nylon can be grouped as follows:

- (1) Heat stabilisers.
- (2) Light stabilisers.
- (3) Plasticisers.
- (4) Lubricants.
- (5) Reinforcing fillers.
- (6) Pigments.
- (7) Fungicides.
- (8) Nucleating agents.
- (9) Flame retarders.
- (10) Impact modifiers.

With the possible exception of pigments, which may be dry-blended by the processor, additives are incorporated by the manufacturers and only a limited amount of information about them is normally made available.

Amongst heat stabilisers are copper salts, phosphoric acid esters,¹³ phenyl- β -naphthylamine, mercaptobenzothiazole and mercaptobenzimidazole. Of these, copper salts in conjunction with halides have been found particularly effective, and some automotive specifications require the use of copper for heat stabilisation. Light stabilisers include carbon black and various phenolic materials.

Plasticisers are comparatively uncommon but plasticised grades are supplied by some manufacturers. Plasticisers lower the melting point and improve toughness and flexibility, particularly at low temperatures. An example of a plasticiser used commercially in Santicizer 8, a blend of *o*- and *p*-toluene ethyl sulphonamide (Figure 18.18).

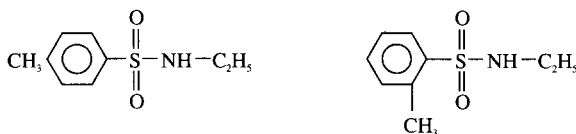


Figure 18.18

Self-lubricating grades are of particular value in some gear and bearing applications. One commercial nylon compound incorporates 0.20% molybdenum disulphide and 1% of graphite whilst many other commercial compounds contain only one of these two lubricants.

Lubricants may also be used to enhance flow and mould release. Materials used are usually of low molecular weight, contain a hydrocarbon component and an amide component, and are typified by ethylene bis(stearamide).

In addition to the nucleating agents discussed in Section 18.4, many other materials have been found to be effective. Whilst the nylons may be self-nucleating, particularly if there is some unmelted crystal structure, seeding with higher melting point polymers can be effective. Thus nylon 66 and poly(ethylene terephthalate) are reported to be especially attractive for nylon 6.

As with many other plastics materials there have been substantial efforts to improve the resistance of nylons to burning. Halogen compounds synergised by zinc oxide or zinc borate have been used whilst compounds containing red phosphorus exhibit very good electrical insulation properties as well as improved flame resistance. They are, however, dark in colour. Furthermore grades of nylons for electrical and electronic applications need to be phosphorus and halogen-free to conform to UL94-V0 requirements, and melamine cyanurate is used as a flame retardant in this instance with unreinforced grades. With glass-filled grades (see below) magnesium hydroxide may be used for this purpose but it is required in substantial quantities and is less effective than typical halogen and phosphorus-containing additives.

Glass-reinforced nylon compounds have become available in recent years and are dealt with in the next section.

There has also been some interest in polymers containing particulate mineral fillers.

Whilst the aliphatic nylons are generally classified as being impact resistant, they are affected by stress concentrators like sharp corners which may lead to brittle failures. Incorporation of rubbers which are not soluble in the nylons and hence form dispersions of rubber droplets in the polyamide matrix but which nevertheless can have some interaction between rubber and polyamide can be most effective. Materials described in the literature include the ethylene-propylene rubbers, ionomers (q.v.), polyurethanes, acrylates and methacrylates, ABS polymers and polyamides from dimer acid.

18.7 GLASS-FILLED NYLONS

There are a number of properties in which the thermoplastics show up to a disadvantage when compared with metals. These include:

- (1) Low rigidity and tensile strength.
- (2) Dimensional instability due to a high temperature coefficient of expansion and a high water absorption.
- (3) Low impact strength to fracture.
- (4) Low maximum service temperature.
- (5) Low creep resistance.
- (6) Low hardness and scratch resistance.

In an attempt to minimise these disadvantages glass-filled varieties of a number of thermoplastics have been successfully introduced. Of these the glass-filled nylons form the most important group and these in turn can be subgrouped into glass-fibre-filled grades and glass-bead-filled varieties.

The glass-fibre-filled types can be obtained in two ways.

One route (the 'long-glass' process) involves passing continuous lengths of glass fibre (as rovings) through a polymer melt or solution to produce a glass-reinforced strand that is chopped into pellets about 0.3 cm ($\frac{1}{8}$ in) dia 0.6–1.2 cm ($\frac{1}{4}$ – $\frac{1}{2}$ in) in length. In this case the fibres will be parallel to the 'long' axis of the pellet. The alternative route involves blending a mixture of resin and glass fibres about 0.6 cm ($\frac{1}{4}$ in) length in an extruder. From 20% to 40% glass is used, usually of the electrical grade (E-grade) and with diameter of about 0.001 cm. Before blending with the nylon the glass fibres are often treated with a lubricant to improve mechanical handling of the roving, a coupling agent such as a silane to improve the resin-glass bond and some poly(vinyl acetate) resin to hold the filaments together as a strand.

Such reinforcement leads to a substantial increase in tensile strength, modulus, hardness, creep resistance, ASTM deflection temperature under load and a sharply reduced coefficient of expansion. Typical figures are shown in *Table 18.7*.

The glass-fibre nylons have a resistance to creep at least three times as great as unfilled polymers. In the case of impact strength the situation is complex since unfilled nylons tend to break showing tough fracture whereas the filled polymers break with a brittle fracture. On the other hand the glass-filled polymers are less notch sensitive and in some tests and service conditions the glass-filled nylons may prove the more satisfactory.

As with other crystalline polymers, the incorporation of glass fibres narrows the gap between the heat deflection temperatures and the crystalline melting point.

Table 18.7 Comparison of glass-fibre-filled and unfilled nylon 66

Property	Units	ASTM test	Glass-filled	Unfilled
Specific gravity	–	D.792	1.38	1.14
Tensile strength	10^3 lbf/in ² (MPa)	D.638	23 159	11.5 79
Elongation at break	%	D.638	3–5	80–100
Flexural modulus	10^5 lbf/in ² (MPa)	D.790	11 8000	4.3 3000
24 h water absorption at saturation	%	D.570	5.6	8.9
Coefficient of linear expansion	in/in °F (cm/cm °C)	D.696	1.65×10^{-5} 2.8×10^{-5}	5.6×10^{-5} 9.9×10^{-5}
Deflection temperature under load				
66 psi	°C	D.648	254	200
264 psi	°C	D.648	245	75

Whilst most glass-fibre-reinforced polyamides have been of the short-glass type, there has been a recent resurgence of interest in the long-glass types. The Verton materials introduced by ICI are claimed to have better impact resistance and higher stiffness than short-glass compounds, together with better impact resistance retention at low temperatures and stiffness retention at higher temperatures. A comparison of some properties of long- and short-fibre materials is given in *Table 18.8*.

Table 18.8 Comparison of short- and long-fibre glass-reinforced nylon 66 (50% fibre loading)

Property	ISO test	Condition	Units	Nylons 66 + 50% short fibre	Nylon 66 + 50% long fibre
Tensile strength	R527	D	MPa	200	230
		C	MPa	155	165
Elongation	R527	D	%	3	4
		C	%	6	6
Flexural modulus	178	D	GPa	12	15.8
		C	GPa	9.6	11.2
Izod impact	180	D	kJ/m ²	11	27
		C	kJ/m ²	13	37
Deflection temp. (1.8 MPa)	75				
		D	°C	250	261
Melting point	1218	D	°C	263	263

D = Dry as moulded; C = conditioned according to ISO 1110, accelerated method: 70°C/62% RH)

Nylons filled with glass beads were also introduced in the late 1960s. Grades filled with 40% of glass spheres have compressive strength some eight-fold higher than those of unfilled nylons as well as showing good improvement in heat distortion temperature, tensile strength and modulus. Compared with glass-fibre, filled grades they are easy to process, with low melt viscosity, uniform and

predictable shrinkage and minimum warpage. They are also more isotropic in their mechanical properties.

Both fibres and sphere fillers tend to improve self-extinguishing characteristics.

18.7.1 Comparison of nylons 6 and 66 in glass-filled compositions

The presence of glass-fibre fillers can to some extent mask the differences between nylons 6 and 66. For example, an advantage of unfilled nylon 66 in injection moulding is that the high T_m leads to a high solidification temperature and shorter cycle times. However, in glass-filled grades the more rapid cooling and crystallisation can lead to a poorer surface finish than obtained with corresponding nylon 6 compounds. It is also considered that abrasive wear on screws is greater with nylon 6.

Water absorption decreases with increasing glass-fibre content at about the same rate with both nylons 66 and 6, and since nylon 6 has an intrinsically higher water absorption than nylon 66 the glass-filled grades also have higher levels at similar glass-fibre loadings.

Mechanical properties of freshly injected compositions are similar for the two nylons but, after conditioning, differences arise largely due to the plasticising effect of the moisture present. Thus for tensile and flexural yield stress, tensile strength and modulus of elasticity, nylon 66 gives slightly higher figures. Yield elongation and elongation at break are greater with nylon 6. Izod impact strengths are similar, with nylon 6 giving marginally higher values.

The above comments refer to comparisons between the two compositions at the same glass-fibre level. If, however, comparison is made between a nylon 66 composition with a glass content of $x\%$ and a nylon 6 compound with a glass content of $(x + 5)\%$, then the differences in mechanical properties become very small. At the same time the nylon 6 material will have slightly easier processing characteristics and surface quality.

Whilst nylon 66 has the higher T_m , the long-term heat resistance of typical copper-stabilised nylon 6 is somewhat superior in such properties as impact strength and bending strength compared to nylon 66. However, it is frequently the case that nylon 66 has better resistance to chemicals at elevated temperatures.

18.8 PROCESSING OF THE NYLONS

In the processing of nylons consideration should be given to the following points:

- (1) The tendency of the material to absorb water.
- (2) The high melting point of the homopolymers.
- (3) The low melt viscosity of the homopolymers.
- (4) The tendency of the material to oxidise at high temperatures where oxygen is present.
- (5) The crystallinity of the solid polymer and hence the extensive shrinkage during cooling.

The above features are particularly marked with nylons 46, 6, 66 and 610 and less marked with nylons 11 and 12. Providing they are dry the copolymers may be processed in much the same way as conventional thermoplastics.

In the injection moulding of nylon 66, for example, it is necessary that the granules be dry. The polymer is normally supplied in sealed containers but should be used within an hour of opening. If reworked polymer is being used, or granules have become otherwise damp, the polymer should be dried in an oven at about 70–90°C. Too high a temperature will oxidise the surface of the granules and result in inferior mouldings.

Injection moulding cylinders should be free from dead spots and a temperature gradient along the cylinder is desirable.

Because of the low melt viscosity of the polymer at processing temperatures it will 'drool' through normal injection nozzles even when the plunger is retracted. Several types of nozzle have been specially designed for use with nylon and all function by sealing the end of the nozzle, either by allowing a pip of polymer to harden, by the use of spring-loaded valve, by the use of sliding side-closure nozzles or by the use of hydraulic nozzle valve activated at the appropriate stages of the moulding cycle. Variations of this last approach have become popular since they are both positive in action and simple to operate. In designs in which solidified polymer is formed at the nozzle it is necessary to make provision for a cold-slug well in the mould, a feature frequently not possible with single-cavity tools. Where spring-loaded closing devices are used the spring should be kept as cool as possible if rapid thermal fatigue is to be avoided.

Because of the crystallisation that occurs on cooling from the melt the polymers show a higher moulding shrinkage than that generally observed with amorphous polymers. With average moulding conditions this is about 0.018 cm/cm with nylon 66 but by increasing the injection pressure and the injection time the shrinkage may be halved. This is because a high initial mould cavity pressure is developed and a large part of the crystallisation process will be complete before the cavity pressure has dropped to zero. The shrinkage will also be affected by the melt temperature, the mould temperature, the injection speed and the design of the mould as well as by the type of nylon used.

The nylons, nylon 66 in particular, may also exhibit a certain amount of after-shrinkage. Further dimensional changes may occur as a result of moulding stresses being relieved by the plasticising effect of absorbed water. It is consequently often useful to anneal mouldings in a non-oxidising oil for about 20 minutes at a temperature 20°C higher than the maximum service temperature. Where this is not known a temperature of 170°C is suitable for nylon 66, with somewhat lower temperatures for the other nylons.

When dimensional accuracy is required in a specific application the effect of water absorption should also be considered. Manufacturers commonly supply data on their products showing how the dimensions change with the ambient humidity.

The particular features of the nylons should also be taken into account in extrusion. Dry granules must be used unless a devolatilising extruder is employed. Because of the sharp melting point it is found appropriate to use a screw with a very short compression zone. Polymers of the lowest melt viscosity are to be avoided since they are difficult to handle. Provision should be made to initiate cooling immediately the extrudate leaves the die.

The polymerisation casting process mentioned in Section 18.3.2 has been adapted to reaction injection moulding (RIM), a process originally developed for polyurethanes. In this process the reacting ingredients are mixed together by impingement of jets of the materials in a small mixing chamber adjacent to the

mould cavity into which the reacting material is then injected. Because of the low injection pressures much lower locking forces are possible than in conventional injection moulding, making the process attractive for large area mouldings.

The first polyamides specifically developed for RIM were introduced by Monsanto in 1981 as Nyrim. They are block copolymers of a polyether (such as a poly(ethylene glycol), poly(propylene glycol) or polybutadiene containing hydroxyl groups) with caprolactam. The reaction components comprise the polyether, caprolactam, adipyl-bis-caprolactam as chain propagator and a caprolactam–magnesium bromide complex as catalyst. The latter has to be protected against moisture, carbon dioxide and oxygen, and thus requires special care in handling. Other polyamide–RIM systems have been developed by Upjohn and Allied Fibers and Plastics.

Unlike polyurethane–RIM processes, nylon–RIM reactions are endothermic and require temperatures of 130–140°C. In contrast to the polyurethane–RIM systems, this enables thick wall parts to be made. Cycle times of 2–3 minutes are comparable to those for polyurethane–RIM. In the development stage, current work is concerned with reducing moulding times and optimising moulding conditions.

18.9 APPLICATIONS

Consumption of polyamide plastics in the late 1990s has been estimated at about 1 300 000 t.p.a. Western Europe and the United States each have about 42% of this market and Japan about 16%. This is probably about 20% of the total production of polyamide materials and virtually all of the rest of polyamide production goes into fibres where the market is shared very roughly equally between nylons 6 and 66. The large-scale production of these materials enables them to be available at a substantially lower price than the other nylons, which do not have the benefit of the economies of scale. Hence the other nylons are usually restricted to applications where nylons 6 and 66 are unsuitable. It has been estimated that in the 1990s in Western Europe, plastics usage was split as follows: nylon 6 48%: nylon 66 40% nylons 11 and 12 10%: the rest 2%. For historical reasons, usage of the various types varies from country to country. For example, in the United States and the United Kingdom, nylon 66 was the first to be developed and remains well entrenched, whilst for similar reasons nylon 6 is more dominant in Germany. The substantial market penetration of nylons 11 and 12 in France also reflects long-standing French commercial activity with these types. It remains to be seen what effect the recent introduction of nylon 46 will have on the balance of usage.

It has been reported that out of a total 1997 Western European consumption of 532 000 tonnes, 387 000 tonnes, i.e. almost 75% of the total, was injection moulded. Film use accounted for 70 000 tonnes, monofilaments 19 000 tonnes, extruded sheet, rod and tube 24 000 tonnes, wire and cable 10 000 tonnes and other processes such as powder coatings, hot melts, blow moulding and monomer casting about 22 000 tonnes. Insofar as data can be compared, patterns in the USA are similar. Over two-thirds of injection moulding usage is in transport and electrical/electronic applications. The polyamides still have the biggest tonnage of the so-called engineering plastics although this could well be overtaken by the polycarbonates in the near future (see Chapter 20). The two classes of materials do, however, have quite dissimilar properties and are seldom directly competitive.

The nylons have found steadily increasing application as plastics materials for speciality purposes where their toughness, rigidity, abrasion resistance, good hydrocarbon resistance and reasonable heat resistance are important. Because of their high cost they have not become general purpose materials such as polyethylene and polystyrene, which are about a third of the price of the nylons.

The largest applications of the homopolymers (nylon 6, 66, 610, 11 and 12) have been in mechanical engineering. Well-known applications include gears, cams, bearings, bushes and valve seats. In addition to the advantageous properties cited above, nylon moving parts may be frequently operated without lubrication, are silent running and may often be moulded in one piece when previously a metal part required assembling of several parts, or alternatively, extensive machining with consequent waste of material.

It may be noted that in this area the newly introduced nylon 46 has become of interest in auto automatic gears, gearboxes, engine differentials and the clutch area because of its exceptional ability (for a polyamide) to withstand severe mechanical and thermal loading.¹⁴

In recent years the nylons have met increased competition from acetal resins (Chapter 19), the latter being superior in fatigue endurance, creep resistance and water resistance. Under average conditions of humidity the nylons are superior in impact toughness and abrasion resistance. When a nylon is considered appropriate it is necessary to consider the relative importance of mechanical properties, water resistance and ease of processing. For the best mechanical properties nylon 66 would be considered but this material is probably the most difficult to process and has a high water absorption value. Nylon 6 is easier to process but has slightly inferior mechanical properties and an even higher water absorption. Nylons 11 and 12 have the lowest water absorption, and are easy to process, but there is some loss in mechanical properties.

Sterilisable mouldings have found application in medicine and pharmacy. Because of their durability, nylon hair combs have found wide acceptance in spite of their higher cost.

Nylon film has been used increasingly for packaging applications for foodstuffs and pharmaceutical products. The value of nylon in this application is due to low odour transmission and to some extent in the ability to boil-in-the-bag. Film of high brilliance and clarity, particularly from nylon 11, is available for point-of-sale displays.

Although the nylons are not generally considered as outstanding electrical insulators, their toughness and, to some extent, their temperature resistance, have led to applications in coil formers and terminal blocks. Indeed, the new nylon 46 materials would appear to be of particular interest here. Acetal resins, polysulphones, modified PPO and polycarbonates, however, present a challenge to applications in this sphere.

Nylon monofilaments have found application in brush tufting, wigs, surgical sutures, sports equipment, braiding and outdoor upholstery. Nylons 610 and 11 have found extensive application in these fields because of their flexibility but nylon 66 is also used for brush tufting less than 0.0035 in. in diameter. Nylon 66/610 copolymer is used in the manufacture of a monofilament for angling purposes.

Extruded applications of nylon, other than film and monofilament, are less commonly encountered because of the low melt viscosity of the polymers. Uses include cable sheathing which requires resistance to abrasion and/or chemical attack, flexible tubing for conveying petrol and other liquids, piping for chemical

plant, rods for subsequent machining, as the tension member of composite belts for high-duty mechanical drive and for bottles requiring resistance to hydrocarbons. Nylons 11 and 12 are frequently preferred because of their ease of processing but the high molecular weight 6, 66 and 610 polymers find occasional use.

The 66/610 and 66/610/6 polymers have also been used in the past where tough leather-like extrudates have been required. Their cost, and perhaps also their obscurity, have resulted in their current use being minimal.

Nylon 11 is also used in powder form in spraying and fluidised bed dipping to produce chemical-resistant coatings. Although more expensive than the polyolefin and PVC powders, it is of interest because of its hardness, abrasion resistance and petrol resistance.

As previously mentioned, mouldings have been produced by the polymerisation casting of caprolactam. The ability to produce large objects in this way enables one to envisage new horizons for the use of plastics engineering and other applications. Such polymerisation-cast polymers also possess certain advantageous properties. The polymers tend to have a somewhat higher molecular weight and also a 45–50% crystallinity, again higher than for melt processed materials. This leads to a higher tensile strength, hardness, modulus and resistance to creep. The comparatively stress-free mouldings also have a reasonably consistent morphological structure. A disadvantage is the shrinkage of 4–4.5% which occurs during polymerisation.

Amongst the products made by polymerisation casting are propellers for small marine craft, conveyor buckets used in the mining industry, liners for coal washing equipment and main drive gears for use in the textile and papermaking industries.

There is persisting interest in nylon–RIM materials as alternatives to polyurethane–RIM. Advantages of the nylon materials are the better shelf life and lower viscosity of the reaction components, ability to mould thick-walled articles, absence of a need for mould lubrication and the ability to avoid using isocyanates with their associated hazards. The main disadvantages of nylon–RIM are the need to have heated storage tanks and elevated temperature reactions, difficulties in catalyst handling and the high water absorption of the product. Possible markets include exterior car body components and appliance and business machine components.

The glass-reinforced nylon plastics are now of substantial importance and take about 30–40% of the UK market. The rigidity, creep resistance, low coefficient of friction and high heat deflection temperature have enabled these materials to replace metals in many applications. Furthermore their good low-frequency electrical insulation properties and non-magnetic characteristics may also be utilised. For these reasons glass-fibre-filled grades are widely used in housings and casings, in domestic appliances, and in car components, including radiator parts. They are also extensively used in the telecommunications field for relay coil formers and tag blocks. Glass-bead-filled nylons have been used in bobbins.

Carbon-fibre-reinforced nylon 6 and nylon 6/12 mixtures have been offered commercially and found use in aerospace and tennis racket applications.

More recently interest has been shown in the appearance of exceptionally tough nylon plastics.

Initial materials of this super-tough type were blends of nylon 66 with an ionomer resin (see Chapter 11). More recent materials are understood to be blends of nylon 66 with a modified ethylene–propylene–diene terpolymer rubber (EPDM rubber—also see Chapter 11). One such modification involves treatment of the rubber with maleic anhydride, this reacting by a Diels–Alder or other

reaction with the double bond in the rubber due to the diene component. A two-phase structure is formed in which the rubber exists not simply as particles embedded in the polyamide matrix but in the form of a reticular structure.

Glass-fibre-filled grades of these toughened polymers are also available but these do not show the same improvement in toughness over normal glass-fibre-filled nylons.

Since large tonnage production is desirable in order to minimise the cost of a polyamide and since the consumption of nylons as plastics materials remains rather small, it is important that any new materials introduced should also have a large outlet as a fibre. There are a number of polyamides in addition to those already mentioned that could well be very useful plastics materials but which would be uneconomical for all but a few applications if they were dependent on a limited outlet in the sphere of plastics. Both nylon 7 and nylon 9 are such examples but their availability as plastics is likely to occur only if they become established fibre-forming polymers. This in turn will depend on the economics of the telomerisation process and the ability to find outlets for the telomers produced other than those required for making the polyamides.

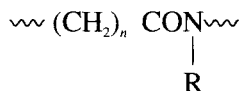
18.10 POLYAMIDES OF ENHANCED SOLUBILITY

Polyamides such as nylon 6, nylon 66, nylon 610, nylon 11 and nylon 12 exhibit properties which are largely due to their high molecular order and the high degree of interchain attraction which is a result of their ability to undergo hydrogen bonding.

It is, however, possible to produce polymers of radically different properties by the following modifications of the molecular structure.

- (1) Replacement of some or all of the —CONH— hydrogens by alkyl or alkoxy-alkyl groups to reduce hydrogen bonding which results in softer, lower melting point and even rubber polymers (*N*-substitution).
- (2) Use of acids or amines containing large bulky side groups which prevent close packing of the molecules.
- (3) Use of trifunctional acids or amines to give branched structures.
- (4) Copolymerisation to give irregular structures.
- (5) Reduction in molecular weight.

The techniques of *N*-alkylation may be effected by the use of *N*-alkylated or *N,N'*-dialkylated diamines, or by the use of an ω -*N*-alkylaminocarboxylic acid of type R_1NHR_2COOH . The polymers thus have repeating units of the general form.



Such *N*-alkyl compounds are not known to be of any current application although fibres from a partially *N*-alkylated derivative of nylon 610 have been described.

Treatment of a nylon with formaldehyde leads to the formation of *N*-methylol groups but the polymers are unstable. If, however, the nylon is dissolved in the solvent such as 90% formic acid and then treated with formaldehyde and an alcohol in the presence of an acidic catalyst such as phosphoric acid a process of alkoxy-methylation occurs (Figure 18.19).

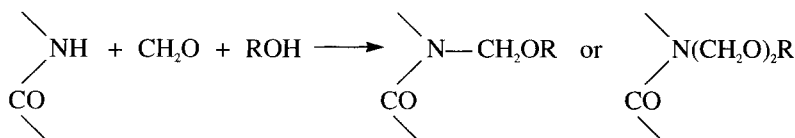


Figure 18.19

Methylmethoxy nylons are commercially available in which about 33% of the —NH— groups have been substituted.

Such materials are soluble in the lower aliphatic alcohols, e.g. ethanol, and in phenols. They also absorb up to 21% of moisture when immersed in water. If this material is heated with 2% citric acid at elevated temperatures, typically for 20 minutes at 120°C, cross-linking will take place (*Figure 18.20*).

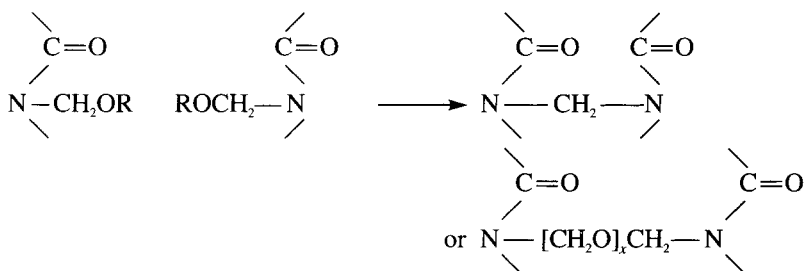


Figure 18.20

This material finds a limited application in films and coatings which require good abrasion and flexing resistance. Some typical properties of cross-linked and uncross-linked polymers are given in *Table 18.9*.

In the early 1950s a new class of polyamides became available differing from the nylons in that they contained bulky side groups, had a somewhat irregular structure and were of low molecular weight (2000–5000). They are marketed under such trade names as ‘Versamids’ and ‘Beckamids’.

Table 18.9 The effect of cross-linking on the properties of methoxymethyl nylon film

Property	Uncross-linked	Cross-linked (conditions as in text)
Tensile strength		
dry 52% RH 22°C Ibf/in ² (MPa)	3980 27.5	6500 45
wet water-saturated 220° (MPa)	1670 11.7	4045 28
Elongation at break % dry 52% RH, 22°C	385	355
Elastic recovery % from 100% elongation	75	73
Resistance to boiling water	gelatinises in less than 5 min	excellent
Colour	colourless	yellow

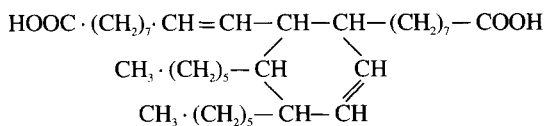


Figure 18.21

A typical example of this class of polymer may be obtained by reacting ethylenediamine and 'dimer fatty acid', a material of inexact structure obtained by fractionating heat-polymerised unsaturated fatty oils and esters. An idealised structure for this acid is shown in *Figure 18.21*. These materials are dark coloured, ranging from viscous liquids to brittle resins and with varying solubility.

They have found use as hardeners-cum-flexibilisers for epoxide resins (see Chapter 26) and are of interest in the production of thixotropic paints and adhesives. Related higher molecular weight materials are tough and flexible and find use as hot melt adhesives (Versalons).

As has been mentioned earlier, a number of copolymers such as nylon 66/610/6 are available. Such a copolymer has an irregular structure and thus interchain bonding and crystallisation are limited. As a consequence the copolymer is soluble in alcohols and many other common polar solvents.

18.11 OTHER ALIPHATIC POLYAMIDES⁷

Although less than a dozen aliphatic polyamide types together with a few miscellaneous copolymers have become available commercially, a very large number have been prepared and investigated. Of the many diamine-dibasic acid combinations those based on intermediates with less than four carbon atoms are unsuitable either because of the tendency to form ring structures or because the melting points are too high for melt spinning (important in fibre production). The many nylons based on amines and acids with 6–10 carbon atoms might also be of interest as fibres and plastics but are not yet attractive commercially because of the costs of synthesis. Similar remarks must also apply to nylons 8, 9 and 10.

Polyamides have also been produced from intermediates with lateral side groups. The effect of such groups is similar to that of *N*-substitution in that there is a decrease in intermolecular cohesion and reduction in the ability of the molecules to pack in a crystal lattice. In some cases the polymers are still fibre-forming but they have much lower melting points. For example the polymer from 12-aminostearic acid (*Figure 18.22*) is fibre-forming but has a low melting point (109°C) and a low moisture-absorbing capacity.

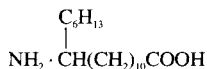


Figure 18.22

One particular type of polyamide produced from intermediates containing lateral side groups are the poly-(α -amino acids). The α -amino acids have the structure shown in *Figure 18.23* (I) and give polymers of the type shown in *Figure 18.23* (II). The proteins may be considered as a special class of such

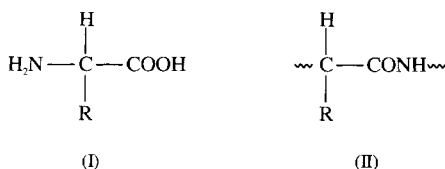


Figure 18.23

polymers in that they are long chain molecules containing the residues of some 25–30 amino acids arranged in a highly specific way in the molecular chain. Table 18.10 gives the structure of some of the α -amino acids that are produced by breakdown of proteins.

Where $\text{R} \neq \text{H}$ the amino acids may be incorporated in either a D- or L-configuration and so it is possible for configurational polymers to be produced. They do not, however, show the same mechanical properties as the configurational homopolymers, which are more regular in structure.

Table 18.10

Name	R
Glycine	H
Alanine	CH_3
Phenylalanine	$\text{CH}_2 \cdot \text{C}_6\text{H}_5$
Cysteine	CH_2SH
Glutamine	$(\text{CH}_2)_2\text{CONH}_2$
Glutamic acid	$(\text{CH}_2)_2\text{COOH}$
Leucine	$(\text{CH}_2)_2\text{CH}(\text{CH}_3)$
Lysine	$(\text{CH}_2)_4\text{NH}_2$

Currently, α -amino acids are prepared by several routes such as by the fermentation of glucose, by enzyme action on several substances and by the hydrolysis of proteins. Many methods for synthesising the polymers are known, of which the polymerisation of *N*-carboxyanhydrides is of particular interest, as it yields products of high molecular weight (Figure 18.24).

These polymers, typical of polyamides with fewer than four main chain carbon atoms in the repeating unit, decompose before melting and have to be processed from solution. Several of the polymers may, however, be spun into fibres. Over thirty years ago Courtaulds produced silk-like fibres on an experimental commercial scale from poly-(L-alanine) and from poly-(α -methyl-L-glutamate). The latter material is also said to be in use as a 'synthetic leather' in Japan. The

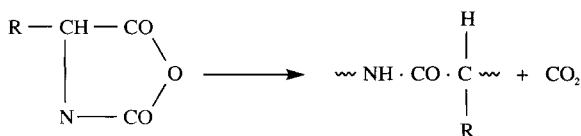


Figure 18.24

Japanese have also shown interest in poly-(L-glutamic acid) for the manufacture of silk-like fibres.

Other polyamides produced experimentally include polymers with active lateral groups (hydroxy, keto groups etc.), polymers with heteroatoms (sulphur and oxygen) in the polyamide-forming intermediates, polymers with tertiary amino groups in the main chain and polymers with unsaturation in the main chain. There does not, however, appear to have been any serious attempt to develop unsaturated polyamide analogues to the polyester laminating resins.

18.12 AROMATIC POLYAMIDES

Until the early 1960s the aromatic and cycloaliphatic polyamides were largely laboratory curiosities. By 1980 they were still only of minor importance to the plastics industry but of rapidly expanding interest as fibre-forming materials with a particular potential as tyre cord materials.

The slow development of these materials is generally ascribed to the slow amidation reactions, the inability of many of the polymers to melt without decomposition and the tendency to colour during polymerisation.

The commercial importance of aromatic polyamides has, however, grown considerably in recent years. These may be classified into three groups:

- (1) Copolymers of high T_g but which are amorphous and thus glassy (the 'glass-clear polyamides').
- (2) Crystalline polymers used as plastics.
- (3) Crystalline polymers primarily of interest as fibres, including some grades which may be considered as liquid crystal polymers.

18.12.1 Glass-clear Polyamides

These materials are also often referred to as glass-clear nylons, which is different from the normal usage of the term nylon for fibre-forming polyamides and their immediate chemical derivatives.

Three commercial types are of interest. They are copolymers of a somewhat irregular structure and are thus non-crystalline and glassy, relying on a fairly high T_g brought about by in-chain ring structures to give reasonable heat deformation resistance. It is reasonable to expect that if these polymers had been regular and crystalline their T_m would have been higher than the decomposition temperature so typical of aromatic polyamides.

The oldest of these materials, a poly (trimethylhexamethylene terephthalamide) was first marketed by Dynamit Nobel in the mid-1960s (Trogamid T). It is a condensation product of trimethylhexamethylenediamine and terephthalic acid (or its dimethyl ester) (*Figure 18.25*). In practice a 1:1 mixture of 2,2,4- and 2,4,4-trimethyldiamines is used, this being produced from acetone via isophorone, trimethyladipic acid and trimethyladiponitrile.

The irregular structure of the polymer indicates that it will be amorphous and glass-like. The presence of the *p*-phenylene group in the main chain and the lone methyl group leads to a high T_g of about 150°C. There is, somewhat surprisingly, a further transition in the range 220–228°C, the nature of which is not really understood. The polymer is more soluble than the crystalline aliphatic nylons. For example it will dissolve in 80/20 chloroform/methanol mixtures.

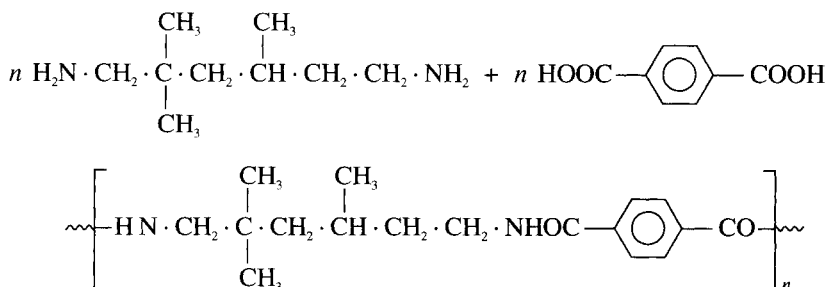


Figure 18.25

Compared with aliphatic nylons it also shows greater rigidity and hardness, lower water absorption, low temperature coefficient of expansion, good resistance to heat and moisture, better electrical insulation properties, particularly under hot and damp condition, and of course transparency.

For transparent applications it is competitive with poly(methyl methacrylate), polycarbonate, polysulphone and MBS. In terms of toughness it is like polycarbonate, polysulphone and MBS and much better than the acrylic materials whilst in terms of heat resistance only the polycarbonate and polysulphone are better. Its good electrical tracking resistance, together with high light and aging resistance and an appropriate chemical resistance, often leads to the aromatic polyamide being the preferred material.

Typical properties are given in *Table 18.11*.

Applications include flow meter parts, transparent housing for electrical equipment, sight glasses, X-ray apparatus windows, gear wheels, racks, counters and containers for solvents.

Table 18.11 Comparison of two glass-clear polyamides

Property	Test method	Units	Grilamid TR-55	Trogamid T
Density	DIN 53479	g/cm ³	1.06	1.12
Refractive index	DIN 53491		1.535	1.566
Water absorption	ISO R62	mg	20	—
	DIN 53472	mg	—	40
T_g , DTA		°C	155	145–153
Deflection temperature (1.82 MPa)	ISO 75	°C	155	130
Vicat temperature	DIN 53460	°C	155	145
Coefficient of expansion	VDE 030414	10 ⁻⁶	68–78	60
Tensile yield strength		MPa	75*	85
Elongation at break		%	8*	70
Tensile modulus		MPa	2300*	3000
Ball indentation hardness	VDE 0302		120*	125
Notched impact	DIN 50453	kJ/m ²	5*	10–15
Volume resistivity	DIN 50482	Ω cm	10 ¹³	>10 ¹⁴
Moulding shrinkage		cm/cm	0.005	0.007

*The mechanical properties for Trogamid T are for dry material at 20°C; those for Grilamid TR-55 at standard atmosphere at 23°C. This will account, in part, for the differences in the figures for mechanical properties of the two polymers.

Another glass-clear polyamide was announced in the mid-1970s by Hoechst; a polynorbornamide, it was marketed as Hostamid. The basic patent suggests that this material is a copolyamide of a mixture of isomeric bisamino-methylnorbornanes (*Figure 18.26* (I) and (II)) with aliphatic or cycloaliphatic dicarboxylic acids with 2–20 carbon atoms or aromatic dicarboxylic acids with 7–20 carbon atoms as well as diamines, amino acids or lactams. The properties of this polymer are similar in many respects to those of Trogamid T, with a T_g of about 150°C, a specific gravity of 1.17 and an apparently somewhat higher tensile strength of 91–95 MPa. It is also glass clear.

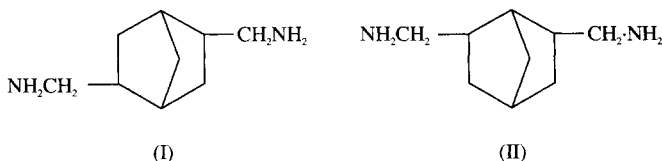


Figure 18.26

The material, Hostamid, LP700, is said to be a melt polycondensate of the diamines (I) and (II) above with terephthalic acid and up to 70% of ϵ -caprolactam but has never been commercially marketed.

A third transparent amorphous polyamide is Grilamid TR55 (Emser Werke). This is also a copolymer, in this case involving both lactam ring opening and the use of a 'nylon-type' salt. It is synthesised by reacting laurinlactam (III) with the salt of isophthalic acid (IV) and the diamine, bis-(4-amino-3-methylcyclohexyl)-methane (V) (*Figure 18.27*). Its T_g of about 160°C is about 10°C above the other commercial glassy polyamides and furthermore it has the lowest specific gravity (1.06). Grilamid TR is also marketed by Mitsubishi and by Union Carbide (as Amidel).

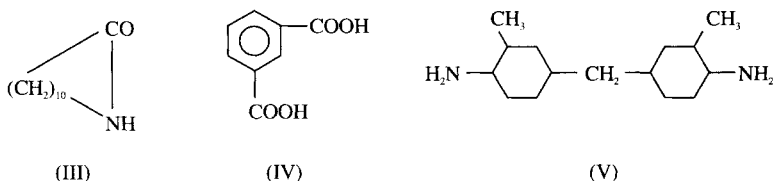


Figure 18.27

Of the transparent polyamides the Grilamid material has the lowest density and lowest water absorption. It is also claimed to have the best resistance to hydrolysis, whilst transparency is unaffected by long-term exposure to boiling water. The properties of Trogamid T and Grilamid TR55 are compared in *Table 18.11*.

The transparent polyamides have increased significantly in importance in recent years. For transparent applications they are competitive with poly(methyl methacrylate), polycarbonates, polysulphones and MBS. In terms of toughness they are like polycarbonates, polysulphones and MBS and much better than the

acrylics. In terms of heat resistance only the polycarbonates and polysulphones are superior. The materials have good tracking resistance and are resistant to a wide range of solvents and chemicals. Some stress cracking may occur on constant exposure to certain liquids, although it is claimed that many of these materials are significantly better than alternative materials in this respect. Grilamid TR55 meets a number of requirements for use in contact with foodstuffs.

Uses for glass-clear polyamides include flow meter parts, filter bowls (air, oil and water), pump casings, sanitary fittings, sight glasses, X-ray apparatus windows, gear wheels, milking machine covers and water gauges for kettle jugs. Modified grades with improved resistance to alcoholic cleaning agents are used for the manufacture of spectacle frames.

In addition several other materials have been reported by industrial companies, but have not at the time of writing been commercialised. These include the product of condensation of 2,2-bis-(*p*-aminocyclohexyl)propane (VI) (*Figure 18.28*) with a mixture of adipic and azelaic acid (Phillips Petroleum), a research material produced in the old German Democratic Republic obtained by melt condensation of *trans*-cyclohexane-1,4-dicarboxylic acid (VII) (*Figure 18.28*) and the two trimethylhexamethylenediamine isomers used in the manufacture of Trogamid T, and another amorphous material (Rilsan N by Ato Chimie).

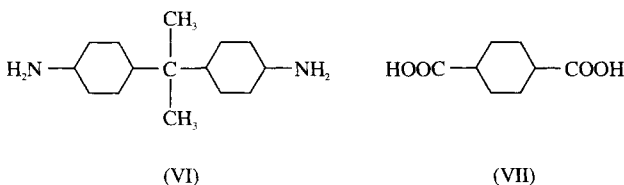


Figure 18.28

A polyether–amide with a heat distortion temperature of 198°C has been prepared by Hitachi by interfacial polycondensation of 2,2-bis-[4-(4-aminophenoxy)phenyl]propane (VIII) with a mixture of isophthaloyl- and terephthaloyl-chloride (IX and X) (*Figure 18.29*).

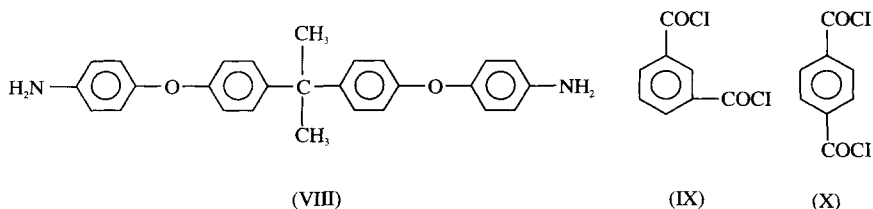


Figure 18.29

The polymer is reported to have a heat deflection temperature of 198°C, and a tensile yield strength of 93.2 MPa, and to be flame retardant.

Another polyetheramide has been produced by another Japanese company, Teijin, under the designation HM-50. The polymer is obtained by condensing

terephthalic acid chloride with a mixture of *p*-phenylene diamine and 3,4'-diaminodiphenylether in polar solvents. The main interest in this polymer, which melts at 515°C, is as a fibre to compete with poly-*p*-phenylene terephthalamide.

18.12.2 Crystalline Aromatic Polyamides

18.12.2.1 Poly-*m*-xylylene adipamide

A rare example of a crystallisable aromatic polyamide used as a plastics material is poly-*m*-xylylene adipamide.

The polymer is produced by condensation of *m*-xylylene diamine with adipic acid (Figure 18.30). The polymer was introduced by Mitsubishi as MXD-6 and is also now marketed by Solvay and by Laporte as Ixef. The polymer has a T_g variously reported in the range 85–100°C, and a crystalline melting point T_m in the range 235–240°C. This is a somewhat lower figure than might be expected in view of the structure and from the glass transition value, with the ratio T_g/T_m having a surprisingly high value of about 0.73 instead of the more usual value of about 0.66.

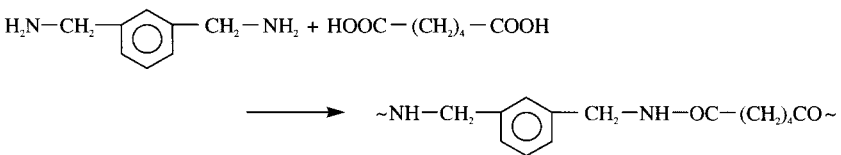


Figure 18.30

As with the aliphatic polyamides, the heat deflection temperature (under 1.82 MPa load) of about 96°C is similar to the figure for the T_g . As a result there is little demand for unfilled polymer, and commercial polymers are normally filled. The inclusion of 30–50% glass fibre brings the heat deflection temperature under load into the range 217–231°C, which is very close to the crystalline melting point. This is in accord with the common observation that with many crystalline polymers the deflection temperature (1.82 MPa load) of unfilled material is close to the T_g and that of glass-filled material is close to the T_m .

Commercial grades of polymer may contain, in addition to glass fibre, fire retardants, impact modifiers and particulate reinforcing fillers. Carbon fibre may be used as an alternative to glass fibre.

The glass-filled grades have a high tensile strength (approx. 185 MPa) and flexural modulus (approx. 10 000 MPa). These two properties, together with their low moulding shrinkage (0.003–0.006 cm/cm) and good surface finish, are emphasised when making comparisons with the aliphatic nylons.

In the absence of fire retardants the material has a limiting oxygen index of 27.5 and may burn slowly. Only some grades will achieve a UL 94 V-1 rating. The Underwriters' Laboratories continuous use temperature index is also somewhat low and similar to the polyarylates with ratings of 135–140°C (electrical) and 105°C (mechanical with impact). Initial marketing has emphasised comparisons with the aliphatic nylons for the reasons given in the previous

paragraph. They have also been favourably compared with poly(butylene terephthalate) in respect of chemical resistance, and poly(phenylene sulphides) because of the lower cost of the polyamide.

Because of their rigidity they are being looked at particularly as replacements for metals such as die-cast zinc alloys. Early uses to become established include portable stereo cassette recorders. Other applications include mowing machine components, electrical plugs, sockets, TV tuner blocks, pulleys, shafts and gears.

18.12.2.2 *Aromatic polyamide fibres.*

In recent years there has been considerable interest in aromatic polyamide fibres, better known as *aramid fibres*. These are defined by the US Federal Trade Commission as 'a manufactured fibre in which the fibre-forming substance is a long chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings.'

The first significant material of this type was introduced in the 1960s by Du Pont as HT-1, later re-named Nomex; a poly-(*m*-phenyleneisophthalamide), it is prepared by condensation of 1,3-phenylenediamine with isophthalic acid (*Figure 18.31*). It may be spun from solution in dimethylformamide containing lithium chloride. It possesses fibre mechanical properties similar to those of nylons 6 and 66 but these are coupled with some very good high-temperature properties. It is claimed to retain half of its room temperature strength at 260°C, resist ignition and be free of after-glow. One disadvantage is that it undergoes pronounced shrinkage when exposed to flame. Although this is acceptable in very loose fitting protective clothing it is not suitable for tailored clothing such as military uniforms.

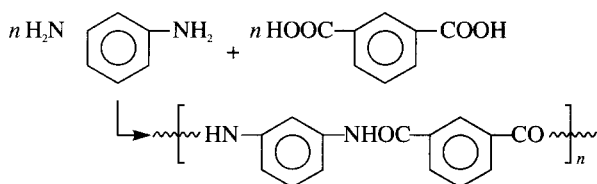


Figure 18.31

In 1973 Du Pont commenced production of another aromatic polyamide fibre, a poly-(*p*-phenyleneterephthalamide) marketed as Kevlar. It is produced by the fourth method of polyamide production listed in the introductory section of this chapter, namely the reaction of a diamine with a diacid chloride. Specifically, *p*-phenylenediamine is treated with terephthalyl chloride in a mixture of hexamethylphosphoramide and *N*-methylpyrrolidone (2:1) at -10°C (*Figure 18.32*).

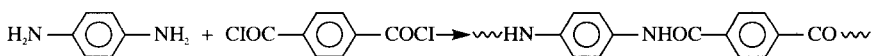


Figure 18.32

The Kevlar polymer may be regarded as a liquid crystal polymer (see Chapter 25) and the fibres have exceptional strength. They are thus competitive with glass, steel and carbon fibres.

Compared with glass fibres, early grades were similar in strength but had twice the stiffness and half the density. The fibres are strong in tension but somewhat weak in compression. Composites have excellent creep resistance and better fatigue resistance than glass-fibre composites. Since their initial availability the tensile strengths achieved with Kevlar polymers have increased from 2.75 to 3.8 GPa, with Kevlar HT, announced in 1987, claimed to be 20% stronger than earlier grades. Announced at the same time was Kevlar HM, claimed to be 40% stiffer than earlier grades.

Originally developed for tyre cords, Kevlar-type materials have also become widely used in composites. Uses include filament-wound rocket motors and pressure vessels, metal-lined Kevlar-overwrapped vessels in the space shuttle, boat and kayak hulls, Kevlar-epoxy helmets for the US military, and as one of the reinforcements in composite lorry cabs.

Rather similar materials have been made available by Monsanto, made by reacting *p*-aminobenzhydrazide with terephthaloyl chloride (*Figure 18.33*). The fibre is marked as PABH-T X-500.

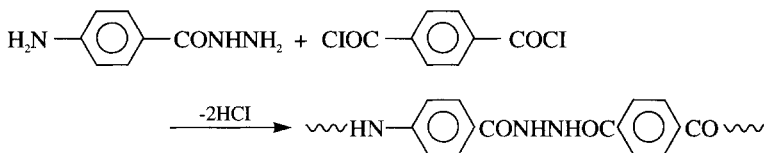


Figure 18.33

Yet another heat- and flame-resistant fibre is the Bayer product AFT-2000. This is classed as a polyquinazolinedione and contains the structural element in *Figure 18.34*.

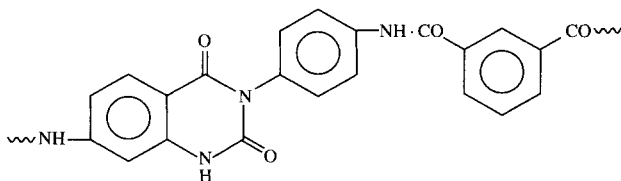


Figure 18.34

Polymers have also been prepared from cyclic amines such as piperazine and bis-(*p*-aminocyclohexyl)methane. An early copolymer, Igamid IC, was based on the latter amine. This amine is also condensed with decanedioic acid, $\text{HOOC}(\text{CH}_2)_{10}\text{COOH}$, to produce to silk-like fibre Quiana (Du Pont).

In addition to the commercial aromatic polyamides described above many others have been prepared but these have not achieved commercial viability. There are, however, a number of other commercial polymers that contain amide groups such as the polyamide-imides. The latter materials are discussed in Section 18.14.

18.12.2.3 Polyphthalamide plastics

As with the aliphatic polyamides such as nylons 6 and 66, the polyphthalamides were developed as plastics materials only after their successful use in the field of fibres. Such materials were introduced in 1991 by Amoco under the trade name of Amodel.

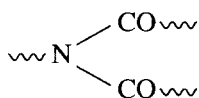
As might be expected of a crystalline aromatic polar polymer, the material has a high T_m of 310°C and a high T_g of 127°C, the ratio of the two having a value close to the 2/3 commonly found with crystalline polymers (see Section 4.4). Also, as to be expected, the material exhibits high strength and rigidity and good chemical resistance, particularly to hydrocarbons. A typical glass-reinforced grade has a continuous use temperature of 180°C, similar to that of polysulphone and only exceeded by a small number of polymers (see *Table 9.1*).

Commercial polymers are generally modified by glass- or mineral-fibre reinforcement. Standard grades have a UL94 Flammability Rating of HB but the use of flame retardants allows grades to be produced with a V-O rating at 0.8 mm thickness. Also of note are such good electrical properties as a high Comparative Tracking Index of 550 V and an ASTM D495 Arc resistance of about 140 s.

The manufacturers stress ease of processing as a particular feature of the material. Recommended melt temperatures are in the range 320–340°C and mould temperatures are 135–165°C. Mould shrinkage of glass-filled grades is usually of the order of 0.2–0.4% in the flow direction and up to twice this value in the transverse direction. The materials are notable for their ability to withstand vapour phase and infrared soldering processes.

18.13 POLYIMIDES^{15,16}

The polyimides have the characteristic functional group below and are thus closely related to the polyamides. However, the branched nature of the



functional group facilitates the production of polymers with a backbone that consists predominantly of ring structures and hence high softening points. Furthermore, many of the structures exhibit a high level of thermal stability so that the polymers have become of some importance in applications involving service at higher temperatures than had been hitherto achieved with plastics materials.

The first commercial materials were introduced by Du Pont in the early 1960s when they marketed a range of products obtained by condensing pyromellitic dianhydride with aromatic amines, particularly di-(4-aminophenyl) ether. These included a coating resin (Pyre ML) film (originally H-film, later named Kapton) and in machinable block form (Vespel). In spite of their high price these materials have found established uses because of their good performance at high temperature. Unfortunately, by their very nature, these polymers cannot be moulded by conventional thermoplastics techniques and this led in the early 1970s to the availability of modified polyimides such as the polyamide imides typified by Torlon (Amoco Chemicals), the polyester imides (e.g. Icdal Ti40 by Dynamit Nobel) and the polybismaleinimides such as Kinel (Rhône-Poulenc).

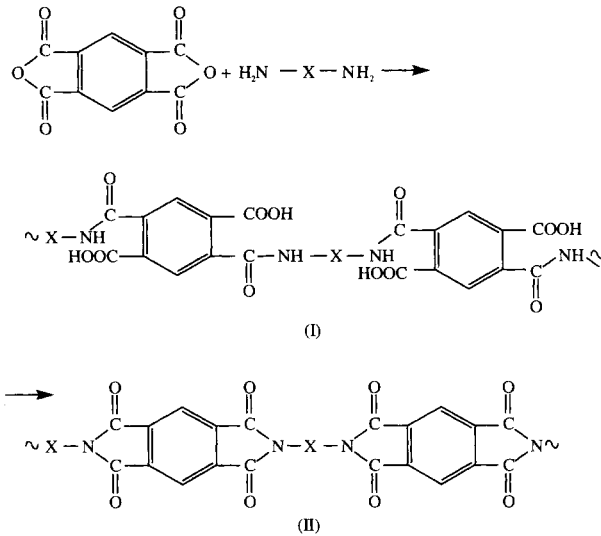


Figure 18.35

By the mid-1970s there were over 20 suppliers in the United States and Western Europe alone although some companies have now withdrawn from the market.

In this section discussion will be confined to the 'true' polyimides whilst the modified materials will be considered in Section 18.14.

The general method of preparation for the original polyimides is shown in Figure 18.35.

The pyromellitic dianhydride is itself obtained by vapour phase oxidation of durene (1,2,4,5-tetramethylbenzene), using a supported vanadium oxide catalyst. A number of amines have been investigated and it has been found that certain aromatic amines give polymers with a high degree of oxidative and thermal stability. Such amines include *m*-phenylenediamine, benzidine and di-(4-amino-phenyl) ether, the last of these being employed in the manufacture of Kapton (Du Pont). The structure of this material is shown in Figure 18.36.

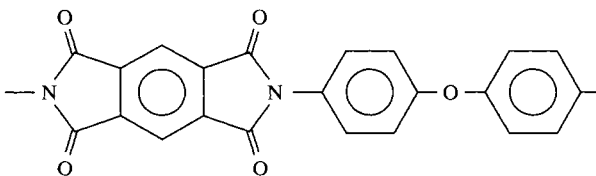


Figure 18.36

For convenience of application it is usual to utilise the two-stage preparation shown above. Initially the soluble prepolymer (I) is formed which is then converted into the insoluble thermally stable polyimide (II) (Figure 18.35). Suitable solvents for the high molecular weight prepolymer (I) include dimethylformamide and dimethylacetamide.

In addition to the *intramolecular* condensation leading to the linear polymer some *intermolecular* reaction may also occur which leads to cross-linking and hence greatly restricts mouldability.

In order to prevent premature gelation the reaction mixture should be anhydrous, free from pyromellitic acid and reacted at temperatures not exceeding 50°C.

Films may be made by casting (I) and heating to produce the polyimide (II). Tough thin film may be obtained by heating for 1–2 hours at 150°C but thicker products tend to become brittle. A substantial improvement can be obtained in some cases if a further baking of solvent-free polymer is carried out at 300°C for a few minutes.

A measure of the heat resistance can be obtained by the weight loss at various temperatures. *Table 18.12* gives details of the weight loss of three polypyromellitimides after various heating times at 325°C.

Table 18.12 Weight loss on heating polypyromellitimides at 325°C.

<i>Polymer based on</i>	<i>Film</i>	<i>Weight loss at 325°C</i>			
		<i>100 h</i>	<i>200 h</i>	<i>300 h</i>	<i>400 h</i>
<i>m</i> -Phenylenediamine	brittle	3.3	4.3	5.0	5.6
Benzidine	flexible	2.2	3.6	5.1	6.5
Di-(4-aminophenyl)ether	flexible	3.3	4.0	5.2	6.6

The first commercial applications of polypyromellitimides were as wire enamels, as insulating varnishes and for coating glass-cloth (Pyre.ML, Du Pont). In film form (Kapton) many of the outstanding properties of the polymer may be more fully utilised. These include excellent electrical properties, solvent resistance, flame resistance, outstanding abrasion resistance and exceptional heat resistance. After 1000 hours exposure to air at 300°C the polymer retained 90% of its tensile strength.

The polymers also have excellent resistance to oxidative degradation, most chemicals other than strong bases and high-energy radiation. Exposure for 1500 hours to a radiation of about 10 rads at 175°C led to embrittlement but the sample retained form stability.

Some typical properties of a fabricated solid grade (Vespel–Du Pont) are given in *Table 18.13* together with some data on a graphite-loaded variety and a commercial polyamide–imide (Torlon 2000—Amoco).

The limited tractability of the polymer makes processing in conventional plastics form very difficult. Nevertheless the materials have been used in the manufacture of seals, gaskets and piston rings (Vespel–Du Pont) and also as the binder resin for diamond grinding wheels.

Laminates produced by impregnation of glass and carbon fibre with polyimide resins followed by subsequent pressing have found important uses in the aircraft industry, particularly in connection with supersonic airliners. Such laminates can be used continuously at temperatures up to 250°C and intermittently to 400°C.

Table 18.13 Typical properties of fabricated unfilled and 15% graphite-loaded polyimide polymers

Property	Units	ASTM test	Vespel, unfilled	Vespel, 15% graphite filled	Torlon 2000, unfilled
Specific gravity	—		1.42	1.49	1.41
Tensile strength		D.638			
25°C	Ibf/in ² (MPa)		13 000 90	9200 63	13 500 93
150°C	Ibf/in ² (MPa)		9700 67	6030 42	— —
315°C	Ibf/in ² (MPa)		5000 35	3890 27	— —
Elongation at break	%	D.638	6–8	5	2.5
Flexural modulus		D.790			
23°C	Ibf/in ² (MPa)		450 000	627 000	710 000
260–300°C	Ibf/in ² (MPa)		26 800 3100	— 4300	450 000 4900
Deflection temperature under load (heat distortion temperature)	°C	D.648	357	—	282
Water absorption (24 h)	%		0.32	—	0.28
Coefficient of friction	—		0.35	—	0.2
Rockwell hardness	H scale	D.785	83–89H	73–75H	104(E-scale)
Volume resistivity	Ωm	D.257	5×10^{18}	$<10^6$	3×10^{14}
Dielectric constant, dry, 23–300°C	—	D.150	3.4	—	3.7
Arc resistance	S	D.495	185	—	—

Methods of preparation of the laminates depend on the particular grade of polyimide resin used but in one process the polyimide precursor is dissolved in acetone and this solution is used to impregnate the glass or carbon fibre and thus produce a 'pre-preg'. The 'pre-preg' is dried and then 'pre-cured' at about 200°C for about 3 hours. This operation reduces the volatile content and also modifies the flow properties to make them more suitable for the subsequent

Table 18.14 Typical properties of a carbon fibre polyimide laminate

Property		Units
Specific gravity	1.67	
Flexural strength (R.T.)	120 000	Ibf/in ²
After 100 h at 200°C tested at R.T.	703	MPa
After 1550 h at 220°C tested at 200°C	120 000	Ibf/in ²
After 1770 h at 300°C tested at 300°C	703	MPa
Flexural modulus (R.T.)	100 000	Ibf/in ²
After 100 h at 200°C tested at R.T.	690	MPa
After 1550 h at 220°C tested at 200°C	50 000	Ibf/in ²
After 1770 h at 300°C tested at 300°C	345	MPa
Interlaminar shear strength (R.T.)	22×10^6	Ibf/in ²
After 100 h at 200°C tested at R.T.	151 600	MPa
After 1550 h at 220°C tested at 200°C	6400	Ibf/in ²
After 1770 h at 300°C tested at 300°C	44	MPa

ICI Development polyimide Resin QX-13 and Morganite Modmor Type 1 (treated) carbon fibre. Unidirectional laminate (52% v/v fibre content)]. Source of data: ICI Trade Literature

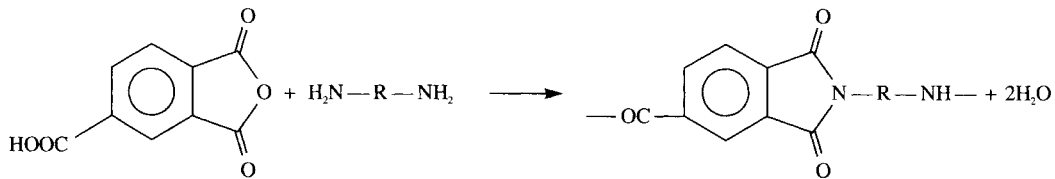


Figure 18.37

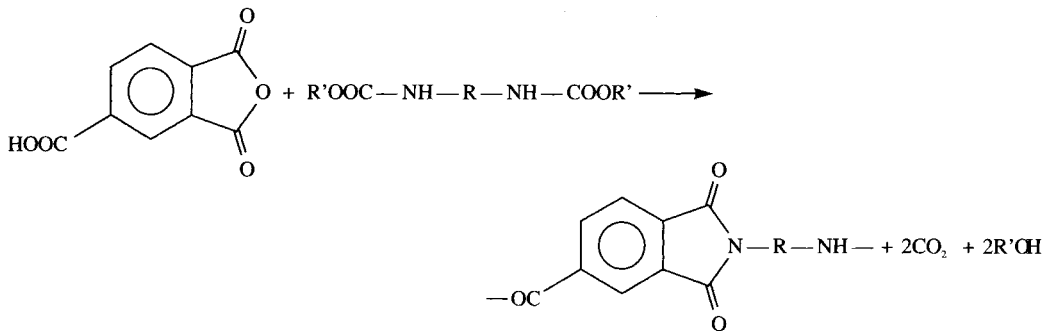
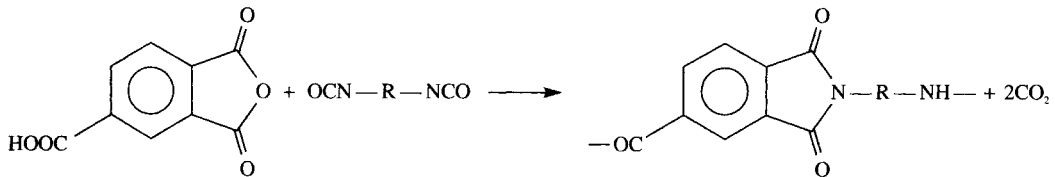


Figure 18.38

laminating operation. This is effected at temperatures in the range 250–300°C for times which vary according to circumstances but where a figure of one hour is fairly typical. After removal from the mould, post-curing at temperatures of up to 350°C is necessary in order to obtain the optimum mechanical properties.

Some properties of a polyimide carbon fibre laminate are given in *Table 18.14*.

At the present time the principal applications of the polyimides are in jet engines, for example in compressor seals. They are also being used in data processing equipment for such purposes as pressure discs, sleeves, bearings, sliding and guide rods and as friction elements. They are also used as valve shafts in shut-off valves whilst their good heat stability and deformation resistance leads to use in soldering and welding equipment. One disadvantage of these materials is their limited resistance to hydrolysis and they may crack in water or steam at temperatures above 100°C. For this reason they have met recent competition from the polyetheretherketones (PEEK), which are not only superior in this respect but are also easier to mould and extrude (see Chapter 21).

18.14 MODIFIED POLYIMIDES

The successful introduction of the polyimides stimulated attempts to produce somewhat more tractable materials without too serious a loss of heat resistance. This led to the availability of a polyamide–imides, polyester–imides and the polybismaleinimides, and in 1982 the polyether–imides.

If trimellitic anhydride is used instead of pyromellitic dianhydride in the reaction illustrated in *Figure 18.35* then a polyamide–imide is formed (*Figure 18.37*). The Torlon materials produced by Amoco Chemicals are of this type.

Both the polyimide and polyamide–imide reactions described above require starting materials of high purity and the use of capped amines (in fact diisocyanates or diurethanes) has been suggested (*Figure 18.38*). It is understood that one of these reactions has been used by Rhone–Poulenc to produce their Kermel fibres. Closely related is the Upjohn process involving the self-condensation of the isocyanate of trimellitic acid, although in this case the product is a true polyimide rather than a polyamide–imide (*Figure 18.39*). Whereas the polyimides are modified polyimides described above are produced by condensation reactions the polybismaleinimides may be produced by rearrangement polymerisation. This avoids the production of volatile low molecular mass by-products.

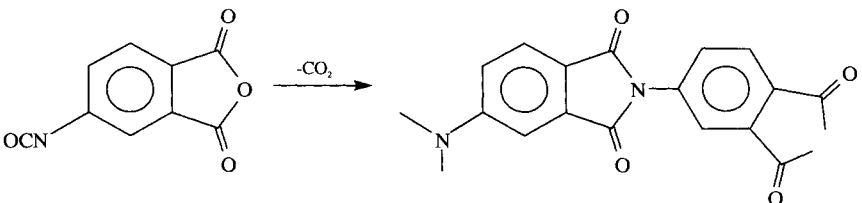


Figure 18.39

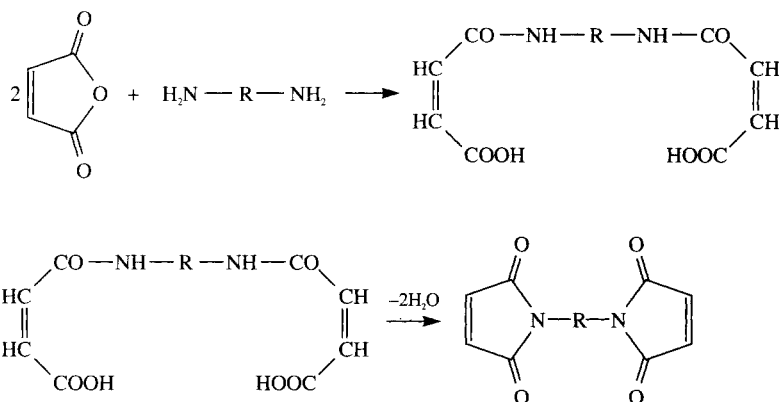


Figure 18.40

The key starting materials in this case are the bismaleimides, which are synthesised by the reaction of maleic anhydride with diamines (Figure 18.40).

A variety of bifunctional compounds react with the bismaleimides to form polymers by rearrangement reactions. These include amines, sulphides and aldoximes (Figure 18.41).

If the bismaleimide-amine reaction is carried out with a deficiency of amine the polymer will have terminal double bonds which allows a cure site to give a thermosetting polymer via a double bond polymerisation mechanism. This approach was developed by Ciba-Geigy with their product P13N (Figure 18.42).

The polybismaleimides, typified by the Rhone-Poulenc material Kinel, may be processed like conventional thermosetting plastics. The original polymers have double bonds at the ends of the chains and polymerisation occurs through them during the moulding process to bring about cross-linking, in this case without the formation of any volatile by-products. The properties of the cured polymers are broadly similar to those of the polyimides and polyamide-imides. Moulding temperatures vary from type to type but are usually in the range 200–260°C followed by post-curing for about 8 h at 250°C.

Unfilled polybismaleimides are used for making laminates, impregnating glass and carbon fibre fabrics, for making printed circuit boards and for filament winding. Grades are also available filled with a diversity of materials such as glass fibre, asbestos, carbon fibre, molybdenum sulphide, graphite and PTFE. They find use in aircraft and spacecraft construction, and in rocket and weapons technology. Specific uses include brake equipment, rings, gear wheels, friction bearings and cam discs.

The polyester-imides form yet another class of modified polyimide. These are typified by the structure shown in Figure 18.43.

Polyimides and related materials have also been used in a number of specialist applications. Polyimide foams (Skybond by Monsanto) have been used for the sound deadening of jet engines. Polyimide fibres have been produced by Rhone-Poulenc (Kermel) and by Upjohn.

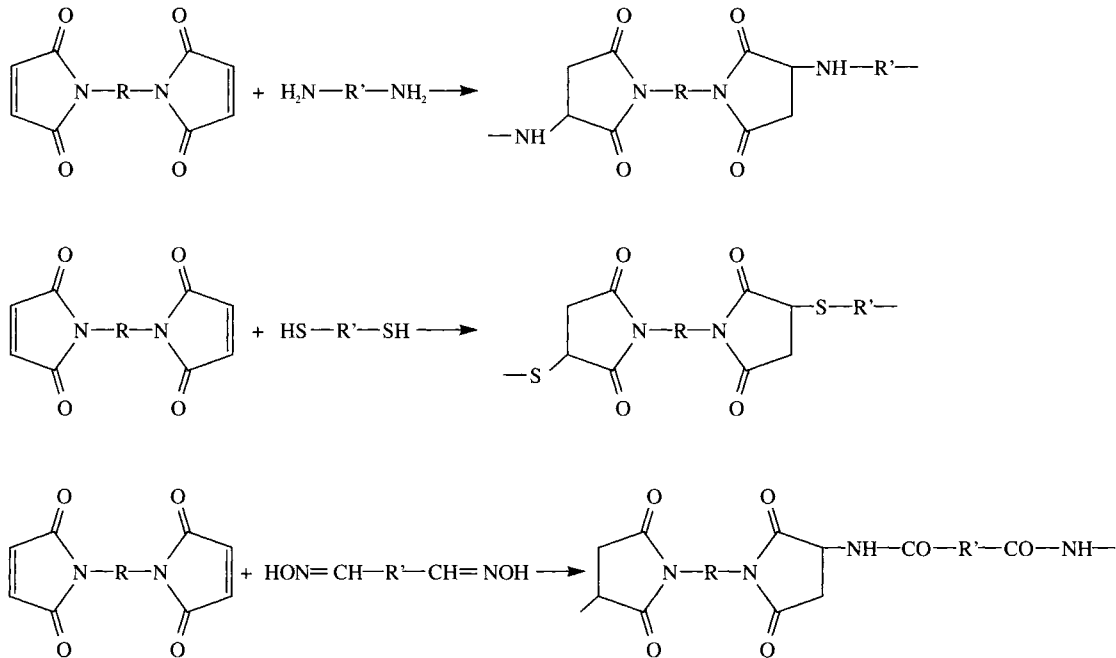


Figure 18.41

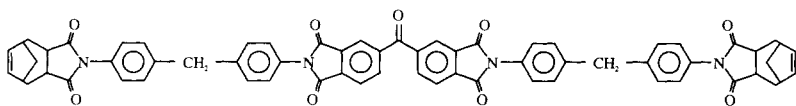


Figure 18.42

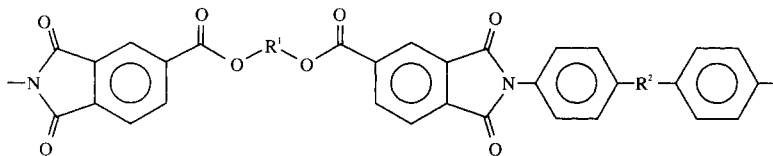


Figure 18.43

18.14.1 Polyamide-imides

The polyamide-imide Torlon was marketed in the early 1970s as a compression moulding material and from the mid-1970s an injection moulding grade has been available. In solution form in *N*-methyl-pyrrolidone it has been used as a wire enamel, as a decorative finish for kitchen equipment and implements and as an adhesive and laminating resin in spacecraft. The compression moulding grade, Torlon 2000, can accept high proportions of filler without serious detriment to many properties.

Polymers of this type have exceptional good values of strength, stiffness and creep resistance (see *Table 18.13*). After 100 h at 23°C and a tensile load of 70 MPa the creep modulus drops only from 4200 to 3000 MPa whilst at a tensile load of 105 MPa the corresponding figures are 3500 and 2500 MPa respectively. If the test temperature is raised to 150°C the creep modulus for a tensile load of 70 MPa drops from 2400 to 1700 MPa in 100 h.

Three months immersion in water leads to a 5% w/w absorption of water which at this level leads to a reduction in the heat distortion temperature (ISO) of 100 Celsius degrees.

Torlon-type polymers are unaffected by aliphatic, aromatic, chlorinated and fluorinated hydrocarbons, dilute acids, aldehydes, ketones, ethers and esters. Resistance to alkalis is poor. They have excellent resistance to radiation. If a total of 10^3 Mrad is absorbed at a radiation dosage of 1 Mrad/h the tensile strength decreases by only 5%.

For compression moulding the moulding compound is preheated at 280°C before moulding at 330–340°C at moulding pressures of 30 MPa (4350 lbf/in²). The mould is cooled to 260°C before removal. For injection moulding melt temperatures are about 355°C, whilst mould temperatures are about 230°C. In order to achieve high-quality mouldings prolonged annealing cycles are recommended. For example, for a 12 mm thick article the annealing cycle is: 36 h at 150°C, 36 h at 177°C, 36 h at 204°C, 36 h at 232°C and finally 48 h at 260°C, a total time of 192 h. For a 6mm section the total recommended time is 120 h and for a 3 mm section, 48 h.

Uses of the polyamide-imides include pumps, valves, gear wheels, accessories for refrigeration plant and electronic components. Interesting materials may be made by blending the polymer with graphite and PTFE. This reduces the coefficient of friction from the already low figure of 0.2 (to steel) to as little as 0.02–0.08.

Polyamide-imides may also be produced by reacting a diacid chloride with an excess of diamine to produce a low molecular mass polyamide with amine end groups. This may then be chain extended by reaction with pyromellitic dianhydride to produce imide linkages. Alternatively the dianhydride, diamine and diacid chloride may be reacted all together.

18.14.2 Polyetherimides

In 1982 General Electric introduced Ultem, a polyetherimide with the following structure:

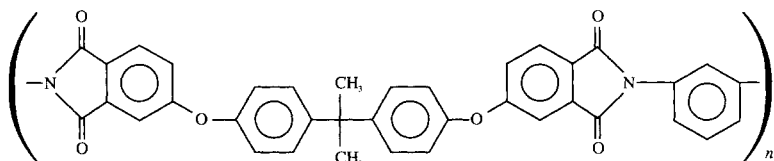


Figure 18.44

The presence of the ether linkages is sufficient to allow the material to be melt processed, whilst the polymer retains many of the desirable characteristics of polyimides. As a consequence the material has gained rapid acceptance as a high-temperature engineering thermoplastics material competitive with the poly-sulphones, poly(phenylene sulphides) and polyketones. They exhibit the following key characteristics:

- (1) Very high tensile strength without the use of reinforcement.
- (2) A glass transition temperature of 215°C, a deflection temperature of 200°C and a Vicat softening point of 219°C.
- (3) A high UL Temperature Index of 170°C (for mechanical with impact).
- (4) Flame resistance (LOI of 47 and UL94 V-0 rating at 0.41 mm thickness).
- (5) Very low smoke emission, superior even to polyethersulphone.
- (6) Excellent hydrolytic stability (a weakness of many polyimides).

Some typical properties of polyetherimides are given *Table 18.15*.

Although the polymer has a regular structure, it is amorphous, the natural polymer being transparent and orange in colour.

The polyetherimides are competitive not only with other high-performance polymers such as the polysulphones and polyketones but also with polyphenylene sulphides, polyarylates, polyamide-imides and the polycarbonates.

Because of its high stability, the processing 'window' (range of processing conditions) is wider than for many other thermoplastics. The main points to bear in mind are:

- (1) The need to use dry granules.
- (2) The need to use high melt temperatures (340–425°C).
- (3) The low moulding shrinkage of 0.005–0.007 cm/cm (typical of an amorphous material).
- (4) The high melt strength, facilitating thermoforming and blow moulding techniques.

Table 18.15 Typical properties of polyetherimide moulding materials (Assessed by use of ASTM test methods)

<i>Property</i>	<i>Unreinforced</i>	<i>30% Glass-fibre reinforced</i>
Specific gravity	1.27	
Tensile yield strength (MPa)	105	165
Tensile modulus (1% secant) (MPa)	3000	9000
Elongation at yield (%)	7–8	—
Elongation at break (%)	60	3
Flexural strength (MPa)	145	230
Izod impact		
Notched ($\frac{1}{8}$ " (ft-lb/in)	1	2
Unnotched	25	8
Dielectric strength ($\frac{1}{16}$ " (v/mil)	710	630
Dielectric constant at 1 kHz 50% RH	3.15	3.7
Dissipation factor at 1 kHz 50% RH	0.0013	0.0015
Volume resistivity ($\frac{1}{16}$ " (ohm . cm)	6.7×10^{17}	3.0×10^{16}

The markets for polyetherimides arise to an extent from stricter regulations concerning flammability and smoke evolution coupled with such features as high strength, toughness and heat resistance. Application areas include car under-the-bonnet uses, microwave equipment, printed circuit boards and aerospace (including carbon-fibre-reinforced laminated materials). The polymer is also of interest in film, fibre and wire insulation form.

General Electric now also offer polyetherimide–polycarbonate blends. Although these materials are not transparent and have a lower specification than the basic polyetherimide, they are less expensive and find use in microwave oven trays and automotive reflectors.

Also of interest is the polysiloxane–polyetherimide copolymer marketed as Ultem Siltem STM1500, which is considered further in Chapter 29.

18.15 ELASTOMERIC POLYAMIDES

Although some of the polyamides described in Section 18.10 are somewhat rubbery, they have never achieved importance as rubbers. On the other hand, the past decade and a half has seen interest aroused in thermoplastic elastomers of the polyamide type which may be considered as polyamide analogues of the somewhat older and more fully established thermoplastic polyester rubbers.

Most of the commercial polymers consist of polyether blocks separated by polyamide blocks. The polyether blocks may be based on polyethylene glycol, polypropylene glycol or, more commonly, polytetramethylene ether glycol. The polyamides are usually based on nylon 11 but may be based on nylons 6 or 66 even a copolymer, e.g. 6/11.

In 1978 Hüls (Mumcu *et al.*¹⁷) described the properties of a block copolymer prepared by condensation of polytetramethylene ether glycol with laurin lactam and decane-1,10-dicarboxylic acid. The materials were introduced as XR3808 and X4006. The polyamide XR3808 is reported to have a specific gravity of 1.02, a yield stress of 24 MPa, a modulus of elasticity of 300 MPa and an elongation of break of 360%. The Swiss company Emser Werke also introduced similar

materials. The currently available grade is Grilamid ELY 60 (formerly ELY 1256). Somewhat related are the Monsanto Nyrin materials processed by reaction injection moulding techniques (see Section 18.8).

A wide range of polyether–polyamide block copolymers were first offered by Atochem in 1981 under the trade name Pebax. These are made by first producing a low molecular weight polyamide using an excess of dicarboxylic acid at a temperature above 230°C and under a pressure of up to 25 bar. This is then combined with a polyether by reaction at 230–280°C under vacuum (0.1–10 Torr) in the presence of a suitable catalyst such as Ti(OR)_4 .

Products varying widely in their properties can be produced by variation of:

- (1) The nature of the polyamide block.
- (2) The nature of the polyether block.
- (3) The lengths of the two blocks.
- (4) The relative amounts of the two blocks present.

Variation in the polyamide block nature and length is a prime influence causing variations in T_m , specific gravity and chemical resistance.

Variation in the polyether block is the prime influence causing variations in T_g , hydrophilic properties and antistatic properties.

Further variation in properties is obtained by incorporating such additives as antistatic agents, ultraviolet stabilisers and antioxidants.

As a result of this flexibility in formulation, the range of physical properties possible is somewhat greater than normally achieved with thermoplastic polyesters (see Section 25.9) or thermoplastic polyurethane rubbers (see Section 27.4.4). For example, hardness can range from Shore A60 (a fairly soft rubber) to Shore D63, which is commonly rated as a moderately hard plastics material. Typical properties of five basic materials in the Pebax range and one hydrophilic grade material (Grade 4011) are given in *Table 18.16* in order to illustrate the range of properties available.

Due to the polyether blocks, these polymers retain their flexibility down to about –40°C and only Grade 6333 breaks in an Izod test at this temperature (using specimens of thickness 3.2 mm). The materials generally show excellent resistance to crack growth from a notch during flexure; some grades are reported

Table 18.16 Selected properties of polyether–polyamide block copolymers of the Pebax type (After Deleens, 1987)

Grade no.	6333	5533	4033	3533	2533	4011
Specific gravity	1.01	1.01	1.01	1.01	1.01	1.10
Hardness (Shore D)	63	55	40	35	25	40
Moisture absorption % (ASTM D570)						
20°C 65% RH	0.5	0.5	0.5	0.5	0.5	4.5
24th in water	1.2	1.2	1.2	1.2	1.2	120
T_m (ASTM D2117)	173	168	168	152	148	195
Def. temp. °C ASTM D648	90	66	52	46	42	—
Tensile strength (MPa)	51	44	36	34	29	—
Elongation at break %	380	455	485	710	715	—
Stress to 25% ext. (MPa)	17.6	11.9	6.5	2.35	1.85	—
Youngs modulus (MPa)	260	145	50	14.6	10.4	—

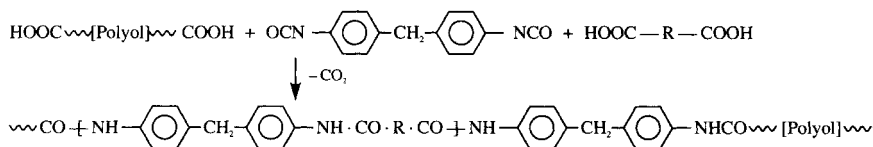
to have withstood 36×10^6 cycles in a de Mattia flexing test. Softer grades are generally more transparent than hard ones as a result of the lower amount of crystalline polyamide block material.

These polymers may be extruded and injection moulded on standard equipment used for thermoplastics. Typical melt temperatures range from about 230°C for the harder grades down to about 200°C for the softer polymers. Mould temperatures are about 25–30°C.

The thermoplastic elastomer polyamides have found use in conveyor and drive belts, ski and soccer shoe soles, computer keyboard pads, silent gears in audio and video recorders and cameras, and thin film for medical applications.

A further range of segmented block copolymers have been developed by Dow through reaction of aromatic di-isocyanates with dicarboxylic acids together with a dicarboxy-terminated polyol using a reaction of type (5) given in Section 18.1 (Nelb *et al.*, 1987). The isocyanate (usually MDI—see Section 27.2) reacts with the dicarboxylic acid (typically adipic or azelaic acid) to give an aromatic polyamide block with a high T_m in the range 230–270°C. This is combined to the polyol (either polyester or polyether—see Chapter 27) via the carboxy terminal groups of the latter.

In a typical process, reaction is carried out at elevated temperatures in a polar solvent. The general polymer reaction scheme is as follows:



Because of the aromatic nature of the polyamide block, the overall polymers can have higher softening points than obtained with other thermoplastic elastomers. For example, some grades will retain a tensile strength of about 15 MPa at 150°C (i.e. about half that of the room temperature strength). The polymers also show good heat aging properties, with, for example, tensile strength increasing after 5 days of exposure at 150°C, due to an annealing process. Where polyester polyols are used there is a good strength retention after exposure to a temperature of 175°C. Although these materials are available in a range of levels of hardness (Shore 88A to 70D), this is in a somewhat harder range of rubbers than the Pebax-type materials, and they are similar to the polyester thermoplastic rubbers discussed in Chapter 25.9.

Other companies interested in thermoplastic polyamide rubbers have been Dow (following on work by Upjohn) and Akzo, whose initial development grades have been trade marked Arnetal.

Applications of the elastomeric polyamides include keyboard pads, sports footwear, loudspeaker gaskets and, in the case of filled grades, watch straps.

18.16 POLYESTERAMIDES

In Chapter 25 it will be shown that polyesters, condensation polymers containing the repeat $-\text{COO}-$ group, may be produced by reactions analogous to the methods used to produce polyamides as summarised in the first section of this chapter. It

is also quite feasible, by using appropriate starting materials to make *polyesteramides*. These materials, which are effectively copolymers, do not have the regularity of the common polyamides and to date have not become of great significance but two types will be mentioned here in passing.

In the 1940s ICI introduced a material marketed as Vulcaprene made by condensing ethylene glycol, adipic acid and ethanalamine to a molecular weight of about 5000 and then chain extending this with a diisocyanate. This rubbery material found some use as a leathercloth and is dealt with further in Chapter 25.

Some 50 years later, in the 1990s Bayer produced their BAK polyesteramides by co-reacting either hexamethylene diamine or ϵ -caprolactam with adipic acid and butane glycol. These materials do have sufficient regularity to be crystallisable and are of interest as biodegradable plastics and are discussed further in Chapter 31.

References

1. *Plastics*, **17**, 64 (1952)
2. FREIDLNA, R. K. and KARAPETYAN, S. A., *Telomerization and New Synthetic Materials*, Pergamon, Oxford (1961)
3. KRALICEK, J., SEBENDA, J., ZADAK, Z. and WICHTERLE, O., *Chem. Prumsyl.*, **11**, 377 (1961); NEUHÄUSL, E. R., *Plastics and Polymers*, **36**, 93 (1968)
4. AÉLION, R., *Ann. Chimq. (Paris)*, **3**, 5 (1948)
5. AÉLION, R., *Ind. Eng. Chem.*, **53**, 826 (1961)
6. COFFMAN D. D., NERCHET, G. J., PETERSON, W. R., and SPANAGEL, E. W., *J. Polymer Sci.*, **2**, 306 (1947)
7. HILL, R. (Ed), *Fibres from Synthetic Polymers*, Elsevier, London (1953)
8. GEIL, P., *Polymer Single Crystals*, Interscience, New York (1963)
9. MANDELKERN, L., *Crystallization of Polymers*, McGraw-Hill, New York (1964)
10. HOLMES, D. R., BUNN, C. W. and SMITH, D. J., *J. Polymer Sci.*, **17**, 159 (1955)
11. MÜLLER, A., and PFLUGER, R., *Plastics*, **24**, 350 (1959)
12. RILEY, J. L., *Eng. Mater. Design*, **1**, 132 (1958)
13. BRASSAT, B. and BUYSIT, H. J., *Kunststoffe*, **70**, 833 (1980)
14. HÜRSCHNITZ, R., EATHER, P. H., DERKS, W. and VAN LEEUWENDAL, R., *Kunststoffe*, **80**, 1272–6 (1990)
15. JONES, J. L., OCHYUSKI, F. W., and RACKLEY, F. A., *Chem. Ind. (London)*, 1686 (1962)
16. BOWER, G. M. and FROST, L. W., *J. Polymer Sci.*, Part A, **1**, 3135 (1963)
17. MUMCU, S., BURZIN, K., FELDMANN, R. and FEINAUER, R., *Angew. Makromol. Chem.*, **74**, 49 (1978)

Bibliography

- ADROVA, N. A. BESSONOV, M. I., LAIUS, L. A. and RUDAKOV, A. P., *Polyimides* (translated from the Russian), Technomic, Stamford (1970)
- FLOYD, D. E., *Polyamide Resins*, Reinhold, New York (1958)
- HILL, R. (Ed), *Fibres from Synthetic Polymers*, Elsevier, London (1953)
- KOHAN, M. I., *Nylon Plastics*, Wiley New York (1973)
- KOHAN, M. I., *Nylon Plastics Handbook*, Carl Hanser Verlag Munich, Vienna, New York (1995)
- NELSON, W. E., *Nylon Plastics Technology*, Newnes-Butterworths, London (1976)
- VIEWEG, R., and MÜLLER, A., *Polyamide*, Carl Hanser Verlag, München (1966) (in German)
- Encyclopaedia of Polymer Science and Technology*, Vol. 10, 347–615. Wiley-Interscience, New York (1965)

Reviews

- BLINNE, G. and PRIEBE, E., *Kunststoffe*, **77**, 988–93 (1987)
- DELEENS, D. Chapter 9B of *Thermoplastic Elastomers* (Eds LEGGE, N. R., HOLDEN, G. and SCHROEDER, H. E.), Hanser, Munich (1987)

- ELIAS, H.-G., Chapters 8, 9 and 10 of *New Commercial Polymers 1969–1975*, Gordon and Breach, New York, London, Paris (1977)
- ELIAS, H.-G., and VOHWINKEL, W., *New Commercial Polymers—2*, Gordon and Breach, New York and London (1986) (Chapters 4 and 9 are particularly relevant to this chapter)
- EL SAYED, A. and STAHLKE, K. R. *Kunststoffe*, **80**, 1107–12 (1990)
- MARGOLIS, J. M. (Ed.), *Engineering Thermoplastics*, Marcel Dekker, New York and Basel (1985) (The following chapters are of particular relevance to this chapter: Chapter 4, R. D. Chapman and J. L. Chruma; Chapter 11, I. W. Serfaty; Chapter 13, F. A. Bystry-King and J. J. King; Chapter 15, C. J. Billerbeck and S. J. Henke)
- MICHAEL, D., *Kunststoffe*, **70**, 629–36 (1980)
- NELB, R. G., CHEN, A. T. and ONDER, K., Chapter 9A of *Thermoplastic Elastomers* (Eds LEGGE, N. R., HOLDEN, G. and SCHROEDER, H. E.), Hanser, Munich (1987)
- POTSCH, G. *Kunststoffe*, **86**(10) 1478–82 (1996)

Polyacetals and Related Materials

19.1 INTRODUCTION

From the time that formaldehyde was first isolated by Butlerov¹ in 1859 polymeric forms have been encountered by those handling the material. Nevertheless it is only since the late 1950s that polymers have been available with the requisite stability and toughness to make them useful plastics. In this period these materials (referred to by the manufacturers as acetal resins or polyacetals) have achieved rapid acceptance as engineering materials competitive not only with the nylons but also with metals and ceramics.

The first commercially available acetal resin was marketed by Du Pont in 1959 under the trade name Delrin after the equivalent of ten million pounds had been spent in research on polymers of formaldehyde. The Du Pont monopoly was unusually short lived as Celcon, an acetal copolymer produced by the Celanese Corporation, became available in small quantities in 1960. This material became commercially available in 1962 and later in the same year Farbwerke Hoechst combined with Celanese to produce similar products in Germany (Hostaform). In 1963 Celanese also combined with the Dainippon Celluloid Company of Osaka, Japan and Imperial Chemical Industries to produce acetal copolymers in Japan and Britain respectively under the trade names Duracon and Alkon (later changed to Kematal). In the early 1970s Ultraform GmbH (a joint venture of BASF and Degussa) introduced a copolymer under the name Ultraform and the Japanese company Asahi Chemical a homopolymer under the name Tenal.

By the late 1990s the main manufacturers were the American-based Du Pont, the Japanese-based Polyplastics and the European-based Ticona with similar plant capacities totalling some 60% of the global capacity which is of the order of 600 000 t.p.a. Among at least eight plants in Asia those of Mitsubishi Gas and Asahi were significant as was also that of BASF (see also Section 19.3.7).

As with other so-called engineering thermoplastics, the polyacetals are available modified with glass fibre, and may contain fire retardants, and some grades are blended with PTFE. In 1982 Hoechst introduced blends of polyacetals

and polyurethanes to give materials of improved toughness yet retaining most of the key features of polyacetals, and they have since been followed by other suppliers.

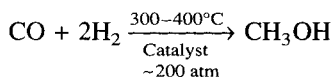
Besides being commercially referred to as polyacetal materials polyformaldehydes are also often known as polyoxymethylenes and are the simplest type of a family of aliphatic polyethers.

Of the many other aliphatic polyethers, polythioethers and polysulphides prepared in the laboratory, some have become commercially available. Those of interest to the plastics industry are dealt with later in this chapter.

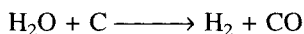
19.2 PREPARATION OF FORMALDEHYDE

Formaldehyde is an important chemical in the plastics industry, being a vital intermediate in the manufacture of phenolic and amino resins. It was also used by Reppe during World War II as an important starting point for the preparation of a wide range of organic chemicals. Consumption of formaldehyde in acetal resins is still a minor outlet for the material but exceptionally pure material is required for this purpose.

The most important route for the production of formaldehyde is from methanol, this normally being prepared by interaction of carbon monoxide and hydrogen.



The two gases involved can be obtained by the 'water-gas reaction' which involves passing water vapour over hot coke.



Methanol is converted into formaldehyde by catalytic vapour phase oxidation over a metal oxide catalyst. In one variation of the process methanol is vaporised, mixed with air and then passed over the catalyst at 300–600°C. The formaldehyde produced is absorbed in water and then fed to a fractionating column. A 37% solution of formaldehyde in water is removed from the bottom of the column with some methanol as a stabiliser whilst excess methanol is taken from the top of the column and recycled.

Formaldehyde is also produced by the oxidation of light petroleum gases, a process which also yields methanol and acetaldehyde. This process is currently used in the Celanese Corporation plant for the production of Celcon.

Formaldehyde is a gas with a boiling point of –21°C. It is usually supplied as a stabilised aqueous solution (~40% formaldehyde) known as formalin. When formalin is used as the source of the aldehyde, impurities present generally include water, methanol, formic acid, methylal, methyl formate and carbon dioxide. The first three of these impurities interfere with polymerisation reactions and need to be removed as much as possible. In commercial polymerisation the low polymers trioxane and paraformaldehyde are convenient sources of formaldehyde since they can be obtained in a greater state of purity.

19.3 ACETAL RESINS

19.3.1 Polymerisation of Formaldehyde

Formaldehyde will polymerise in a number of ways, as indicated in *Figure 19.1*

The cyclic trimer (trioxane) and tetramer are obtained by a trace of sulphuric acid acting on hot formaldehyde vapour (i) (*Figure 19.1*). Linear polymers with degrees of polymerisation of about 50 and a terminal hydroxyl group are obtained by evaporation of aqueous solutions of formaldehyde (ii). In the presence of strong acid the average chain length may be doubled. Evaporation of methanol solution leads to products of type (iii).

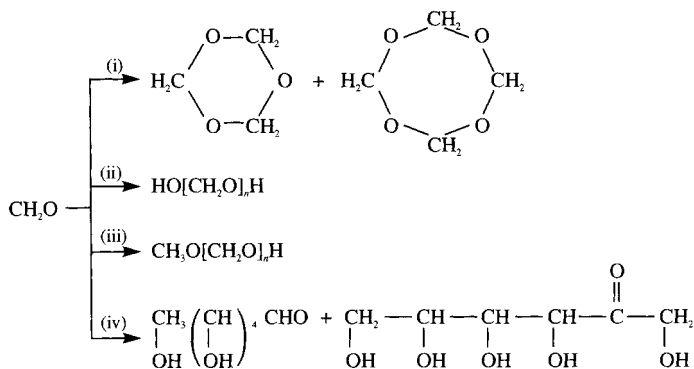


Figure 19.1

In the presence of lime water more complex reactions occur, leading to the formation of aldoses and hexoses (iv). This particular reaction is of interest to the biochemist as it is now generally held that optically active plant carbohydrates are obtained from carbon dioxide and water via formaldehyde.

During the 1920s Staudinger and his collaborators² prepared linear polymers of formaldehyde in some classic researches which demonstrated for the first time the molecular structure of high polymers. When prepared by a solution polymerisation technique, brittle, pulverisable and thermally unstable products were obtained, but Staudinger also prepared polymers by allowing the material to polymerise in bulk at -80°C . These products, though still thermally unstable, possessed some degree of toughness.

In the early 1940s an intensive research programme on the polymerisation of formaldehyde was initiated by the Du Pont Company. As a consequence of this work polymers, both tough and adequately stable to processing conditions, were prepared and eventually marketed^{3,4} (Delrin).

In order to manufacture such polymers, it is first necessary to produce a very pure form of formaldehyde. This is typically produced from an alkali-precipitated low molecular weight polyformaldehyde which has been carefully washed with distilled water and dried for several hours under vacuum at about 80°C . The dried polymer is then pyrolysed by heating at 150 – 160°C , and the resultant formaldehyde passed through a number of cold traps (typically four) at -15°C . Some prepolymerisation occurs in these traps and removes undesirable

impurities from the monomer. The monomer is then introduced into the polymerisation vessel over a rapidly stirred and carefully dried inert medium such as heptane. A number of polymerisation initiators have been cited in the literature and include Lewis acids, amines, phosphines,⁵ arsines and stibines. A typical initiator is triphenylphosphine used to the extent of 20 ppm based on the inert medium. A polymer stabiliser such as diphenylamine may also be present to a concentration of 100 ppm. Polymerisation is carried out until a 20% solids content is obtained. The polymer is then isolated by filtration, washed in turn with heptane and pure acetone and then dried in a vacuum oven at 80°C. Control of molecular weight may be made by adding traces of water, which is an effective chain transfer agent. It is because of this particular property of water that it is necessary to work under conditions where the water content is carefully controlled.

Polymers produced by methods as described above have thermal stabilities many times greater than those obtained by the earlier bulk and solution methods of Staudinger. Staudinger had, however, shown that the diacetates of low molecular weight polyoxymethylenes (I) (polyformaldehydes) were more stable than the simple polyoxymethylene glycols (II) (*Figure 19.2*).

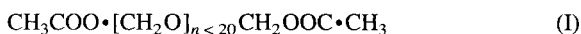


Figure 19.2

Staudinger also found that diacetates of polyoxymethylenes with a degree of polymerisation of about 50 were less stable. Truly high molecular weight polyoxymethylenes (degree of polymerisation ~1000) were not esterified by Staudinger; this was effected by the Du Pont research team and was found to improve the thermal stability of the polymer substantially.

The esterification reaction may be carried out with a number of different anhydrides but the literature^{4,6} indicates that acetic anhydride is preferred. The reaction is catalysed by amines and the soluble salts of the alkali metals. The presence of free acid has an adverse effect on the esterification reaction, the presence of hydrogen ions causing depolymerisation by an unzipping mechanism. Reaction temperatures may be in the range of 130–200°C. Sodium acetate is a particularly effective catalyst. Esterification at 139°C, the boiling point of acetic anhydride, in the presence of 0.01% sodium acetate (based on the anhydride) is substantially complete within 5 minutes. In the absence of such a catalyst the percentage esterification is of the order of only 35% after 15 minutes.

The following extract is taken from an example in British Patent 770,717 to the Du Pont Company as an illustration of a typical method of esterification:

‘Into a reaction vessel there is placed 500 g of a high molecular weight formaldehyde polymer, 4 litres of acetic anhydride and 1.6 g of anhydrous sodium acetate. The mixture is stirred and heated to 160°C. Nitrogen gas at 12 to 15 p.s.i. gauge pressure is maintained in the space above the reaction mixture during the heating period to prevent boiling. The polymer is completely dissolved in the reaction mixture at this temperature. The mixture is allowed to cool slowly with stirring and the polymer precipitates from the solution at about 133°C, the total time in solution being about 90

minutes. The acetylated polymer is removed by filtration and washed on the filter with 3 litres of acetone. It is then re-slurried in 3 litres of water using high speed agitation and the slurry is filtered again. The water washing is repeated two more times. It is then washed with 3 litres of acetone and 3 litres of acetone containing 2.0 g of beta-conidendrol. The product is then dried in a vacuum oven at 67°C.

The beta-conidendrol is incorporated as an antioxidant and is frequently referred to in the patent literature, as is also di- β -naphthyl-*p*-phenylenediamine for this purpose. It is claimed that in the example given above the degradation rate at 222°C is only 0.09% per minute compared with typical values of 0.6–0.8% for unesterified polymer.

An alternative approach to the production of thermally stable polyoxymethylenes was made by chemists of the Celanese Corporation of America and the commercial products were marketed as Celcon, Hostaform and Duracon. The principle of thermal stability in this case is the copolymerisation of formaldehyde with a second monomer⁷ which is a cyclic ether of the general form shown in Figure 19.3 (I).

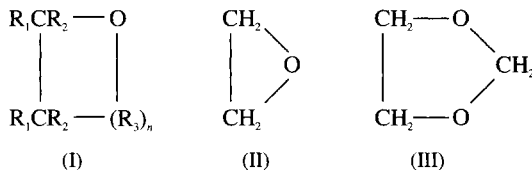


Figure 19.3

It is stated in the basic patent that ethylene oxide (II) and 1,3-dioxolane (III) are the preferred materials. By the occasional incorporation of molecules containing two successive methylene groups the tendency of the molecules to unzip is markedly reduced.

In one example⁷ 25.0 g of cyclohexane were added to 25.0 g of trioxane (a cyclic trimer of formaldehyde) and cooled to -70°C; 0.03 ml of dioxolane were added together with 0.10 ml boron fluoride etherate (stated in the basic patent to be the preferred catalyst). The tube was then sealed and immersed in a water bath at 66–68°C for 4 hours. After washing the product the polymer was dried and a 20% yield obtained. On heating this sample for 2 hours at 225°C there was weight loss of 27.8%. Experiments were also carried out using 0.25 parts and 1.25 parts of dioxolane, but in these cases there was a higher weight loss and, in addition, a lower melting point.

In another example, trioxane and dioxolane were blended in such a ratio as 'to provide one oxyethylene group for each 8.45 oxymethylene groups'. The boron trifluoride etherate comprised 0.089% by weight of the mixture which was then heated in a tube in a bath of boiling water for 2.16 hours. A polymer was produced in a yield of 42.5% by weight, it had a melting point of 158–163°C and a degradation rate at 222°C of only 0.06% by weight per minute.

The stability of the copolymers may be enhanced by alkaline hydrolysis following polymerisation to remove oxymethyl end-groups and replace them with the more stable oxyethyl groups.

It is to be noted that there appear to be four processes which lead to degradation of polyacetals.

- (1) Stepwise thermal- or base-catalysed hydrolytic depolymerisation initiated from the hemi-formal chain end with the evolution of formaldehyde. The main reasons for end-capping and copolymerisation mechanisms described above are carried out in order to minimise this reaction.
- (2) Oxidative attack at random along the chain leading to chain scission and subsequent depolymerisation. Initial chain scission is reduced by the use of antioxidants (see Chapter 7) and in recent formulations hindered phenols seemed to be preferred. It is reported that 2,2'-methylenebis-(4-methyl-6-t-butylphenol) is present in Celcon and 4,4'-butylidene bis-(3-methyl-6-t-butylphenol) in Derlin. The copolymerisation helps to reduce the rate of depolymerisation where initiation of depolymerisation is not completely prevented.
- (3) Acid-catalysed cleavage of the acetal linkage. Traces of acid may arise as residues from polymerisation and end-capping stages and through oxidation of formaldehyde to formic acid. Acid acceptors are believed to be used in commercial practice and epoxides, nitrogen-containing compounds and basic salts are all quoted in the patent literature. Polyacetals should not be processed in equipment which has been used for processing PVC unless the equipment has been cleaned because of the serious effect of trace HCl at elevated temperatures.
- (4) Thermal depolymerisation through scission of C—O bonds can occur catastrophically above 270°C and care must be taken not to exceed this temperature during processing.

19.3.2 Structure and Properties of Acetal Resins

It is difficult to resist a comparison between the structure and properties of acetal polymers and those of polyethylene.

Both polymers are linear with a flexible chain backbone and are thus both thermoplastic. Both the structures shown (*Figure 19.4*) are regular and since there is no question of tacticity arising both polymers are capable of crystallisation. In the case of both materials polymerisation conditions may lead to structures which slightly impede crystallisation; with the polyethylenes this is due to a branching mechanism, whilst with the polyacetals this may be due to copolymerisation.

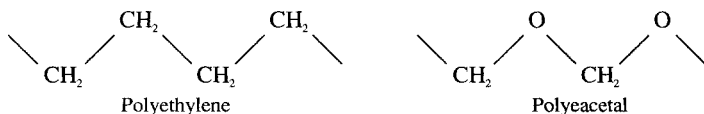


Figure 19.4

The acetal polymer molecules have a shorter backbone (—C—O)—bond and they pack more closely together than those of polyethylene. The resultant polymer is thus harder and has a higher melting point (175°C for the homopolymer). The position of the glass transition is a subject of debate since at least two transitions in addition to the melting point are discernible. The true glass transition is usually associated with the temperature at which movement of segments of about 50–150 backbone atoms becomes relatively easy, in the

amorphous zone. Unfortunately (from the sense of trying to identify T_g) there are not a large number of such segments in a highly crystalline polymer and the T_g only has secondary effects. It is possible that a transition about -13°C is of the true T_g type. Another transition at about -73°C is more prominent but is believed by the author to be associated with the mobility of much smaller units via, for example, the Schatzki crackshaft effect (Chapter 3).

As is typical for crystalline polymers incapable of specific interactions with liquids, there are no solvents at room temperature but liquids which have a similar solubility parameter ($\delta = 22.4 \text{ MPa}^{1/2}$) will cause a measure of swelling, principally in the amorphous region.⁸

At room temperature there is only a small decrease in free energy on conversion of monomer to polymer. At higher temperatures the magnitude of the free energy change decreases and becomes zero at 127°C ⁹; above this temperature the thermodynamics indicate that depolymerisation will take place. Thus it is absolutely vital to stabilise the polyacetal resin both internally and externally to form a polymer which is sufficiently stable for processing at the desired elevated temperatures.

The backbone bonds are polar but the structure is balanced and the polymer is quite a good dielectric. Reported data on resistivity indicate only moderate values presumably because of ionic fragments, impurities and additives.

Table 19.1 Crystallinity data for homopolymer acetal resins¹¹

Unit cell dimensions	$a = 4.46 \text{ \AA}$ $c = 17.30 \text{ \AA}$
Molecular configuration	helical
No. of repeat units in identity period	9
Crystal cell density	1.506
Polymer densities (observed)	1.40–1.45
% crystallinity	75–85

Both the molecular¹⁰ and fine structure¹¹ of the Du Pont polyoxymethylenes have been investigated and reported. Koch and Lindvig¹⁰ have demonstrated that the repeating unit of the polymer is $-\text{CH}_2\cdot\text{O}-$ and that the end groups of the unmodified polymer are either acetate or methoxyl (derived from methanol which is present in trace in the formaldehyde during polymerisation). The number average molecular weights of these polymers are normally in the range of 20 000–110 000. Values for molecular weight determined by end-group analysis and by osmotic methods show close agreement. This agreement, together with the fact that no structures which could be possible branch points in the molecule have been discovered, indicates that the polymers are substantially linear.

Commercial polymers are made so that they possess terminal end groups for enhanced stability. Differences in the nature of these end groups have been claimed to be the main reason for the higher hot water and alkali resistance of the copolymers over the homopolymers (see section 19.3.3).

The acetal polymers exhibit a high crystallinity.¹¹ The percentage crystallinity will depend on the quench temperature and will range from about 77%, when quenched at 0°C , to about 80% when quenched at 160°C . Annealing will increase the crystallinity, this being most marked at 150°C (Figure 19.5).

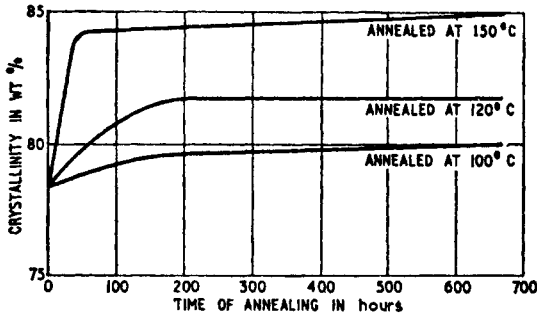


Figure 19.5. Effect of annealing on room temperature crystallinity of acetal homopolymer resin. (Films moulded at 210°C, quenched to 50°C.) (After Hammer et al¹¹)

The greater the percentage crystallinity the higher the yield point and tensile modulus. It has also been shown that by raising the quench temperature the spherulite size is increased and that this greatly decreases the impact toughness.

19.3.3 Properties of Acetal Resins^{9,12,13}

The principal features of acetal resins leading to commercial application may be summarised as follows:

- (1) Stiffness.
- (2) Fatigue endurance.
- (3) Resistance to creep.
- (4) Low coefficient of friction (with equal dynamic and static coefficients).
- (5) Good appearance.

Table 19.2

Property	ASTM test	Acetal homopolymer	Acetal copolymer	Unit
Specific gravity	D.792	1.425	1.410	
Tensile strength (23°C)	D.638	10 000 70	8500 58	lbf/in ² MPa
Flexural modulus (23°C)	D.790	410 000 2800	360 000 2500	lbf/in ² MPa
E_p (23°C)	D.638	15–75	23–35	%
Deflection temperature				
264 lbf/in ² (1.82 MPa)	D.648	100	110	°C
66 lbf/in ² (0.48 MPa)		170	158	°C
Vicat softening point	D.569	185	162	°C
Impact strength (23°C)	D.256	1.4–2.3	1.1	ft lbf in ⁻¹ notch
Crystalline melting point	—	175	163	°C
Water immersion				
(24 h immersion)	D.570	0.4	0.22	%
(50% RH equilibrium)	—	0.2	0.16	%
(continuous immersion—equilibrium)	—	0.9	0.8	%
Coefficient of friction	—	0.1–0.3	0.2	—

Although in many respects acetal resins are similar to the nylons, they may be considered to be superior to them in their fatigue endurance, creep resistance, stiffness and water resistance. The nylons (except under dry conditions) are superior in impact toughness and abrasion resistance.

Some mechanical and thermal properties of acetal polymers are listed in *Table 19.2*. The value quoted are those supplied by the manufacturers.

It must, however, be stressed that for design purposes such data have little value. Like the nylons, which are also widely used for load-bearing light engineering applications, the polyacetals exhibit a small but finite creep under load. It is thus necessary to consider mechanical properties under those main headings.

- (1) Short-term failure—in particular impact resistance.
- (2) Long-term deformation such as shown by creep curves and/or the derived isochronous stress–strain and isometric stress–time curves, and also by studies of recovery for deformation.
- (3) Long-term failure. A sample under continuous load for a year may break at a stress about half of that required in a short-term tensile test (*Figure 19.6*).

These aspects were discussed in Chapter 9 and further details regarding polyacetal resins may be found from manufacturers, literature and in the various monographs cited at the end of this chapter.

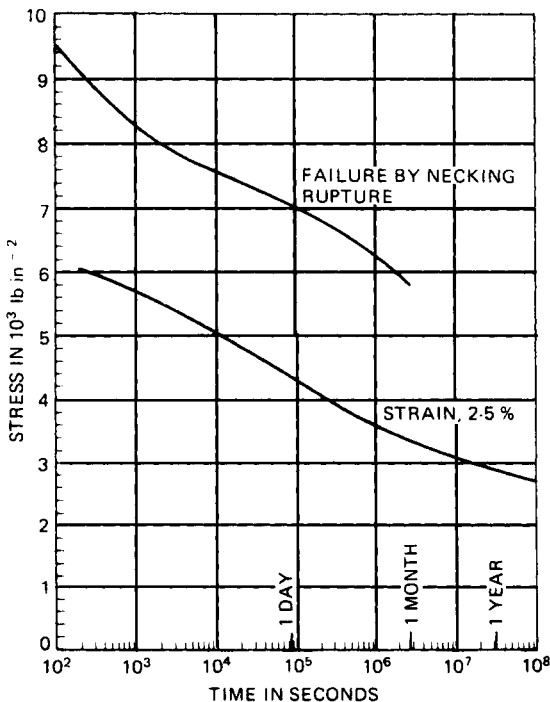


Figure 19.6. Acetal copolymer: static fatigue: failure vs time at 20°C (R.H. ca 65%) (ICI Publicity and Reports)

In addition, service properties such as abrasion resistance are of interest.

The data presented in *Figure 19.7* were obtained on a Sonntag-Universal machine which flexes a beam in tension and compression. Whereas the acetal resin was subjected to stresses at 1800 cycles per minute at 75°F and at 100% RH, the nylons were cycled at only 1200 cycles per minute and had a moisture content of 2.5%. The polyethylene sample was also flexed at 1200 cycles per minute. Whilst the moisture content has not been found to be a significant factor it has been observed that the geometry of the test piece and, in particular, the presence of notches has a profound effect on the fatigue endurance limit.

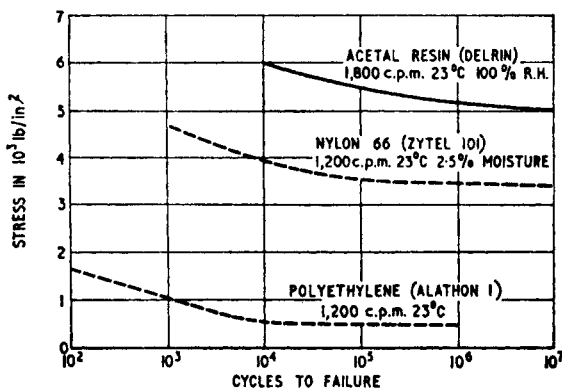


Figure 19.7. Fatigue resistance of acetal resin compared with nylon 66 and with polyethylene. Measured as the cycles to failure at a given applied stress. (Du Pont trade literature)

The acetal resins show superior creep resistance to the nylons but are inferior in this respect, to the polycarbonates. It is to be noted, however, that limitations in the load-bearing properties of the polycarbonates restrict their use in engineering applications (see Chapter 20). Another property of importance in engineering is abrasion resistance—a property that is extremely difficult to assess. Results obtained from various tests indicate that the acetal polymers are superior to most plastics and die cast aluminium, but inferior to nylon 66 (see also Section 19.3.6 and Chapter 18).

The electrical insulation properties of the acetal resins may be described as good but not particularly outstanding. There are available alternative materials which are better insulators and are also less expensive. There are, however, applications where impact toughness and rigidity are required in addition to good electrical insulation characteristics, and in these instances acetal resins would be considered. *Table 19.3* lists some of the more important electrical characteristics of 'Delrin' acetal resin. Data for the trioxane-based copolymer resin (e.g. Celcon) are virtually identical.

Acetal homopolymer resins show outstanding resistance to organic solvents, no effective solvent having yet been found for temperatures below 70°C. Above this temperature some phenolic materials such as the chlorophenols are effective. Stress cracking has not been encountered in organic solvents. Swelling occurs with solvents of similar solubility parameter to that of the polymer ($\delta = 22.4 \text{ MPa}^{1/2}$).

The resistance of these polymers to inorganic reagents is not, however, so outstanding and they should not be used in strong acids, strong alkalis or oxidising agents. Staining resistance is generally good although hot coffee will

Table 19.3

	ASTM test method	Value
Dielectric strength (short time)	D.149	(0.125 in thick) 197 kV/cm (0.010 in thick) 670 kV/cm
Volume resistivity	D.257	$6 \times 10^{16} \Omega\text{m}$ (0.2% water) $4.6 \times 10^{15} \Omega\text{m}$ (0.9% water)
Surface resistivity	D.257	$10^{16} \Omega$
Dielectric constant (73°F)	D.150	$3.7(10^2-10^4 \text{ Hz})$
Power factor	D.150	0.004 (10^2-10^4 Hz)

cause staining. Acetal copolymer resins are somewhat more resistant to hot alkalis but resistance to acids is still comparatively poor. There do not appear to be any toxic or dermatitic hazards under normal conditions of use with either homopolymers or copolymers. Water does not cause any significant degrading hydrolysis of the polymer but may swell it or permeate through it. *Figure 19.8* shows the relation between humidity, time and temperature on the water absorption whilst *Figure 19.9* shows the effect of water absorption on dimensions for homopolymer resins.

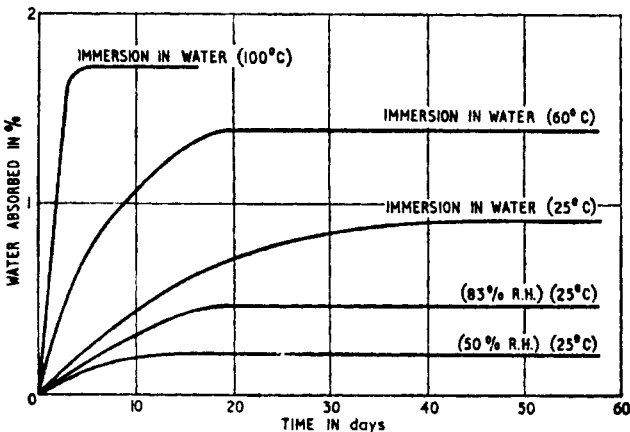


Figure 19.8. Effect of humidity, time and temperature on the water absorption of acetal homopolymer resin (Delrin). (Du Pont Trade Literature).

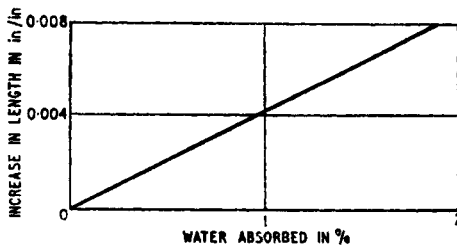


Figure 19.9. Effect of absorbed water on the dimensions of acetal homopolymer resins ('Delrin'). (Du Pont Trade Literature)

The polyacetals have a good record of performance in uses involving hot air and hot water. Plumbing components have been used for hot water service in the range 60–80°C and applications in hot air well in excess of 90°C. Recommended maximum continuous use temperatures are given in *Table 19.4*

Table 19.4 Recommended maximum continuous use temperatures for polyacetals

	<i>In air</i> (°C)	<i>In water</i> (°C)
Homopolymer	82	65
Copolymer	104	82

Underwriters' Laboratories Thermal Index ratings are 105°C for electrical, 90°C for mechanical without impact and 90°C (copolymer)/85°C (homopolymer) for mechanical with impact.

Prolonged exposure to ultraviolet light will induce surface chalking and reduce the molecular weight, leading to gradual embrittlement. As with the polyolefins it is found that the incorporation of a small amount of well-dispersed carbon black increases resistance of ultraviolet degradation. Amongst miscellaneous properties it may be noted that the resins do not appear to be attacked by fungi, rodents and insects. The polymer burns slowly with a soot-free flame.

The homopolymer and the trioxane-based copolymers are generally similar in properties. The copolymer has better thermal stability, better hydrolytic stability at elevated temperatures, easier mouldability and better alkali resistance. The homopolymer has slightly better mechanical properties, e.g. higher tensile strength, higher flexural modulus and greater surface hardness. As may be expected, the homopolymer has a slightly higher crystalline melting point.

19.3.4 Processing

Acetal resins may be processed without difficulty on conventional injection moulding, blow moulding and extrusion equipment. The main points to be considered are:

- (1) Overheating leads to the production of formaldehyde gas and if this is produced in sufficient quantities within the confines of an injection cylinder or extruder barrel the gas pressure may become sufficiently high that there is a risk of damage or injury. The time for which acetal resin may be heated at any given temperature will vary from grade to grade according to the method and degree of stabilisation. A typical copolymer may be kept in an extruder barrel for 110 min at 190°C before serious discolouration occurs. Dead spots must be carefully avoided.
- (2) Although less hygroscopic than the nylons, acetal resins must be stored in a dry place.
- (3) With most homopolymers and copolymers the apparent viscosity is less dependent on temperature and shear stress (up to 10^6 dyn/cm²) than that of the polyolefins, thus simplifying die design. On the other hand the melt has a low elasticity and strength and this requires that extruded sections be

supported and brought below the melting point as soon as possible consistent with obtaining a satisfactory crystalline texture.

The lack of melt strength leads to particular problems with blow moulding because of the extensive drawing down of the parison under gravity. To overcome these problems copolymers have become available with slightly branched molecules which have a greater melt elasticity and tenacity. Such materials, which also have more stress-dependent viscosities, are not only of specific value in blow moulding but extrudates generally are easier to handle.

- (4) The high crystallinity which develops on cooling results in a shrinkage of about 0.020 cm/cm. Because of the low glass transition temperature, crystallisation can take place quite rapidly at room temperatures and after-shrinkage is usually complete within 48 hours of moulding or extrusion. In processing operations injection moulds, blow moulding moulds and sizing dies should be kept at about 80–120°C in order to obtain the best results.
- (5) Because of the low glass transition temperature it is not possible to make clear film, stable at room temperature, by quenching. Some improvement in clarity may be obtained by cold rolling as this tends to dispose the crystal structure into layers (see Chapter 6).

Both homopolymers and copolymers are available in a range of molecular weights (M_n 20 000–100 000). The materials are normally characterised by the melt flow index using basically the same test as employed for polyethylene. For general purpose work polymers with an MFI of about 9 are employed but high-precision work and complex mouldings polymers with MFIs as high as 27 (viz. lower molecular weight polymers) may be used. For extrusion and thick-walled mouldings a polymer with MFI about 2.5 (M_n ca 45 000) is often employed although for extrusion blow moulding the special polymers used have MFIs of about 1.0.

19.3.5 Additives

The acetal polymers are probably never supplied for use without any additives being incorporated. As mentioned in Section 19.3.1 antioxidants of the phenol alkane type are present in both homopolymers and copolymers. Acid acceptors are also believed to be widely used to absorb traces of acidic materials which attack the acetal linkage. Epoxides, nitrogen compounds and basic salts⁹ have been successfully employed.

Since acetal resins are degraded by ultra violet light, additives may be included to improve the resistance of the polymer. Carbon black is effective but as in the case of polyethylene it must be well dispersed in the polymer. The finer the particle size the better the ultra violet stability of the polymer but the poorer the heat stability. About 1.5% is generally recommended. For white compounds and those with pastel colours titanium dioxide is as good in polyacetals as most transparent ultraviolet absorbers, such as the benzophenone derivatives and other materials discussed in Chapter 7. Such ultraviolet absorbers may be used for compounds that are neither black, white nor pastel shade in colour.

In order to reduce the coefficient of friction in bearing applications small amounts of molybdenum disulphide are incorporated although in quantity this material may cause problems through acidic impurities. Blends of polyacetal and PTFE (20–25% PTFE) have a very low coefficient of friction (as low as 0.02)

and may be operated under much more severe conditions than is possible with unfilled materials.

Lower cost alternatives to PTFE-modified polymers have also been introduced for low-friction applications. These materials use graphite and 'chemical lubricants' of undisclosed composition.

Glass-filled polyacetals (20–30% glass fibre) are available when such properties as high creep resistance, enhanced stiffness and low coefficient of expansion are important. Properties of the filled compound depend considerably on the glass-fibre dimensions, the nature of surface coatings on the glass and the goodness of mixing. The main difficulties with these compounds arise from their inferior impact strength and the anisotropic nature of mouldings. Grades are also available in which the glass is available in ballotini (i.e. small bead) form and as ballotini-fibre mixtures.

19.3.6 Acetal–Polyurethane Alloys

Blends or alloys of polyacetals with polyurethane elastomers were first introduced by Hoechst in 1982, who were then followed by other manufacturers. The key features of these materials are their improved toughness with little change in other important properties. There are two aspects with respect to the impact toughness:

- (1) A high strength under impact.
- (2) Good elastic recovery.

Where the polyurethane comprises <30% of the blend, the polyurethane remains in discrete droplets within the polyacetal matrix. In this range the particle size and particle size distribution of the elastomer particles are of importance. Where the elastomer component is in excess of 30%, interpenetrating polymer networks exist in the sense that there are two interpenetrating continuous phases (as opposed to two cross-linked interpenetrating polymer systems).

Charpy notched impact strengths in excess of 55 kJ/m² have been reported for alloys with homopolymers and in excess of 20 kJ/m² for copolymers.

19.3.7 Applications of the Acetal Polymers and Copolymers

There has been a steady increase in demand for polyacetals over the years, with global nameplate capacity increasing from about 260 000 t.p.a. at the beginning of the 1980s to about 600 000 t.p.a. at the end of the century. In the same period consumption has risen from about 140 000 t.p.a. to about 480 000 t.p.a. In terms of nameplate capacity the acetal copolymers dominate the homopolymers by a ratio of the order of 3:1.

About 95% of the polymers are processed by injection moulding. Virtually all the remainder is extruded into sheet and rods for subsequent machining into finished parts.

The acetal resins may best be considered as engineering materials. They therefore become competitive with a number of plastics materials, nylon in particular, and with metals.

Because of their light weight, ability to be moulded into intricate shapes in one piece, low coefficients of friction and absence of slip–stick behaviour, acetal resins find use as bearings.

An approximate rule of thumb guide as to whether acetal resin may be suitable for a particular bearing application may be obtained from *PV* data. The *PV* value is the product of pressure on the projected bearing area (in lb/in^2) and the velocity (surface speed in ft/min). For sleeve bearings the projected area is that of a plane running through the axis of a bearing of the same length as, and of width equal to the diameter of, the bearing. Therefore a bearing 2 in long and 1 in in diameter would have a projected area of 2 in^2 . It can easily be calculated that for a shaft rotating at 200 rev/min with a bearing load of 50 lb the *PV* value will be about 1300. Approximate maximum *PV* values for a steel shaft on an acetal homopolymer bearing are:

	<i>Max. PV</i>
Completely unlubricated	1600–2000
Lubricated at installation	2000–5000
Repeated lubrication	5000–10 000
Continuous lubrication	10 000–15 000
Unlubricated polyacetal-PTFE blend	15 000–45 000

These figures are somewhat higher than those obtained with the nylons.

The lowest coefficients of friction and wear are obtained with acetal resin against steel. With other metals, in particular with aluminium, greater wear and higher friction occur. From the design point of view it is not generally desirable to use acetal to acetal in bearings because of the tendency to heat build-up, except with very light loads. Where the use of a non-metallic material is desirable it is found that better results are obtained using acetal and nylon in conjunction rather than either on its own.

Acetal resins find a number of applications in gears, where they come into competition with the nylons. Acetal gears are superior to those made from nylon in fatigue resistance, dimensional stability and stiffness, whereas nylon gears in conditions of average humidity have greater resistance to impact fatigue and abrasion.

Amongst the many other applications for acetal resins should be mentioned links in conveyor belts, moulded sprockets and chains, blower wheels, cams, fan blades, check valves, pump impellers, carburettor bodies, blow-moulded aerosol containers and plumbing components such as valve stems and shower heads.

It may therefore be seen that acetal resins are primarily engineering materials being used to replace metals because of such desirable properties as low weight, corrosion resistance, resistance to fatigue, ease of fabrication and low coefficient of friction. Because of their comparatively high cost they cannot be considered as being general purpose thermoplastics alongside polyethylene, polypropylene, PVC and polystyrene.

In the late 1990s it was estimated that in Western Europe usage breakdown was as follows:

Transportation	35.7%
Industrial uses	13.6%
Consumer products	12.0%
Appliances/power tools	9.3%
Electrical/electronics	8.6%
Plumbing, hardware	2.9%
Other	17.9%

In North America somewhat less is used in transportation applications and rather more in plumbing.

Whilst usage of polyacetals is substantially less, in tonnage terms, than that of the major polymers such as polyethylene, polypropylene, PVC and polystyrene, it is perhaps worth noting that they are used in a very large number of applications. This, however, commonly is in the form of small mouldings. For instance, there was an example quoted in the 1970s of a small Italian car that contained some 450 components made from polyacetals, weighing only one kilogram in total.

19.4 MISCELLANEOUS ALDEHYDE POLYMERS

A large number of polymers from aldehydes have been reported in the literature¹⁴⁻¹⁶ but, apart from those polymers already described, they are not of commercial importance.

With the exception of formaldehyde, the aldehydes may polymerise to give varying molecular configurations and, depending on the stereo-regulating influence of the catalysts, either amorphous rubber or crystalline polymers may be obtained. It may, however, be mentioned that in such cases as isobutyraldehyde, n-heptaldehyde and chlorinated acetaldehydes the steric hindrance of side groups allows polymerisation to proceed only when the molecules are in certain configurations. In these cases a degree of stereo-regularity may be imposed.

Care has to be taken in the polymerisation of aldehyde polymers in order to achieve reproducible results. It is also difficult to stabilise most of the products since thermodynamics frequently favour depolymerisation at temperatures a little above or at room temperature.

In the immediate future it is unlikely that any of these polymers will attain commercial significance. Hopes that polyhaloaldehydes such as polychloral might be of some use because of their good acid stability have not been realised. This is because polymers prepared to date have poor alkali and thermal resistance, decomposing without melting. Chloral-dichloroacetaldehyde copolymers have also proved similarly disappointing.

19.5 POLYETHERS FROM GLYCOLS AND ALKYLENE OXIDES

If ethylene glycol is subjected to vigorous dehydrating conditions, simple molecules such as dioxan and acetaldehyde may be prepared (*Figure 19.10*).

Under appropriate conditions it is possible to obtain linear polymers, the poly(ethylene oxides), from either glycol or oxide (*Figure 19.11*).

Controlled polymerisation of ethylene oxide under alkaline conditions will produce a range of polymers marketed under the trade name Carbowax. These have molecular weights in the range 1500–20 000 and are greases or waxes according to their degree of polymerisation. Lower molecular weight polymers

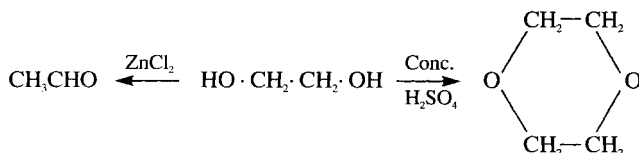


Figure 19.10

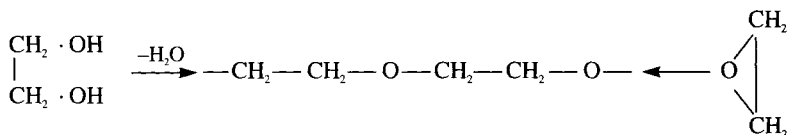


Figure 19.11

have also been prepared, of which carbitol, $\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, may be considered as the limiting dimer.

In 1958 the Union Carbide Corporation introduced high molecular weight, highly crystalline ethylene oxide polymers under the trade name Polyox.¹⁷ Although similar in appearance to polyethylene they are miscible with water in all proportions at room temperature.

Unlike the lower molecular weight poly(ethylene oxide)s these materials are tough and extensible, owing to their high molecular weight and their crystallinity. Typical mechanical properties of the polymer are given in *Table 19.5*

Table 19.5 Some properties of a medium-high molecular weight ethylene oxide polymer¹⁷

Tensile strength	1800–2400 lbf/in ² (13–22 MPa)
Yield strength	1000–1500 lbf/in ² (7–11 MPa)
Ultimate elongation	700–1200%
Shore A hardness	99
Melting point	66°C
Brittle temperature	–50°C

The tensile strength will depend to a large extent on the rate of extension and the relative humidity. There is a severe drop in tensile values as the relative humidity exceeds 80%.

Unlike other water-soluble resins the poly(ethylene oxide)s may be injection moulded, extruded and calendered without difficulty. The viscosity is highly dependent on shear rate and to a lesser extent on temperature. Processing temperatures in the range 90–130°C may be used for polymers with an intrinsic viscosity of about 2.5. (The intrinsic viscosity is used as a measure of molecular weight.)

The polymers are of interest as water-soluble packaging films for a wide variety of domestic and industrial materials. (Additional advantages of the poly(ethylene oxide)s are that they remain dry to the feel at high humidities and may be heat sealed.) The materials are also of use in a number of solution application such as textile sizes and thickening agents. As a water-soluble film they are competitive with poly(vinyl alcohol) whereas in their solution applications they meet competition from many longer established natural and synthetic water-soluble polymers.

19.5.1 Elastomeric Polyethers

The flexible backbone of an aliphatic polyether chain can lead to polymers with a low glass transition temperature. Providing crystallisation can be inhibited by

either copolymerisation or by the polymers having a substantially atactic structure, many of these materials are rubbery. Incorporation of chlorine atoms into the structure will give materials of good hydrocarbon oil resistance and, providing such attachments are not too close to the chain backbone, the glass transition temperature will not be greatly raised.

This approach was used in the development of the epichlorhydrin rubbers which became commercially available around 1965 from Goodrich (Hydrin) and Hercules (Herclor). Both homopolymers of epichlorhydrin (Hydrin 100, Herclor H) and copolymers of epichlorhydrin with ethylene oxide (Hydrin 200, Herclor C) became available. (In 1986 Hercules sold their interest in these materials to Goodrich, who in turn later sold this to Nippon Zeon).

Initiation of polymerisation is said to be effected by zinc diethyl–water and aluminium trialkyl–water–acetyl acetone systems to give the structures indicated in *Figure 19.12*.

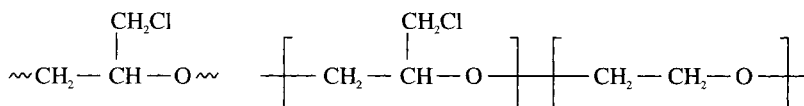


Figure 19.12

The polymers are amorphous with brittle points (quite closely related to the T_g) of about -15°C and -40°C respectively.

Vulcanisation can be effected by diamines, polyamines and lead compounds such as lead oxides and basic lead phosphite. The homopolymer vulcanisate is similar to butyl rubber in such characteristics as low air permeability, low resilience, excellent ozone resistance, good heat resistance and good weathering resistance. In addition the polyepichlorohydrins have good flame resistance. The copolymers have more resilience and lower brittle points but air impermeability and oil resistance are not so good. The inclusion of allyl glycidyl ether in the polymerisation recipe produces a sulphur-curable elastomer primarily of interest because of its better resistance to 'sour gas' than conventional epichlorhydrin rubbers.

Epichlorhydrin rubbers, whilst being speciality materials, have a useful combination of properties which leads to their use in many applications such as gaskets, oil-field components, fuel pump diaphragms, oil seals, fuel and hydraulic hose and printing rollers.

Copolymers of propylene oxide with a cure site monomer (usually allyl glycidyl ether used to a level of about 10% of the total monomer) were first described in 1963 and first marketed by General Tire and Rubber as Dynagen XP-139 in the 1960s. This material was then marketed as Parel by Hercules until 1986 when they sold their interest in the material to Goodrich. (As with the epichlorhydrin rubbers, this interest was later sold on to Nippon Zeon). This material has a strong structural resemblance to the epichlorhydrin rubbers, the absence of the chlorine atoms reducing oil and flame resistance but improving low-temperature flexibility. Although sulphur-cured, the rubbers have very good heat resistance and an operating range of -60°C to $+150^\circ\text{C}$. They are similar to natural rubber in exhibiting high resilience and excellent flex life, but in addition show excellent low-temperature properties together

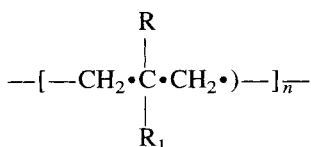
with good heat resistance, good ozone resistance and moderate oil resistance.

A number of other polyethers derived from polyfunctional hydroxy compounds or alkylene oxides are important intermediates in the manufacture of polyurethanes. These are dealt with in Chapter 27.

19.6 OXETANE POLYMERS

In the early 1950s novel polyethers were prepared in the laboratories of the Hercules Powder Company and of Imperial Chemical Industries Limited from oxacyclobutane derivatives. One such polyether that from 3,3-dichloromethyl-1-oxacyclobutane, was marketed by the first named company in 1959 under the trade name of Penton. Commercial manufacture of this material had, however, ceased by the end of 1972.

The polymers are of the general form



and some properties of specific polymers are given in *Table 19.6*.

Table 19.6 Properties of some oxetane polymers¹⁸

R	R ₁	Melting point (°C)	Nature	Solubility
CH ₂ Cl	CH ₂ Cl	180	crystalline	gen. insoluble
CH ₂ Cl	CH ₂ OAc	—	amorphous	insoluble in H ₂ O
CH ₂ OAc	CH ₂ OAc	—	amorphous	soluble in H ₂ O
CH ₂ OH	CH ₂ OH	>280	crystalline	insoluble
CH ₃	CH ₃	47	crystalline	insoluble

The chloromethyl derivatives may be prepared from pentaerythritol via the trichloride or trichloride monoacetate (*Figure 19.13*).

The monomer, 3,3-dichloromethyl-1-oxacyclobutane, has the following characteristics¹⁹

Boiling point	83°C at 11 mmHg
Melting point	18.75°C
Density (25°C)	1.2951 g/cm ³
Refractive index (20°C)	1.4858

The patent literature²⁰ indicates that polymerisation may be carried out in the range -80 to +25°C using boron trifluoride or its etherate as catalyst.

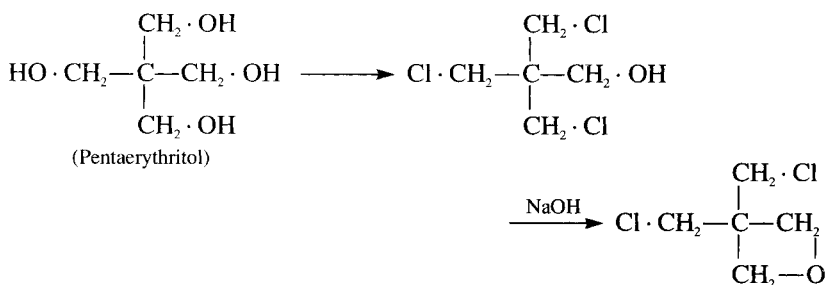


Figure 19.13

Solvents mentioned include hexane, benzene, liquid sulphur dioxide, chloroform, methylene dichloride and ethyl bromide. Where chlorinated solvents are employed the polymer is separated by addition of methanol, filtered, washed with methanol and the product dried *in vacuo* at 60°C.

The commercial polymer was said to have a number average molecular weight of 250 000–350 000.²¹ Because of its regular structure (Figure 19.4) it is capable of crystallisation.

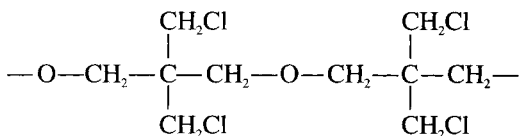


Figure 19.14

Two crystalline forms have been observed.²² One is formed by slow cooling from the melt and the other by slow heating of the amorphous polymer. The properties of the commercial products were therefore to some extent dependent on their heat history. Glass transition temperatures observed range from 7 to 32°C and depend on the time scale of the method of measurement.²²

Typical properties of Penton are given in Table 19.7.²¹

Consideration of the figures given in Table 19.7 shows that the physical properties of the chlorinated polyethers are not particularly outstanding when compared with other plastics materials. On the other hand, apart from a somewhat low impact strength, these figures reveal no particular limitation.

The principal applications of these plastics arose from their very good chemical resistance, as they are resistant to mineral acids, strong alkalis and most common solvents. They were, however, not recommended for use in conjunction with oxidising acids such as fuming nitric acid, fuming sulphuric acid or chlorosulphonic acid, with fluorine or with some chlorinated solvents, particularly at elevated temperatures.

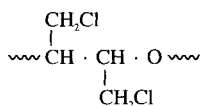
It was claimed that the maximum continuous operating temperature in most chemical environments was 120°C and even 140–150°C in some instances.²¹

The major chemical applications were in the form of pipe and tank linings and injection moulded valve and pump parts. Coatings could be applied to metals by means of fluidised bed, water suspension and organic dispersion techniques.

Table 19.7 Properties of Penton

Property	ASTM test	Value	Units
Tensile strength (23°C)	D.638	6000	lbf/in ²
		41	MPa
Modulus of elasticity (23°C)	D.638	150 000	lbf/in ²
		1100	MPa
E_b	D.638	130	%
Flexural strength (23°C)	D.790	5000	lbf/in ²
		900	MPa
Izod impact strength (23°C)	D.758	0.4	ft lb per in notch
Deflection temperature	D.648		
264 lbf/in ²		99	°C
66 lbf/in ²		140	°C
Thermal conductivity	D.696	0.13	W/mK
Volume resistivity	D.257	1.5×10^{18}	Ω m
Power factor			
60–10 ⁶ Hz (23°C)		~0.011	
60 Hz (100°C)		0.045	
10 ⁴ –10 ⁶ Hz (100°C)		0.003	
Dielectric constant (varying according to temperature and frequency)		2.8–3.5	
Dielectric strength		155	Kv/cm
Flammability	D.635		self extinguishing

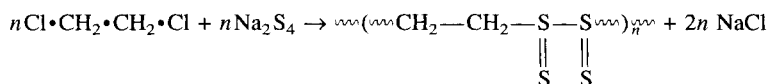
In 1975 the Hercules company announced²³ the preparation of a polymer very similar in structure to the discontinued Penton. The new polymer is poly-(1,2-dichloromethyl)ethylene oxide:



It may be prepared in two stereo-regular forms, *cis*- and *trans*-. The *cis*-polymer, which crystallises in zig-zag form, has a T_m of 235°C, whilst the *trans*-polymer, which crystallises in helical form, melts at the much lower temperature of 145°C. Tensile strengths of both forms are reportedly similar to that of Penton whilst the tensile modulus of 2300 MPa is about twice as high. Unfortunately the material is rather brittle with an impact strength only about half that of polystyrene although this may be improved by orientation.

19.7 POLYSULPHIDES

In 1928 J. C. Patrick attempted to produce ethylene glycol by reacting ethylene dichloride with sodium polysulphide. In fact a rubbery polymer was formed by the reaction:



This polymer became the first commercially successful synthetic rubber, with the trade name Thiokol A.

Other commercial products were produced using different dihalides as indicated in *Table 19.8*.

Table 19.8

<i>Dihalide</i>	<i>Trade names of polymer</i>
(1) Di-2-chloroethyl ether $\text{Cl}\cdot(\text{CH}_2)_2\cdot\text{O}\cdot(\text{CH}_2)_2\text{Cl}$	Thiokol B Perduren G Novoplas
(2) Di-2-chloroethyl formal $\text{Cl}\cdot(\text{CH}_2)_2\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot(\text{CH}_2)_2\text{Cl}$	Perduren H Thiokol ST
(3) 1,3-Glycerol dichlorohydrin $\text{Cl}\cdot\text{CH}_2\cdot\underset{\text{OH}}{\text{CH}}\cdot\text{CH}_2\cdot\text{Cl}$	Vulcplas

All these materials could be vulcanised into rubbers with good oil resistance but with a high compression set.

Further variations in the properties of the polysulphides were also achieved by the following means:

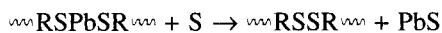
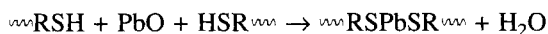
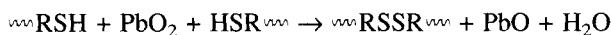
- (1) The use of mixtures of dihalides, Thiokol FA, which has less odour and a lower brittle point than Thiokol A, is produced from a mixture of ethylene dichloride and di-2-chloroethyl formal.
- (2) By varying the value of the ranking x in the polysulphide Na_2S_x . The tetrasulphide is necessary to obtain a rubber with ethylene dichloride, but disulphides may be used with other dichlorides.
- (3) By incorporation of some trihalide to give a branched polymer such as Thiokol ST (about 2% of 1,2,3-trichloropropane is used in this instance). The resultant vulcanisates have lower cold flow and compression set than obtained with Thiokol A.
- (4) By reduction in the degree of polymerisation. To produce processable rubbers the original polymers are masticated with substances such as benzothiazole disulphide and tetramethylthiuram disulphide. The more severe degradation techniques to produce liquid polysulphides are mentioned below.

The general method of preparation of the polysulphides is to add the dihalide slowly to an aqueous solution of sodium polysulphide. Magnesium hydroxide is often employed to facilitate the reaction, which takes 2–6 hours at 70°C.

The early polysulphides were made more elastic, after shaping, by a chain extension process rather than by cross-linking. As a result of producing polymers of much higher molecular weight in this way some chain entanglements occurred to give what were in effect physical cross-links. However, the rubber, even when 'vulcanised', showed a high compression set, particularly at elevated temperatures.

By introducing branch points into the polymer chains, for example by incorporating about 2% of 1,2,3,-trichloropropane into the polymerisation recipe, chain extension may proceed in more than two directions and this leads to the formation of networks by chemical cross-links. However, with these structures interchange reactions occur at elevated temperatures and these cause stress relief of stressed parts and in turn a high compression set.

Early examples of such branched polysulphides, e.g. Thiokol FA, are believed to possess hydroxyl end groups and are coupled by means of zinc compounds such as the oxide, hydroxide, borate and stearate by a mechanism which is not understood. Later elastomers, e.g. Thiokol ST, have been modified by a restricted reductive cleavage (see below) and this generates thiol (mercaptan) end groups. These may be vulcanised by oxidative coupling as illustrated below with lead peroxide:

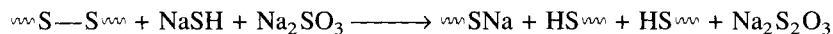


Vulcanisation may also be brought about by zinc and calcium peroxides, *p*-quinone dioxime, epoxide resins, phenolic resins and di-isocyanates.

Other mild oxidising agents which abstract the terminal hydrogen atoms and thus facilitate disulphide formation may be used as vulcanising agents. They include benzoyl peroxide, *p*-nitrosobenzene and *p*-quinone dioxime.

The applications of polysulphide rubbers are due to their excellent oil and water resistance and their impermeability to gases. Because of other factors, including their unpleasant odour, particularly during processing, they are much less used than the two major oil-resistant synthetic rubbers, the polychloroprenes and the nitrile rubbers.

From the point of view of the plastics technologist the most useful products are the low molecular weight polysulphides^{24,25} with molecular weights ranging from 300 to 7500. These are produced by reductive cleavage of the disulphide linkage of high molecular weight polysulphides by means of a mixture of sodium hydrosulphide and sodium sulphite. The reaction is carried out in water dispersion and the relative amounts of the hydrosulphide and sulphite control the extent of cleavage.

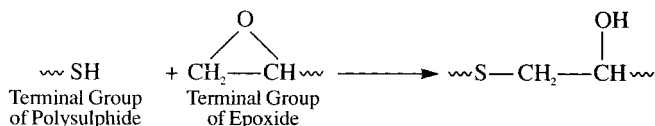


The sodium salt of the polysulphide is converted back to the free thiol on coagulation with acid.

These polymers are liquids which may usefully be cast or used for impregnation and caulking compounds. In addition they may be 'vulcanised' by a variety of agents, ostensibly by a chain lengthening process. It should, however, be noted that these polymers normally contain small quantities of trichloropropane in the original monomer mix so that the three-dimensional chain extension will lead to cross-linking.

Similar reactions also occur with organic peroxides, dioximes, paint driers such as cobalt naphthenate and furfural. It is interesting to note that the cure time is dependent on the humidity of the atmosphere. With lead peroxide the rate doubles by increasing the relative humidity from 40 to 70%. The most important

reaction is, however, that with epoxy resins (Chapter 26). These contain epoxide rings and chain linkage occurs by a 'polyaddition' mechanism.

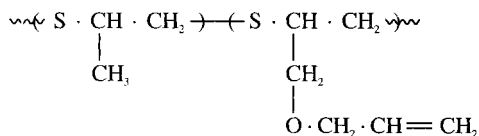


The normal amine hardeners used with epoxy resins are employed in conjunction with the polysulphides. The resulting products become more flexible the greater the percentage of polysulphide present and therefore a range of materials may be produced which vary from brittle resins to soft rubbers. Incorporation of relatively small amounts of polysulphide (20%) considerably increases the impact strength of the epoxy resins. The viscosity of the uncured epoxy resin is also reduced and so polysulphides can be used with advantage for laminating, adhesives and castings. In the latter case the slightly inferior electrical properties resulting may be of some limitation.

A number of other aliphatic sulphide polymers have appeared with the general structure (I) as opposed to the older materials of type (II) typified by the Thiokol materials:



These include copolymers of propylene sulphide with 3–10% of allyl glycidyl thioether and which may be considered as a thio-analogue of the propylene oxide-allyl glycidyl ether rubber briefly mentioned in Section 19.5:



These materials are also rubbery but are not believed to be in commercial production.

Another type consists of mixtures of polythiols and polyenes with at least two functional groups per molecule but of undisclosed structure. The prepolymers, supplied by W R Grace, range from low-viscosity fluids to grease-like substances. On exposure to radiation (e.g. electron beams or ultraviolet light) a combination reaction involving a double bond and a mercaptan group occurs, leading to gelation. The resultant cross-linked polymer may be elastic, hard or stiff depending on the prepolymer used. They are being promoted as coatings, adhesion agents and encapsulating agents for electronic components.

References

Acetal polymers

1. BUTLEROV, A., *Ann.* **III**, 242 (1859)
2. STAUDINGER, H., *Die Hochmolekularen Organischen Verbindungen*, Julius Springer, Berlin (1932).

3. *U.S. Patent*, 2,768,994 (October 1956)
4. *British Patent*, 770, 717 (July 1957)
5. *British Patent*, 742, 135 (1956)
6. SCHWEITZER, C. E., MACDONALD, R. N., and PUNDERSON, J. O., *J. Appl. Polymer Sci.*, **1** (2), 158 (1959)
7. *U.S. Patent* 3,027,352
8. ALSUP, R. G., PUNDERSON, J. O., and LEVERETT, G. F., *J. Appl. Polymer Sci.*, **1** (2), 185 (1959)
9. SITTIG, M., *Polyacetal Resins*, Gulf Publishing, Houston (1963)
10. KOCH, T. A., and LINDVIG, P. E., *J. Appl. Polymer Sci.*, **1** (2), 164 (1959)
11. HAMMER, C. F., KOCH, T. A., and WHITNEY, J. F., *J. Appl. Polymer Sci.*, **1** (2), 169 (1959)
12. LINTON, W. H., and GOODMAN, H. H., *J. Appl. Polymer Sci.*, **1** (2), 179 (1959)
13. LINTON, W. H., *Trans. Plastics Inst.*, **28** (75), 131 (June 1960)
14. FURUKAWA, J., and SAEGUSA, T., *Polymerisation of Aldehydes and Oxides*, Interscience, New York (1963)

Miscellaneous aldehyde polymers and polyethers

15. BEVINGTON, J. C., *Brit. Plastics*, **35**, 75 (1962)
16. BEVINGTON, J. C., *Chem. Ind.*, 2025 (1961)
17. DAVIDSON, R. L., and SITTIG, M., *Water Soluble Resins*, Reinhold, New York (1962)

Oxetane polymers

18. FARTHING, A. C., *J. Appl. Chem.*, **8**, 186 (1958)
19. FARTHING, A. C., and REYNOLDS, R. J. W., *J. Polymer Sci.*, **12**, 503 (1954)
20. *British Patent* 723,777 (ICI), *British Patent* 769,116 (Hercules); *U.S. Patent* 2,722,340; *U.S. Patent* 2,722,492; *U.S. Patent* 2,722,487; *U.S. Patent* 2,722,493; *U.S. Patent* 2,722,520 (Hercules); *British Patent* 758,450; *British Patent* 764,053; *British Patent* 764,284 (Hercules)
21. FLETCHER, F. T., *Trans. Plastics Inst.*, **30**, 127 (1962)
22. SANDIFORD, D. J. H., *J. Appl. Chem.*, **8**, 188 (1958)
23. VANDENBERG, E. J., *J. Polymer Sci. (Chem)*, **13**, 2221 (1975)

Polysulphides

24. FETTES, E. M., and JORCZAK, J. S., *Ind. Eng. Chem.*, **42**, 2217 (1950)
25. JORCZAK, J. S., and FETTES, E. M., *Ind. Eng. Chem.*, **43**, 324 (1951)

Bibliography

- AKIN, R. B., *Acetal Resins*, Reinhold, New York (1962)
- BAILEY, F. E., and KOLESKE, J. V., *Poly(ethylene oxide)*, Academic Press, New York (1976)
- BARKER, S. J., and PRICE, M. B., *Polyacetals*, Iliffe, London (1970)
- DAVIDSON, R. L., and SITTIG, M., *Water Soluble Resins*, Reinhold, New York (1962)
- FURUKAWA, J., and SAEGUSA, T., *Polymerisation of Aldehydes and Oxides*, Interscience, New York (1963).
- SERLE, A. G., Chapter 6 in *Engineering Thermoplastics* (Ed. MARGOLIS, J. M.), Marcel Dekker, New York (1985)
- SITTIG, M., *Polyacetal Resins*, Gulf Publishing, Houston (1963)

Reviews

- ECKENBERGER J. *Kunststoffe*, **86** (10), 1514–16 (1996)
- SABEL, H.-D., *Kunststoffe*, **70**, 641–5 (1980)
- SABEL, H.-D., and STRUTH, U., *Kunststoffe*, **80** (10), 1118–22 (1990).
- WOLTERS, E., and SABEL, H.-D., *Kunststoffe*, **77**, 997–1000 (1987)

Polycarbonates

20.1 INTRODUCTION

Reaction of polyhydroxy compounds with polybasic acids gives rise to condensation polymers containing ester ($-\text{COO}-$) groups. Because of the presence of these groups such polycondensates are known as polyesters and find use in such diverse applications as fibres, surface coatings, plasticisers, rubbers and laminating resins. These materials are discussed in detail in Chapter 25.

By reaction of polyhydroxy compounds with a carbonic acid derivative, a series of related polymers may be produced with carbonate ($-\text{O}\cdot\text{CO}\cdot\text{O}-$) linkages, the polymers being referred to as polycarbonates. Carbonic acid, $\text{CO}(\text{OH})_2$, itself does not exist in the free state but by means of ester exchange (*Figure 20.1*) (I) and phosgenation techniques (II) it is possible to produce useful products.

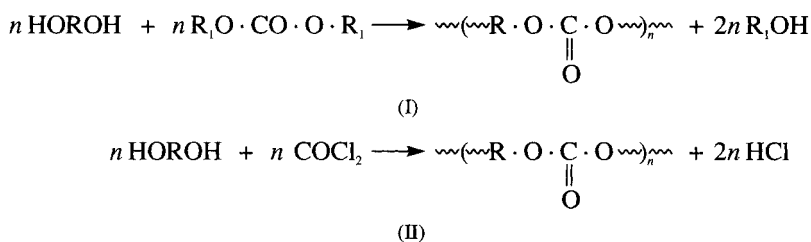


Figure 20.1

Polycarbonates were first prepared by Einhorn¹ in 1898 by reacting the dihydroxybenzenes, hydroquinone and resorcinol, separately with phosgene in solution in pyridine. The hydroquinone polycarbonate was an infusible and insoluble crystalline powder whereas the resorcinol polymer was an amorphous material melting at about 200°C. The third dihydroxybenzene, catechol, yields a cyclic carbonate only, which is not surprising bearing in mind the proximity of

the two hydroxy groups to each other. By the use of diphenylcarbonate, Bischoff and von Hedenström² prepared similar products by an ester-exchange reaction in 1902.

In 1930 Carothers and Natta³ prepared a number of aliphatic polycarbonates using ester-interchange reactions. These materials had a low melting point, were easily hydrolysed and did not achieve commercial significance.

Carothers also produced a number of aliphatic linear polyesters but these did not fulfil his requirements for a fibre-forming polymer which were eventually met by the polyamide, nylon 66. As a consequence the polyesters were discarded by Carothers. However, in 1941 Whinfield and Dickson working at the Calico Printers Association in England announced the discovery of a fibre from poly(ethylene terephthalate). Prompted by the success of such a polymer, Farbenfabriken Bayer initiated a programme in search of other useful polymers containing aromatic rings in the main chain. Carbonic acid derivatives were reacted with many dihydroxy compounds and one of these, bis-phenol A, produced a polymer of immediate promise.

Independently at the General Electric Company in America, work was being carried out in search of thermally and hydrolytically stable thermosetting resins. As a by-product from this work the research team at General Electric also produced polycarbonates from bis-phenol A so that by 1958 production of bis-phenol A polycarbonates was being carried out in both Germany and the USA.

Today about 75% of the market is held by General Electric and Bayer with their products Lexan and Makrolon respectively. Other manufacturers are ANIC (Italy), Taijin Chemical Co., Mitsubishi Edogawa and Idemitsu Kasei in Japan and, since 1985, Dow (USA) and Policarbonatos do Brasil (Brazil). Whilst this market is dominated by bis-phenol A polycarbonates, recent important developments include alloys with other thermoplastics, polyester carbonates and silicone-polycarbonate block copolymers.

20.2 PRODUCTION OF INTERMEDIATES

As already indicated, the polycarbonates may be produced from a wide range of polyfunctional hydroxy compounds. In practice only the diphenyl compounds have proved of much interest and the only polycarbonate of commercial significance is derived from bis-phenol A 2,2-bis-(4-hydroxyphenyl) propane.

Bis-phenol A may be produced by the condensation of phenol with acetone under acidic conditions (*Figure 20.2*).

Schnell⁴ states that the initial product is isopropenylphenyl which then reacts with a further molecule to form the bis-phenol A.

At elevated temperatures the second stage of the reaction takes place in the reverse direction and so reactions are carried out below 70°C. In order to achieve

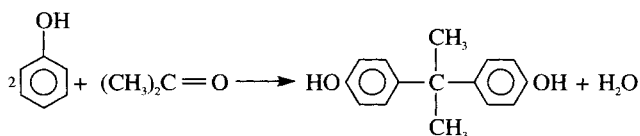


Figure 20.2

a high yield, an excess of phenol is employed and the initial reaction product is a bis-phenol A-Phenol adduct. The bis-phenol A may be separated from the adduct by crystallisation from appropriate solvents or by distilling off the phenol.

Improvements in the rate of the condensation reaction have been claimed with the use of co-catalysts such as an ionisable sulphur compound⁵ and by pre-irradiation with actinic light.⁶

Unless great care is taken in control of phenol/acetone ratios, reaction conditions and the use of catalysts, a number of undesirable by-products may be obtained such as the *o*-,*p*- and *o*-,*o*- isomers of bis-phenol A and certain chroman-type structures. Although tolerable when the bis-phenol A is used in epoxy resins, these have adverse effects on both physical properties and the colour of polycarbonate resins.

Residual traces of these impurities must thus be removed by some technique such as recrystallisation from chlorobenzene or aqueous alcohol. The melting point is a useful measure of purity and for polycarbonate resins the melting point should be in the range 154–157°C compared with values of 140–150°C for epoxy resin grade bis-phenol A.

Phosgene, employed in both of the main processes, is prepared commercially from carbon monoxide and chlorine.

Diphenyl carbonate, an alternative source of the carbonate group to phosgene, may be obtained by reacting phenol with phosgene in aqueous caustic soda solution, the reaction being accelerated by tertiary amines. The diphenyl carbonate can be purified by redistillation.

20.3 POLYMER PREPARATION

There are four possible practical routes to linear polycarbonates:

- (1) Ester exchange of dihydroxy compounds with diesters of carbonic acid and monofunctional aromatic or aliphatic hydroxy compounds.
- (2) Ester exchange of bis-alkyl or bis-aryl carbonates of dihydroxy compounds with themselves or with other dihydroxy compound.
- (3) Reaction of dihydroxy compounds with phosgene in the presence of acid acceptors.
- (4) Reaction of the bis-chlorocarbonic acid ester of dihydroxy compounds with dihydroxy compounds in the presence of acid acceptors.

Of these four routes the first and third have been studied intensively, in particular in the preparation of the bis-phenol A polycarbonates. Since this polycarbonate is at present the only one of major commercial importance the following remarks will apply to this only unless otherwise stated.

20.3.1 Ester Exchange

The equation for the ester-exchange reaction (1) is shown in *Figure 20.3*.

In this method the reaction is typically carried out at 180–220°C at 20–30 mmHg pressure until 80–90% of the phenol of condensation has been removed. The temperature is then gradually raised to 290–300°C and the pressure reduced to 1 mmHg or below. The melt viscosity increases considerably

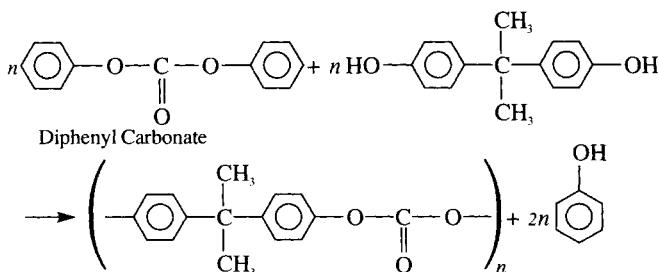


Figure 20.3

during this period and the reaction is stopped while the material can still be forced out of the kettle by an inert gas.

The high melt viscosity limits the molecular weights obtainable and although number average molecular weights of 50 000 can be obtained it is difficult to attain values of above 30 000 without special equipment.

Because bis-phenol A is somewhat unstable at elevated temperature it is desirable to work with an excess of diphenyl carbonate so that the bis-phenol A is rapidly used up. The reaction may be conveniently carried out using twice or more than twice the theoretical quantity of diphenyl carbonate so that the initial reaction product is the bis(phenyl carbonate) of bis-phenol A (Figure 20.4 (a)).

Polymerisation then proceeds by splitting out of diphenyl carbonate to give the polycarbonate resin (Figure 20.4 (b)).

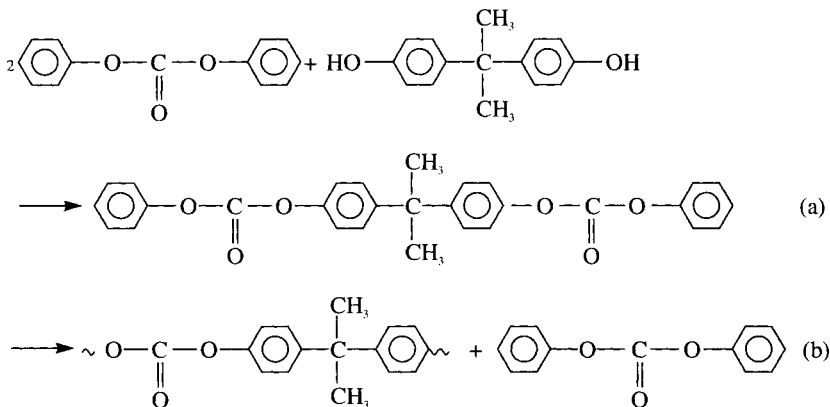


Figure 20.4

This variation has the obvious disadvantage that the less volatile diphenyl carbonate is more difficult to remove than phenol.

A number of basic materials such as hydroxides, hydrides and amides of alkaline and alkaline earth metals and metal oxides such as zinc oxide and antimony oxide are useful catalysts for the reaction.⁷ Acid ester-exchange catalysts such as boric acid, *p*-toluene sulphonic acid and zinc chloride are less

effective. Catalyst systems are not essential when diaryl carbonates are used as carbonate sources and do in fact cause problems in their subsequent removal.

Although of importance in the early days of polycarbonate production the transesterification process was virtually abandoned in the mid-1970s. This was because although it avoids the use of solvents (as required in the phosgenation process described below) it has the disadvantages of special equipment being required for the high reaction temperatures, good vacuum systems in order to work at very low pressures, the need to handle highly viscous melts and a tendency to give a yellow colour due to high temperature side reactions. Interestingly in the mid-1990s improvements were made to the process details and a plant using the transesterification process has been reported to be in operation in Japan (GE/Mitsui)

20.3.2 Phosgenation Process

High molecular weight polycarbonates may be produced without undue difficulty by the phosgenation process. The basic reaction is as shown in *Figure 20.5*.

For this reaction to proceed it is obviously necessary to remove the hydrochloric acid formed, preferably by means of hydrohalide acceptor.

The attractive possibility of dissolving the bis-phenol A in caustic soda solution and bubbling phosgene into it is not practical since the polymer is insoluble in the caustic soda and precipitates out at a low and variable molecular weight.

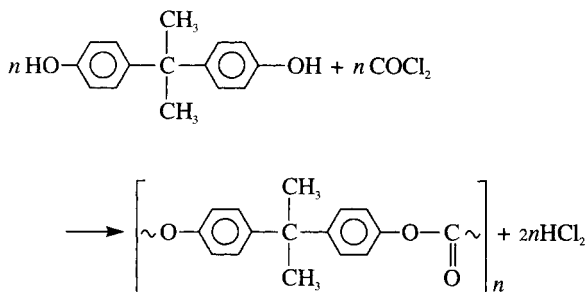


Figure 20.5

Greater success has been achieved with organic solvents which are also hydrohalide acceptors, pyridine being a specific example.

Typically in such a process the bis-phenol A is dissolved in about ten times its weight of pyridine and vigorously stirred at 25–35°C. Phosgene is then bubbled into the solution and in a few minutes the pyridine hydrochloride starts to precipitate. As polymer is formed the viscosity of the solution increases and eventually becomes too great for stirring. The polymer is then recovered by the addition of a solvent such as methyl alcohol which dissolves the pyridine hydrochloride but precipitates the polymer.

A variation of this process involves the formation of a preformed pyridine-phosgene complex. Polymerisation will then be effected by adding a solution of bis-phenol A.

Because of the cost of pyridine the phosgenation process may be carried out with a mixture of pyridine and a non-hydrohalide-accepting solvent for the polymer and the growing complexes. Suitable solvents include methylene dichloride, tetrachlorethane and chloroform. Although unsubstituted aromatic hydrocarbons may dissolve the solvent they are not effective solvents for the acid chloride-pyridine complexes.

Today the most important process is that of *interfacial polymerisation* first described in Ger Patent 959 497⁸. In a typical process the disodium salt of bisphenol A in an alkaline aqueous solution or suspension is reacted with phosgene in the presence of an inert organic solvent such as methylene chloride, chlorobenzene, tetrahydrofuran or dioxane. While initially a solvent for the phosgene it dissolves arylchloroformates and oligocarbonates formed as the polycondensation reaction proceeds at the interface or just inside the aqueous phase. The arylchloroformates and oligocarbonates then condense to form a high molecular weight polymer in the presence of a catalyst such as triethylamine or tri-*n*-propylamine. Reaction temperatures are in the range 10–35°C. The polymer is recovered by washing the organic phase with water, neutralisation of the caustic soda and either precipitation of the polymer by a non-solvent or evaporation of the solvent by thorough washing. The molecular weight is controlled by the use of monofunctional phenols, particularly branched phenols such as *iso*-octyl phenol.

While the interfacial polycondensation-by-phosgenation process has hazards involving the use of phosgene and solvents, the need for solvent recovery and the requirement for purifying and densifying the polymer it does have the advantage of being able to produce colourless high molecular weight polymers using fairly simple processing equipment under moderate preparation conditions and as indicated above is the most important process for making polycarbonates on a commercial scale.

20.4 RELATION OF STRUCTURE AND PROPERTIES

A study of the molecular structure of bis-phenol A polycarbonates enables one to make fairly accurate predictions of the bulk properties of the polymer. The relevant factors to be considered are:

- (1) The molecule has a symmetrical structure and therefore questions of stereospecificity do not arise.
- (2) The carbonate groups are polar but separated by aromatic hydrocarbon groups.
- (3) The presence of benzene rings in the chain restricts flexibility of the molecule.
- (4) The repeating unit of the molecule is quite long.

Because of its regularity it would be expected that the polymer would be capable of crystallisation. In practice, however, the X-ray pattern characteristics of crystalline polymer is absent in conventionally fabricated samples. On the other hand films which have been prepared by slow evaporation from solvent or by heating for several days at 180°C do exhibit both haziness and the characteristic X-ray diagram. The amount of crystallisation and the size of the crystallite structures decrease with an increase in the molecular weight of

the polymer. These effects are no doubt associated with both the stiffness of the molecule and its long repeat unit.

The crystalline structure of bis-phenol A polymers has been thoroughly studied by Prietschk⁹ and some of the data he obtained on the crystal structure are summarised in *Table 20.1*.

Table 20.1 Crystal structure data of bis-phenol A polycarbonates (after Prietschk)⁹

Crystal type	rhombic
Cell constants	$a = 11.9$ $b = 10.1$ $c = 21.5$
No. of units in elementary cell	8
Crystal density	1.3 g/cm ³
Macroscopic density	1.2 g/cm ³

Figure 20.6 shows the disposition of the molecules in the elementary cell as determined by Prietschk. It will be seen that in the crystalline zone the molecules pack in such a way that the methyl groups attached to the pivotal carbon atom extend toward the back of the carbonate group of the neighbouring chain.

The rigid molecular backbone of the bis-phenol A polycarbonates leads to a high melting temperature ($T_m = 225\text{--}250^\circ\text{C}$) and glass transition temperature ($T_g = 145^\circ\text{C}$). That this molecular rigidity and not the polar interchain attraction of the ester group or of the benzene rings is the predominating influence may be inferred by comparison of the polycarbonate resin with poly(ethylene terephthalate). This latter polymer has similar chemical groups but has much lower values for T_g and T_m .

It is found that observed values of T_g for the bis-phenol A polycarbonate are somewhat higher than estimated from T_m data by the general rule-of-thumb relation:

$$T_g = \frac{2}{3}T_m$$

propounded in Chapter 4 (temperatures in K). This may well be connected with the fact that the polycarbonate has a higher free volume at its T_g than normally observed with organic polymers. This in turn is probably due to the fact that although the chain is basically frozen some in-chain movement of phenylene, isopropylidene and carbonate groups can occur. These groups have secondary transitions which tend to merge to give a diffuse band in the range -200 to 0°C . When transitions occur over a temperature range in a polymer the polymer does not immediately respond to application of a stress but the small in-chain motions which become possible at temperatures above the secondary transitions allow the stress to be taken up by deformations much greater than would be possible if such motions did not exist. There is accumulating evidence that the toughness of polycarbonate is related to the high free volume below the T_g and its damping capacity over a wide temperature range.

In this respect it should be mentioned that the impact strength may be reduced by annealing, crystallisation and aging. If the polymer is annealed by heating between 80 and 130°C there is a small increase in density and hence there must be a decrease in free volume. It is therefore not surprising to find that there is a large drop in impact strength.

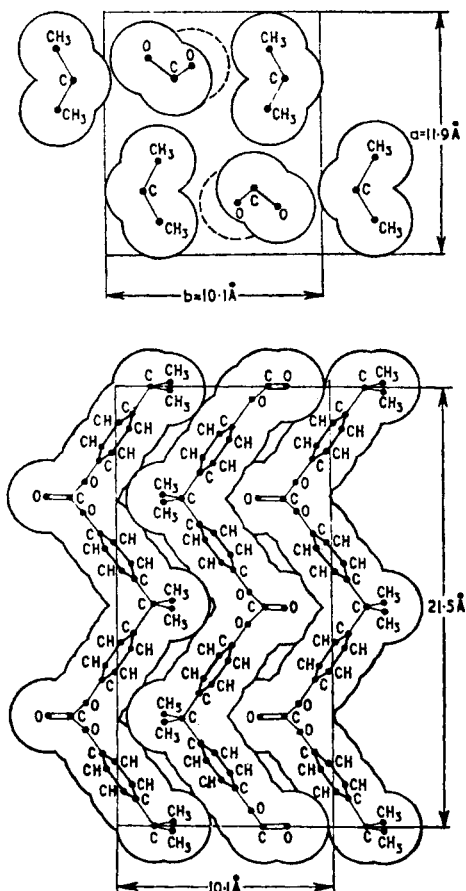


Figure 20.6. Unit cell diagrams for polycarbonate based on bis-phenol A. (After Prietschk⁹)

The limited degree of crystallinity is another factor contributing to the toughness of the polymer. Interchain attraction, particularly in the crystalline zones, contributes to a high yield strength but too much crystallinity would not only reduce free volume but also lead to weak planes at highly stressed spherulite interfaces. Again it is not surprising to find that highly crystalline samples prepared by heating for prolonged periods above their T_g or by precipitating from solutions are quite brittle.

Aging of samples also leads to brittleness but at the present time there appears to be no information on how this affects either free volume or the secondary transitions.

Both the chemical solubility and the electrical properties are consistent with those expected of a lightly polar polymer, whilst reactivity is consistent with that of a polymer containing hydrolysable carbonate ester linkages partially protected by aromatic hydrocarbon groupings. The influence of these factors on specific properties is amplified in subsequent sections.

20.4.1 Variations in Commercial Grades

The range of polycarbonates commercially available has increased greatly in recent years. The main differences between these grades are largely due to:

- (1) Differences in molecular weight.
- (2) The presence or otherwise of a second polyhydroxy compound.
- (3) Differences in additives.

In the usual range of moulding and extrusion materials an increase in molecular weight leads to comparatively small improvements in such properties as tensile strength. It does, however, lead to the usual steep increase in melt viscosity and to an increase in impact strength. This is indicated in *Table 20.2*, which also indicates the recommended processing method. Polymers with number average molecular weights below 20 000 are generally unsuitable as plastics whilst those with molecular weights above 50 000 (particularly those in range of $\bar{M}_n = \text{ca } 70\,000$) are mainly processed into film by solution casting methods.

Table 20.2

\bar{M}_n	Melt Index ASTM D.1238 (300°C) g/10 min	Notched impact strength ASTM D.256 Izod ft lbf in ⁻¹ $\frac{1}{8}$ in	Recommended processing method
23 100–27 700	23.9–12.0	11–13	} Injection moulding
27 700–32 200	11.9–6.0	12–16	
32 000–35 700	5.9–3.0	15–17	} Extrusion blow moulding
35 700–39 100	2.9–1.5	16–18	

Easy flow grades with \bar{M}_n values in the range 18 000–32 000 are particularly useful for thin wall mouldings and where low injection moulding cycle times are of particular importance but as the molecular weight is reduced toward the lower end of this range the polymers become more brittle and more liable to stress cracking. The molecular weight is controlled by the use of monofunctional additives such as *iso*-octyl phenols to give branched alkyl phenyl end groups.

Structurally viscous grades are based on branched polymers (branching being effected by the use of tri- or higher functional phenols). These polymers exhibit a sharp decrease in viscosity with increasing shear rate which makes them particularly suitable for extrusion and blow moulding and also, it is claimed, in reducing drip in case of fire.

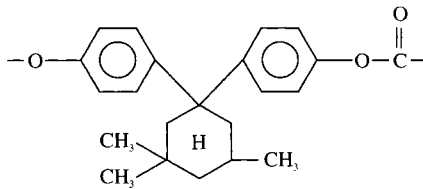
Flame retardant grades usually employ additives (but see below), e.g. sodium 2,4,5-trichlorobenzene sulphonate, sometimes in conjunction with an *anti-dripping agent* which, it is claimed, cross-links the polymer as it burns thus reducing the tendency to drip.

UV-stabilised grades exhibit reduced tendency to yellowing by the use of stabilisers such as benzophenone and benzotriazole compounds (see also Section 7.5.4).

Whilst remaining speciality materials, several copolymers have been marketed over the years in order to enhance certain specific properties whilst retaining the general characteristics of polycarbonates. There are also a number of homopolymers in which the bis-phenol A has been replaced by another bis-phenol compound. The most important of these are summarised below.

- 1) To enhance *flame retardancy* without use of additives, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)propane (tetrabromobis-phenol A) has been used in copolymers with bis-phenol A.
- 2) To enhance *refractive index*, copolymers of bis-phenol S (thiodiphenol) with bis-phenol A have been employed. The refractive index of the copolymer n_o is 1.610 compared with 1.590 for the homopolymer.
- 3) To reduce *melt viscosity* an aliphatic dicarboxylic acid may be used to partially replace the carbonic acid derivative. Easy-flow grades with a melt flow rate of 80 are now available in order to meet the stringent flow requirements involved in compact disc production. Such an improvement in flow rate is, however, at the expense of heat distortion temperature.
- 4) To produce resins for *paints and for electrical insulation, film cast from solution* copolymers based on bis-phenol A and bis-phenol Z (1,1-bis-(4-hydroxyphenyl)cyclohexane) have been used.
- 5) To enhance the *resistance to heat softening* bis-phenol A is substituted by a stiffer molecule. Conventional bis-phenol A polycarbonates have lower heat distortion temperatures (deflection temperatures under load) than some of the somewhat newer aromatic thermoplastics described in the next chapter, such as the polysulphones. In 1979 a polycarbonate in which the bis-phenol A was replaced by tetramethylbis-phenol A was test marketed. This material had a Vicat softening point of 196°C, excellent resistance to hydrolysis, excellent resistance to tracking and a low density of about 1.1 g/cm³. Such improvements were obtained at the expense of impact strength and resistance to stress cracking.

Another approach is to copolymerise bis-phenol A with the bis-phenol of trimethylcyclohexanone (bis-phenol TMC); commercial materials were introduced in 1992.



Bis-phenol TMC segment
in copolymer

The TMC polycarbonate homopolymer has a glass transition temperature of 238°C, nearly 100°C above that of the bis-phenol A polycarbonate. Therefore, copolymers will have intermediate glass transitions depending on the relative proportions of TMC and bis-phenol A. Commercial grades (marketed by Bayer as Apec HT) have Vicat softening points from 158 to

205°C. Other properties are broadly similar to those of conventional bisphenol A polycarbonates. For example, the polymer is clear, with a light transmittance of about 90% at 1 mm thickness. The polymer is also tough, although the notched impact strength is somewhat lower. Being copolymers, the materials are amorphous. These materials are of particular interest where the material is subject to extensive thermal stressing, such as in car headlights, lamps, household appliances and medical applications (where the copolymers are suitable for superheated steam sterilisation at 134°C). There is at present no other plastics material which provides the particular combination of high heat resistance, high transparency, high impact strength and good flow properties at such a level.

A more recent development of interest with this material is that scratch-resistant coatings may be stoved on at temperatures not feasible with conventional bisphenol A polycarbonates to give products with a scratch resistance comparable to glass.

Another approach to increase the heat distortion temperature is to produce cocondensates of bisphenol A with bishydroxyphenyl fluorene. Some variations of this copolymer had heat distortion temperatures in excess of 200°C and with the potential to be produced at lower cost than such temperature-resistant thermoplastics as polysulphones and polyetherimides. Plans to develop this material were however abandoned when it was found, during trials of test materials, that workers developed skin rashes said to be similar to those encountered on contact with poison ivy.

- (6) Polycarbonates with superior *notched impact strength*, made by reacting bisphenol A, bis-phenol S and phosgene, were introduced in 1980 (Merlon T). These copolymers have a better impact strength at low temperatures than conventional polycarbonate, with little or no sacrifice in transparency. These co-carbonate polymers are also less notch sensitive and, unlike for the standard bis-phenol A polymer, the notched impact strength is almost independent of specimen thickness. Impact resistance increases with increase in the bis-phenol S component in the polymer feed. Whilst tensile and flexural properties are similar to those of the bis-phenol A polycarbonate, the polycarbonates have a slightly lower deflection temperature under load of about 126°C at 1.81 MPa loading.

Another recent development is the preparation of a polyester-polycarbonate copolymer. The polymers involve a polyester component based on the reaction between bis-phenol A and iso- or terephthalic acid with the carbonate component arising from the reactions described in Section 20.3 (see Section 20.9).

In common with other polymers the polycarbonates have been blended with other polymers in recent years. The most well-known blends are those with ABS but more recently elastomer-modified grades have made their appearance, some of which may be copolymers (See Section 20.8).

Whilst conventional polycarbonate based on bis-phenol A is essentially linear, branched polymers have recently been introduced. These materials have flow properties and a melt stability that makes them particularly suitable for large (20 litre) water and milk containers. Branched polymers have also been used in the manufacture of twin-walled sheet for the building industry.

Comparatively little information is available concerning the use of additives in commercial grades of polycarbonate. Pigments, heat and ultraviolet stabilisers, blowing agents and fire retardants are used but the range of materials available

is very restricted because of the high processing temperatures involved. It has been found that benzophenone and benzotriazole ultraviolet absorbers are only effective if the polycarbonate composition is treated to become slightly acidic. Very small amounts (ca 0.005%) of stabilisers such as metaphosphoric acid, boron phosphate and phenyl neopentyl phosphite may also be used. Glass fibre is now used in special grades. Depending on the concentration and type of glass fibres, mouldings have increased hardness, flexural strength, modulus of elasticity and fatigue strength but lower moulding shrinkage and coefficient of thermal expansion. The last two properties in particular permit the production of mouldings with high dimensional accuracy and stability. As with all instances involving reinforcement with glass fibres it is necessary to treat the fibre surfaces with a finish to promote adhesion between resin and glass. In the case of polycarbonates very good results are reported with (β -3,4-epoxycyclohexylethyl) trimethoxysilane.

The addition of carbon fibre to polycarbonate can lead to composites with flexural strength three times and flexural modulus seven times that of unfilled resin. Notched Izod impact values are amongst the highest for any fibre-filled thermoplastics material. Flexural creep after 2000 hours loading at 10 000 psi (68.97 MPa) is also minimal. Carbon-fibre-reinforced grades also exhibit enhanced deflection temperatures (149°C for 30% fibre loading under 1.8 MPa loading), low volume and surface resistivities, facilitating dissipation of static charge, lower coefficient of friction and increased wear resistance.

Incorporation of PTFE, silicone resins and glass or carbon fibres can lead to important internally lubricated composites. One grade available from LNP containing 13% PTFE, 2% silicone and 30% glass fibre showed a 100-fold improvement in wear resistance, a 45% reduction in static coefficient of friction, and a 36-fold increase in PV value compared with an unmodified polymer. Traditionally not considered good bearing materials, such modified grades may be used effectively in demanding gear, cam and sliding applications.

Flame retardant grades may not only use additives such as sodium 2,4,5-trichlorobenzene sulphonate but also an *anti-dripping agent* which can cause cross-linking as the polymer burns, thus reducing the tendency to drip.

20.5 GENERAL PROPERTIES

Although somewhat more expensive than the general purpose thermoplastics, polycarbonates have established themselves in a number of applications. The desirable features of the polymer may be listed as follows:

- (1) Rigidity up to 140°C.
- (2) Toughness up to 140°C.
- (3) Transparency.
- (4) Very good electrical insulation characteristics.
- (5) Virtually self-extinguishing.
- (6) Physiological inertness.

The principal disadvantages may be listed as:

- (1) More expensive than polyethylene, polystyrene and PVC.
- (2) Special care required in processing.

Table 20.3 Comparison of mechanical properties of typical commercial bis-phenol A polycarbonates

	Units	Test method	Unfilled grades		Glass-filled grades	
			Low	Medium-high		
MW-range			Low	Medium-high	—	—
% glass fibre			Nil	Nil	20	35
Specific gravity		DIN 53479	1.2	1.2	1.33	1.44
Tensile strength -30°C	lbf/in ² (MPa)	DIN 53455	12 000–13 000 83–90	12 000–13 000 83–90	—	—
+23°C	lbf/in ² (MPa)	ASTM D.638	9500 65	9500 65	16 000 110	18 500 127
+100°C	lbf/in ² (MPa)		5000 35	5000 35	—	—
Elongation at yield	%	DIN 53455	6	6–7	4.5	—
at break	%	DIN 53455	110–120	80–120	8.5	2.7
Modulus of elasticity (tensile)	lbf/in ² (MPa)	DIN 53455	345 000 2400	345 000 2400	860 000 5900	1 350 000 10 000
Flexural strength at yield	lbf/in ² (MPa)	DIN 53452	13 500 93	13 500 93	—	—
at break	lbf/in ² (MPa)		— —	— —	21 000 150	30 000 210
Izod impact strength	ft lbf per in notch	ASTM D.256–56 ½in – ¼in bar	12–16	15–18	ca 2.5	ca 2.5
Unnotched impact strength	kgf cm cm ⁻²	DIN 53453 (22°C)	no fail	no fail	—	50

- (3) Pale yellow colour (now commonly masked with dyes).
- (4) Limited resistance to chemicals and ultraviolet light.
- (5) Notch sensitivity and susceptibility to crazing under strain.

Such a tabulation of advantages and limitations is an oversimplification and may in itself be misleading. It is therefore necessary to study some of these properties in somewhat more detail.

Typical mechanical properties for bis-phenol A polycarbonates are listed in *Table 20.3*.

Of these properties the most interesting is the figure given for impact strength. Such high impact strength figures are in part due to the ductility of the resin.

Great care must be taken, as always, in the interpretation of impact test results. It is important to be informed on the influence of temperature, speed of testing and shape factor on the tough–brittle transitions and not to rely on results of a single test. A number of examples of the misleading tendency of quoting single results may be given. In the first instance, while $\frac{1}{2}$ in \times $\frac{1}{8}$ in bars consistently give Izod values of about 16, the values for $\frac{1}{2}$ in \times $\frac{1}{2}$ in bars are of the order of 2.5 ft lbf per inch notch. There appears to be a critical thickness for a given polycarbonate below which high values (~16 ft lbf per in notch) are obtained but above which much lower figures are to be noted. The impact strengths of bis-phenol A polycarbonates are also temperature sensitive. A sharp discontinuity occurs at about -10°C to -15°C , for above this temperature $\frac{1}{2}$ in \times $\frac{1}{8}$ in bars give numerical values of about 16 whilst below it values of 2 to $2\frac{1}{2}$ are to be obtained. Heat aging will cause similar drops in strength.

It should, however, be realised that this lower value (2.5 ft lbf per in notch) is still high compared with many other plastics. Such values should not be considered as consistent with brittle behaviour. Comparatively brittle mouldings can, however, be obtained if specimens are badly moulded.

An illustration of the toughness of the resin is given by the fact that when 5 kg weights were dropped a height of 3 metres on to polycarbonate bowls, the bowls, although dented, did not fracture. It is also claimed that an $\frac{1}{8}$ in thick moulded disc will stop a 0.22 calibre bullet, causing denting but not cracking.

The resistance of polycarbonate resins to ‘creep’ or deformation under load is markedly superior to that of acetal and polyamide thermoplastics. A sample loaded at a rate of one ton per square inch for a thousand hours at 100°C deformed only 0.013 cm/cm. Because of the good impact strength and creep resistance it was felt at one time that the polycarbonates would become important engineering materials. Such hopes have been frustrated by the observations that where resins are subjected to tensile strains of 0.75% or more cracking or crazing of the specimen will occur. This figure applies to static loading in air. When there are frozen-in stresses due to moulding, or at elevated temperatures, or in many chemical environments and under dynamic conditions crazing may occur at much lower strain levels. Aging of the specimen may also lead to similar effects. As a result moulded and extruded parts should be subjected only to very light loadings, a typical maximum value for static loading in air being 2000 lbf/in² (14 MPa).

The electrical insulation characteristics of bis-phenol A polycarbonates are in line with those to be expected of a lightly polar polymer (see Chapter 6).

Because of a small dipole polarisation effect the dielectric constant is somewhat higher than that for PTFE and the polyolefins but lower than those of polar polymers such as the phenolic resins. The dielectric constant is almost

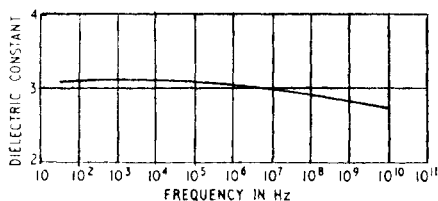


Figure 20.7. Effect of frequency on dielectric constant of bis-phenol A polycarbonate

unaffected by temperature over the normal range of operations and little affected by frequency changes up to 10^6 Hz. Above this frequency, however, the dielectric constant starts to fall, as is common with polar materials (see Figure 20.7).

In common with other dielectrics the power factor is dependent on the presence of polar groups. At low frequencies and in the normal working temperature range (20–100°C) the power factor is almost surprisingly low for a polar polymer (~0.0009). As the frequency increases, the power loss increases and the power factor reaches a maximum value of 0.012 at 10^7 Hz (see Figure 20.8). The polycarbonates have a high volume resistivity and because of the low water absorption these values obtained are little affected by humidity. They do, however, have a poor resistance to tracking. A summary of typical electrical properties of bis-phenol A polycarbonates is given in Table 20.4.

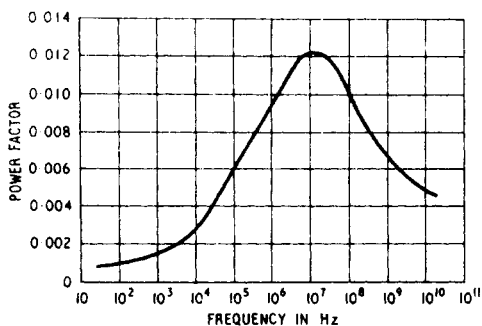


Figure 20.8. Effect of frequency on the power factor of bis-phenol A polycarbonate

Although the general electrical properties of the polycarbonates are less impressive than those observed with polyethylene they are more than adequate for many purposes. These properties, coupled with the heat and flame resistance, transparency and toughness, have led to the extensive use of these resins in electrical applications.

Early grades tended to be yellow in colour due to impurities in the bis-phenol A. Some darkening also occurred during processing and service. Later grades masked the yellowness with the use of a small amount of blue dye whilst modern grades are of much higher purity and virtually water-white. The polymer has a refractive index of 1.586 at 25°C. As may be expected of a polar polymer the dielectric constant (3.17 at 60 Hz) is greater than the square of the refractive index (2.51) but does tend towards this value at very high frequencies (see Chapter 6).

Table 20.4

Property	Units	ASTM test	Value
Power factor at 73°F (23°C)			
60 Hz	—	D.150	0.0009
1 kHz	—		0.0011
10 kHz	—		0.0021
100 kHz	—		0.0049
1 MHz	—		0.010
Dielectric constant			
60 Hz	—	D.150	3.17
1 kHz	—		3.02
10 kHz	—		3.00
100 kHz	—		2.99
1 MHz	—		2.96
Volume resistivity (23°C)	Ω_m		2.1×10^{18}
Dielectric strength short time, $\frac{1}{8}$ in sample	kV/cm	D.149	157

Typical figures for the basic thermal properties of polycarbonates are summarised in Table 20.5.

Peilstöcker¹⁰ has studied in some detail the dependence of the properties of bis-phenol A polycarbonate on temperature. He found that if the resin is heated to just below the glass transition temperature some stiffening of the sample takes place owing to some ordering of the molecules. The degree of molecular ordering did not, however, affect the form of the X-ray diagram. The annealing effect takes place quite rapidly and is complete within 80 minutes at 135°C. This effect may be partially reversed by heating at about the transition temperature, viz. (140–160°C), and completely reversed by raising the temperature of the sample to its optical melting point. The rubbery range extends from the glass transition temperature to the optical melting point. Samples maintained at this temperature, i.e. the T_g , will slowly crystallise. The maximum rate of crystallisation occurs at about 190°C, spherulitic structures being formed at this temperature within eight days.

The chemical resistance of polyester materials is well recognised to be limited because of the comparative ease of hydrolysis of the ester groups. Whereas this ease of hydrolysis was also observed in aliphatic polycarbonates produced by

Table 20.5

Property	Standard	Units	Value
Deflection temp. under load			
method a	ASTM D.648	°C	135–140
method b		°C	140–146
Martens heat distortion point	DIN 53458	°C	115–127
Vicat heat distortion point	VDE 0302	°C	164–166
Specific heat	—	J g ⁻¹ °C ⁻¹	1.18
Thermal conductivity	—	W/mk	0.19
Coeff. of thermal expansion (linear)	ASTM D.696	cm cm ⁻¹ °C ⁻¹	7×10^{-5}
Glass transition temperature	—	°C	~145
Crystal melting point (by optical methods)	—	°C	220–230

Carothers and Natta in 1930, the bis-phenol A polycarbonates are somewhat more resistant. This may be ascribed to the protective influence of the hydrophobic benzene rings on each side of the carbonate group. The resin thus shows a degree of resistance to dilute (25%) mineral acids and dilute alkaline solutions other than caustic soda and caustic potash. Where the resin comes into contact with organophilic hydrolysing agents such as ammonia and the amines the benzene rings give little protection and reaction is quite rapid.

The absence of both secondary and tertiary C—H bonds leads to a high measure of oxidative stability. Oxidation does take place when thin films are heated in air to temperatures above 300°C and causes cross-linking but this is of little practical significance. The absence of double bonds gives a very good but not absolute resistance to ozone.

Although moulded polycarbonate parts are substantially amorphous, crystallisation will develop in environments which enable the molecules to move into an ordered pattern. Thus a liquid that is capable of dissolving amorphous polymer may provide a solution from which polymer may precipitate out in a crystalline form because of the favourable free energy conditions.

For solvation to take place it is first of all necessary for the solvent to have a solubility parameter within about 1.4 units of the solubility parameter of the polycarbonate (19.4–19.8 MPa^{1/2}). A number of solvents (see Chapter 5) meet the requirement but some are nevertheless poor solvents. The reason for this is that although they may tend to dissolve the amorphous polymer they do not interact with the polycarbonate molecule, which for thermodynamic reasons will prefer to crystallise out. If, however, some specific interaction between the resin and the solvent can be achieved then the two species will not separate and solution will be maintained. This can be effected by using a solvent which has a proton-donating ability (e.g. symtetrachlorethane $\delta = 19.2 \text{ MPa}^{1/2}$ or methylene dichloride, $\delta = 19.8 \text{ MPa}^{1/2}$), as a weak bond can be formed with the proton-accepting carbonate group, thus preventing crystallisation. Other good solvents are *cis*-1,2-dichloroethylene, chloroform and 1,1,2-trichloroethane. Thiophene, dioxane and tetrahydrofuran are rated as fair solvents.

A number of materials exist which neither attack the polymer molecule chemically nor dissolve it but which cannot be used because they cause cracking of fabricated parts. It is likely that the reason for this is that such media have sufficient solvent action to soften the surface of the part to such a degree that the frozen-in stresses tend to be released but with consequent cracking of the surface.

The very low water absorption of bis-phenol A polycarbonates contributes to a high order of dimensional stability. *Table 20.6* shows how the water absorption of $\frac{1}{8}$ in thick samples changes with time and environmental conditions and the consequent influence on dimensions.

Table 20.6

Environment	Water absorption (%)			Equilibrium swelling (cm/cm)
	25 h	50 h	150 h	
59% RH 23°C	0.05	0.1	0.15	0.0004
Water immersion 23°C	0.2	0.27	0.35	0.0008
Boiling water immersion	0.58	0.58	0.58	0.0013

Table 20.7 Permeability

Water vapour	$3.8 \times 10^{-8} \text{ g cm h}^{-1} \text{ cm}^{-2} \text{ mm Hg}^{-1}$
Nitrogen	$0.012 \times 10^{-8} \text{ cm}^3 \text{ (S.T.P.) mm s}^{-1} \text{ cm}^{-2} \text{ cmHg}^{-1}$
Carbon dioxide	$0.32 \times 10^{-8} \text{ cm}^3 \text{ (S.T.P.) mm s}^{-1} \text{ cm}^{-2} \text{ cmHg}^{-1}$

The permeability characteristics of the bis-phenol A polycarbonates are shown in Table 20.7.

Stannett and Meyers¹¹ have reported that crystallisation may reduce the nitrogen permeability by 50%. The moisture vapour permeability of the polycarbonate from 1,1-bis-(4-hydroxyphenyl)cyclohexane has been quoted by Schnell⁷ as being somewhat below half that of the bis-phenol A polymer (1.7, c.f. 3.8 units).

When fabricated polycarbonate parts are exposed to ultraviolet light, either in laboratory equipment or by outdoor exposure, a progressive dulling is observed on the exposed surface. The dullness is due to microscopic cracks on the surface of the resin. If the surface resin is analysed it is observed that it has a significantly lower molecular weight than the parent polymer.

Such degradation of the surface causes little effect on either flexural strength or flexural modulus of elasticity but the influence on the impact properties is more profound. In such instances the minute cracks form centres for crack initiation and samples struck on the face of samples opposite to the exposed surface show brittle behaviour. For example, a moulded disc which will withstand an impact of 12 ft lbf without fracture before weathering will still withstand this impact if struck on the exposed side but may resist impacts of only 0.75 ft lbf when struck on the unexposed face.

Because polycarbonates are good light absorbers, ultraviolet degradation does not occur beyond a depth of 0.030–0.050 in (0.075–0.125 cm). Whilst this is often not serious with moulded and extruded parts, film may become extremely brittle. Improvements in the resistance of cast film may be made by addition of an ultraviolet absorber but common absorbers cannot be used in moulding compositions because they do not withstand the high processing temperatures.

Heat aging effects are somewhat complex. Heating at 125°C will cause reduction in elongation at break to 5–15% and in Izod impact strength from 16 down to 1–2 ft lbf per in notch and a slight increase a tensile strength in less than four days. Further aging has little effect on these properties but will cause progressive darkening. Heat aging in the presence of water will lead to more severe adverse effects.

Unmodified polycarbonates are usually rated as slow burning, with an oxygen index of 26 and a UL-94 V-2 rating. Flame-retarding grades are available with an oxygen index as high as 35 and with a UL-94 V-0 rating. Some of these grades also have limited smoke and toxic gas emission on burning.

20.6 PROCESSING CHARACTERISTICS

Satisfactory production of polycarbonate parts may be achieved only if consideration is given to certain characteristics of the polymer.

In the first place, although the moisture pick-up of the resin is small it is sufficient to cause problems in processing. In the extruder or injection moulding

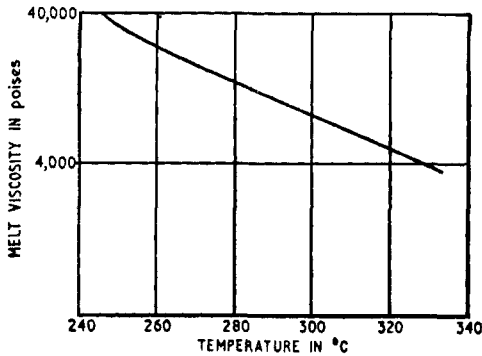


Figure 20.9. Influence of temperature on the melt viscosity of a typical bis-phenol A polycarbonate (shear stress = $\sim 1 \times 10^6$ dyn/cm²). (After Christopher and Fox¹²)

machine it will volatilise into steam and frothy products will emerge from die and nozzle. It is therefore necessary to keep all materials scrupulously dry. Commercial materials are supplied in tins that have been vacuum sealed at elevated temperatures. These tins should be opened only after heating for several hours in an oven at 110°C and the granules should be used immediately. The use of heated hoppers is advocated.

The melt viscosity of the resin is very high and processing equipment should be rugged. The use of in-line screw plasticisers is to be particularly recommended. The effect of increasing temperature on viscosity is less marked with polycarbonates than with other polymers (see Figure 20.9¹²). The apparent melt viscosity is also less dependent on the rate of shear than usual with thermoplastics (Figure 20.10). Because of the high melt viscosities, flow path ratios are in the range 30:1 to 70:1, which is substantially less than for many

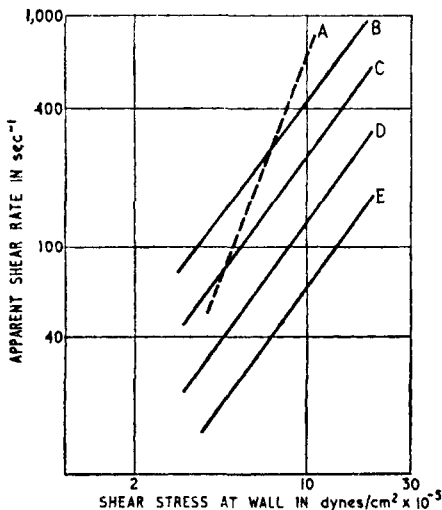


Figure 20.10. Shear stress-shear rate relationships for a polystyrene at 440°F (A) and polycarbonate resin at 650°F (B), 600°F (C), 550°F (D) and 500°F (E). (After Fiedler *et al.*¹³).

more general purpose thermoplastics (e.g. polypropylene 175:1–350:1, ABS 80:1–150:1, nylon 66 180:1–350:1, polyacetals 100:1–250:1).

Processing temperatures are high and fall between the melting point (~230°C) and 300°C, at which temperature degradation occurs quite rapidly.

Polycarbonate melts adhere strongly to metals and if allowed to cool in an injection cylinder or extrusion barrel may, on shrinkage, pull pieces of metal away from the wall. It is therefore necessary to purge all equipment free of the resin, with a polymer such as polyethylene, after processing.

There is little crystallisation on cooling and after-crystallisation has not been observed. Mould shrinkage is consequently of the order of 0.006–0.008 cm/cm and is the same both along and across the flow.

In the case of glass-filled polymers, moulding shrinkage is somewhat lower (0.003–0.005 cm/cm).

The rigidity of the molecule means that molecules may not have time to relax before the temperature drops below the glass transition point. Frozen-in strain may be gauged by noting how well the sample will withstand immersion in carbon tetrachloride. In general, moulding strain will be reduced by using high melt temperatures, preplasticising machines, high injection rates, and hot moulds (~100°C); where used, inserts should be hot. Annealing at 125°C for up to 24 hours will be of some value.

Provided due care is taken with respect to predrying and to crazing tendencies, polycarbonates may also be thermoformed, used for fluidised bed coating and machined and cemented. Like metals, but unlike most thermoplastics, polycarbonates may be cold formed by punching and cold rolling. Cold rolling can in fact improve the impact resistance of the resin.

Film casting is comparatively straightforward but when film is produced above a critical thickness it tends to become cloudy. This is presumably because with such a thickness the solvent remains in the film longer, giving the molecules freedom for a longer period to move into a crystalline state. Since we have already found that the higher the molecular weight of polyethylene and of polypropylene the more difficult does crystallisation become, it is not surprising to find that the critical thickness with polycarbonate film increases with an increase in molecular weight. For polymers with molecular weights (M_n) in the range 75 000–100 000 the critical thickness can be as high as 275 μm .

One recent development is rotational moulding. This process has enabled large mouldings of polycarbonate to be made using reasonably simple and inexpensive equipment.

20.7 APPLICATIONS OF BIS-PHENOL A POLYCARBONATES

In spite of their rather complicated chemical structure, which consequently involves rather expensive production costs, the bis-phenol A polycarbonates have achieved an important place amongst the speciality plastics materials.

Global production capacity at the end of the 1990s is of the order of 1 600 000 tonnes per annum. This is about twice that quoted in the sixth edition of this book, four times the amount given in the fifth edition and eight times that for the fourth edition indicating both a high and consistent rate of growth, and consumption is now approaching that of the market leader in engineering plastics, the nylons (polyamides). About 15% of bisphenol A polycarbonates are used in alloys with other thermoplastics such as ABS (see Section 20.8)

Table 20.8 Usage patterns for polycarbonates and polycarbonate/ABS alloys in Western Europe and the USA 1997. (Based on information published in *Modern Plastics International*)

	Polycarbonate		Polycarbonate/ABS Alloy	
	Western Europe	USA	Western Europe	USA
Consumption (tonnes)	506 000	358 000	156 000	78 000
Application breakdown (%)				
Glazing	28.7	23.5	—	—
Electric/electronic	21.8	7.5	34	25.6
Optical media	17.8	16.2	—	—
Lighting	8.7	2.5	1.3	—
Appliances	5.2	8.4	7.1	10.3
Transportation	4.3	17.0	52.0	57.7
Packaging	3.6	4.2	—	—
Recreation	2.6	7.3	1.3	5.1
Medical	2.6	9.5	—	1.3
Other	4.7	3.9	4.4	—

Western Europe has about 45% of the market with the United States 30% and Japan 25%. It is interesting to note that there are differences in the pattern of consumption in the two areas (*Table 20.8*).

Such success in the use of polycarbonates arises from the advantages of toughness, rigidity, transparency, self-extinguishing characteristics, good electrical insulation characteristics and heat resistance. The main factors retarding growth are the cost, the special care needed in processing, limitations in chemical and ultraviolet light resistance, moderate electrical tracking resistance and notch sensitivity.

Other polymers are as rigid, others are as transparent, others are even both more rigid and as transparent, but the bis-phenol A polycarbonate is the only material that can provide such a combination of properties, at least at such a reasonable cost. The application of polycarbonates therefore largely arise where at least two and usually three or more of the advantageous properties are required and where there is no cheaper alternative.

The largest single field of application for moulded polycarbonates is in electronics and electrical engineering. Covers for time switches, batteries and relays, for example; utilise the good electrical insulation characteristics in conjunction with transparency, flame resistance and durability. The polymer is widely used in making coil formers. In this case the ability to wind the wire tightly without deformation of the former, the heat stability, the oxidation resistance and the good electrical insulation characteristics have proved invaluable. Polycarbonate mouldings have also been made for computers, calculating machines and magnetic disc pack housing, terminals, contact strips, starter enclosures for fluorescent lamps, switch plates and a host of other miscellaneous electrical and electronic applications. Polycarbonate films of high molecular weight are used in the manufacture of capacitors.

The polymers are extensively used in telecommunications equipment, a major use being in telephone switching mechanisms. Polycarbonates now dominate the

compact disc market, where material of very high purity is required. Fibre-filled lubricated grades have become of interest in business machine applications such as ribbon cartridges, paper tractors and printed circuit boards.

Polycarbonates have proved attractive in domestic appliances. Examples include food processor bowls, coffeemaker cold water reservoirs, vacuum cleaner housings, food mixer housings, power tool housings, hair drier and electric razor housings, and microwave cookware.

In the photographic field polycarbonates now compete with ABS for projector housings, whilst in cameras polycarbonates are now used in the shutter assembly, film drive, flash-cube sockets and lens holders. One popular low-cost camera recently introduced into the UK market had at least eight parts moulded from polycarbonate. Polycarbonate film is also used for photographic purposes, e.g. for quality colour fine engravings.

The chronic development of vandalism in recent years has led to the substantial growth of the market for polycarbonate glazing. Bus shelters, telephone kiosks, gymnasium windows, strip-lighting covers at foot level, riot squad helmets and armour have all used such material successfully and further extensive growth may be expected in these areas. Lamp housings, both for general street lighting and on traffic lights and automobiles, are also areas where growth may be expected to continue. Nevertheless in these glazing applications the limited scratch and weathering resistance of the polycarbonates remain a serious drawback and much effort is being expended to try and overcome these problems. One approach is to coat the polycarbonate sheet with a material glass-like in chemical composition and structure which provides hardness and long-term protection against abrasion and weathering. Success with such systems depends on the priming system used to ensure good adhesion between coating and base material. One such material is now marketed by the General Electric company of America as Margard. This system uses a siloxane-based coating. Alternatively as already mentioned in Section 20.4.1 Bayer have developed techniques to facilitate the ability to stove scratch-resistant coatings onto bisphenol TMC polycarbonates. As a sign of the huge potential for polycarbonates in auto glazing applications GE and Bayer in 1998 set up a joint venture, Exatec, to exploit this potential.

The use of the polymer in safety goggles, helmets and machine guards gained a boost with the application of the bis-phenol A polycarbonate as the visor worn by lunar astronauts. This is arguably the most famous application of a plastics material. The use of polycarbonates for some safety applications has not always proved satisfactory. In particular, concern has been expressed about the use of the material for motor cyclists' helmets. This arises largely as a result of helmet owners' predilections for embellishing the helmets by painting or attachments stuck on by adhesives. In both cases the liquids used often cause a weakening through stresscracking. In fact the use of any oriented polycarbonate sheet which may come into contact with stress cracking liquids is to be discouraged.

Another area which is of considerable interest is the development of rotationally moulded products. These mouldings include air ducting housing and a 700-litre frozen food container, both of which are greater than 20 kg in weight.

The toughness and transparency of polycarbonates has also led to a number of other industrial applications. In Great Britain one of the first established uses was for compressed air lubricator bowls. In the first five years of commercial

production it was estimated that over 100 000 breeding cages for rats were produced. Transparent milking pail lids have also been moulded.

Polycarbonates have also found applications in domestic mouldings. Cups, saucers and tumblers are adequately tough and are not stained by the usual domestic beverages and fruit juices. They are thus competitive with melamine-formaldehyde mouldings, the latter having superior resistance to scratching. Tough transparent babies' bottles may be blow moulded at very high rates because of the high setting-up temperatures. Medical uses of polycarbonates include transparent filter bowls used in transferring blood and intravenous fluids. Because of the option of disposability or sterilisation, they have also replaced some stainless steel surgical equipment.

In 1973 polycarbonate structural foams, i.e. expanded or cellular polycarbonates, became available. Densities as low as 0.6 g/cm^3 are possible whilst the rigidity of the stress-free mouldings is such that the flexural strength to weight ratio is twice that of most metals. Furthermore the products may be nailed and screwed like wood. Initial applications were largely in business machine housings but glass-reinforced grades have extended the range of use. For example they are used in water ski shoes because of the high rigidity and resistance to fatigue.

20.8 ALLOYS BASED ON BIS-PHENOL A POLYCARBONATES

Alloys of bisphenol A polycarbonates with ABS and MBS resins have been known for many years. Subsequently many other alloys containing polycarbonates have been introduced so that by the mid-1990s they comprised at least 15% of the polycarbonate market.

The styrene-based terpolymers were originally used to the extent of some 2–9% in order to reduce the notch sensitivity of the polycarbonate and to improve the environmental stress cracking resistance. More recently emphasis has been on alloys with 10–50% of SAN or ABS. Alloys of polycarbonates with ASA have also become available (Luran SC-BASF)

Vicat softening points are usually in the range 110–135°C, depending on the level of ABS or MBS (decreasing with increasing ABS or MBS content). The Bayer ABS-PC alloy (Bayblend) retains its high impact strength and notched impact strength down to -50°C. The alloys are also claimed to be 'non-splintering'. The hardness of the alloys is comparable to that of polycarbonate.

Because of the above properties, together with other features such as the ability to mould to close dimensional tolerances, low warpage, low shrinkage, low moisture absorption and good surface finish, polycarbonate-ABS alloys have become widely used in the automotive industry, for electrical applications and for housings of domestic and business equipment.

Examples of applications in the automotive industry include instrument panels, air vents and ventilation systems, cowl panels, wheel covers, rear light chassis, headlamp housings, central electrical control boxes, electroplated insignia, loudspeaker grilles, double rear spoilers and window trim. Electrical applications include fuse switch housings, plug connectors, safety sockets, fuse switch housings, power distribution fittings, control switch housings, thermostat housings, switches, appliance connectors and telephone dials. The alloys are also used for housings of typewriters, small radio receivers and hair dryers, steam iron handles and vacuum cleaner motor bearings.

Table 20.9 Selected properties of PC-ABS and PC-PBT alloys

Grade	PC-ABS			PC-PBT basic Grade
	High ABS	Low ABS	GF-reinforced Low ABS (20% glass)	
Vicat softening point (°C)	111	130	130	125
Notched impact (kJ/m ²)	25	35	8	46
Specific gravity	1.1	1.16	1.2	1.22
Water absorption (ISO 62) (%)	0.7	0.6	0.6	0.35
Oxygen index (%)	21	24	24	<21
Tensile strength (MPa)	40	50	75	55
Elongation at break(%)	60	85	2	75
Flexural modulus (MPa)	2000	2200	6000	2200
Ball hardness (H_{30} (ISO 2039) (N/mm ²))	80	90	125	96
Vol. resistivity (ohm.cm)	10 ¹⁶	10 ¹⁶	10 ¹⁶	>10 ¹⁴

In addition to standard grades varying in the ABS/PC ratio, fire-retarded, glass-fibre-reinforced and glass-fibre-reinforced fire-retarded grades are available. Typical properties of three grades of ABS-PC alloys are given in *Table 20.9*.

Polycarbonate-polybutylene terephthalate alloys (Macroblend—Bayer; Xenoy—General Electric) were also introduced in the 1980s. The blends are particularly notable for their high levels of toughness (down to -40°C) and resistance to petrols and oils. Initial interest was for car bumpers and front ends but the alloys have found intensive competition from polypropylene-based materials and more recently emphasis has been placed on the suitability of these materials for demanding uses such as lawn mower and chain saw housings. Typical properties of a general purpose grade are given in *Table 20.8*.

Polycarbonate-polyethylene terephthalate (PC-PET) alloys have also recently been announced by DSM.

Polycarbonates based on tetramethylbisphenol A are thermally stable and have a high Vicat softening point of 196°C. On the other hand they have lower impact and notched impact resistance than the normal polymer. Blends with styrene-based polymers were introduced in 1980, and compared with PC/ABS blends, are claimed to have improved hydrolytic resistance, lower density and higher heat deflection temperatures. Suggested applications are as dishes for microwave ovens and car headlamp reflectors.

Yet another recent development has been the alloying of polycarbonates with liquid crystal polymers such as Vectra (see Section 25.8.1). These alloys are notable for their very good flow properties and higher strength and rigidity than conventional bisphenol A polycarbonates.

20.9 POLYESTER CARBONATES AND BLOCK COPOLYMERS

In the 1980s a number of copolymers became established, known as polyester carbonates, which may be considered as being intermediate between bisphenol A polycarbonates and the polyarylates discussed in Chapter 25.

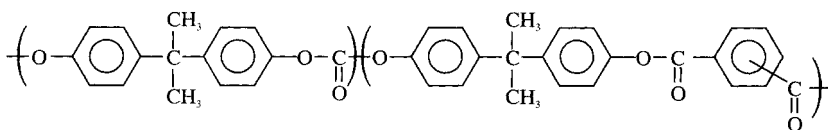


Figure 20.11

These materials have the general structure shown in *Figure 20.11* and are prepared by reaction of bisphenol A with iso- and/or terephthalic acid and a carbonate group donor (e.g. phosgene or diphenyl carbonate).

Because of the irregular structure the copolymers are amorphous and transparent. The higher the polyester component the higher the softening point, typical grades having values in the range 158–182°C compared with 148°C for unmodified polymer. On thermal aging the polyester carbonates also show a lower tendency to embrittlement than polycarbonate. This is, however, at the cost of a reduction in notched Izod impact strength (35–28 kJ/m², compared to 45 kJ/m² for unmodified polymer) and increased melt viscosity. As with the poly(carbonates) based on bisphenol A and bisphenol S, the polyester carbonates have a low level of notch sensitivity. The polyester carbonates are easier to process than the polyarylates.

Block copolymers of polycarbonates and silicone polymers have also been commercially marketed (e.g. Makrolons KU 1–1198 and KU 1–1207). These block copolymers show a marked increase in toughness at low temperatures coupled with reduced notch sensitivity. (They show little improvement in toughness at normal ambient temperatures.)

20.10 MISCELLANEOUS CARBONIC ESTER POLYMERS

Unless the hydroxyl groups have such proximity that cyclisation takes place, polycarbonates will normally be produced whenever phosgene or a carbonate ester is reacted with a polyhydroxy compound. This means that a very large range of polycarbonate resins are possible and in fact many hundreds have been prepared.

Aliphatic polycarbonates have few characteristics which make them potentially valuable materials but study of various aromatic polycarbonates is instructive even if not of immediate commercial significance. Although bisphenol A polycarbonates still show the best all-round properties other carbonic ester polymers have been prepared which are outstandingly good in one or two specific properties. For example, some materials have better heat resistance, some have better resistance to hydrolysis, some have greater solvent resistance whilst others are less permeable to gases.

It is particularly interesting to consider the influence of the substituents R and R₁ in diphenylol alkanes of the type shown in *Figure 20.12*. Such variations will influence properties because they affect the flexibility of the molecule about the central C-atom, the spatial symmetry of the molecule and also the interchain attraction, the three principal factors determining the physical nature of a high polymer.

Thus where R and R_{1P} are hydrogen the molecule is symmetrical, the absence of bulky side groups leads to high intermolecular attraction and the flexibility of

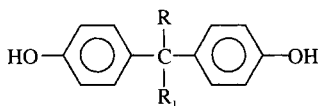


Figure 20.12

the molecule enables crystallisation to take place without difficulty. The resultant material is highly crystalline, with a melting point of above 300°C, and is insoluble in known solvents.

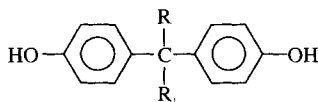
Where R is hydrogen and R₁ a methyl group the molecule is less symmetrical and less flexible and the intermolecular attraction would be slightly less. The melting point of this polymer is below 200°C. In the case where R and R₁ are both methyl groups the molecule is more symmetrical but the flexibility of the molecule about its central carbon atom is reduced. Because of these two factors this polymer, the commercial bis-phenol A polycarbonate, has glass transition temperatures and melting points slightly above that of the aforementioned material.



The higher aliphatic homologues in this series show lower melting points, the reduction depending on symmetry and on the length of the side group. The symmetrical methyl, ethyl and propyl disubstituted materials have similar glass transition temperatures presumably because the molecules have similar degrees of flexibility.

Introduction of aromatic or cycloaliphatic groups at R and/or R₁ gives further restriction to chain flexibility and the resulting polymers have transition temperatures markedly higher than that of the bis-phenol A polycarbonate.

The melting ranges and glass transition temperatures of a number of polycarbonates from di-(4-hydroxyphenyl)methane derivatives are given in Table 20.10.

Table 20.10 Melting range and glass transition temperatures of polycarbonates from di-(4-hydroxyphenyl)methane derivatives



R	R ₁	Melting range (°C)	Glass temperature (°C)
—H	—H	300	—
—H	—CH ₃	185–195	130
—CH ₃	—CH ₃	220–230	149
—CH ₃	—C ₂ H ₅	205–222	134
—C ₂ H ₅	—C ₂ H ₅	175–195	149
—CH ₃	—CH ₂ —CH ₂ —CH ₃	200–220	137
—CH ₂ —CH ₂ —CH ₃	—CH ₂ —CH ₂ —CH ₃	190–200	148
		250–275	200

Polycarbonates have also been prepared from diphenyl compounds where the benzene rings are separated by more than one carbon atom. In the absence of bulky side groups such polymer molecules are more flexible and crystallise very rapidly. As is to be expected, the more the separating carbon atoms the lower the melting range. This effect is shown in data supplied by Schnell⁴ (Table 20.11).

Table 20.11

<i>Diphenyl compound (i.e. linkage between rings)</i>	<i>Melting range of polymer (°C)</i>	<i>Solubility of polymer in ordinary solvents</i>
—CH ₂ —	over 300	insoluble
—CH ₂ —CH ₂ —	290–300	insoluble
—CH ₂ —(CH ₂) ₈ —CH ₂ —	135–150	insoluble

Polymers have been prepared from nuclear substituted di-(4-hydroxyphenyl)-alkanes, of which the halogenated materials have been of particular interest. The symmetrical tetrachlorobis-phenol A yields a polymer with a glass transition temperature of 180°C and melting range of 250–260°C but soluble in a variety of solvents.

Crystallisable polymers have also been prepared from diphenylol compounds containing sulphur or oxygen atoms or both between the aromatic rings. Of these the polycarbonates from di-(4-hydroxyphenyl)ether and from di-(4-hydroxyphenyl)sulphide crystallise sufficiently to form opaque products. Both materials are insoluble in the usual solvents. The diphenyl sulphide polymer also has excellent resistance to hydrolysing agents and very low water absorption. Schnell⁴ quotes a water absorption of only 0.09% for a sample at 90% relative humidity and 250°C. Both the sulphide and ether polymers have melting ranges of about 220–240°C. The di-(4-hydroxyphenyl)sulphoxide and the di-(4-hydroxyphenyl)sulphone yield hydrolysable polymers but whereas the polymer from the former is soluble in common solvents the latter is insoluble.

Further variations in the polycarbonate system may be achieved by copolymerisation. The reduced regularity of copolymers compared with the parent homopolymers would normally lead to amorphous materials. Since, however, the common diphenylol alkanes are identical in length they can be interchanged with each other in the unit cell, providing the side groups do not differ greatly in their bulkiness.

Christopher and Fox¹² have given examples of the way in which polycarbonate resins may be tailor-made to suit specific requirements. Whereas the bis-phenol from *o*-cresol and acetone (bis-phenol C) yields a polymer of high hydrolytic stability and low transition temperature, the polymer from phenol and cyclohexanone has average hydrolytic stability but a high heat distortion temperature. By using a condensate of *o*-cresol and cyclohexanone a polymer may be obtained with both hydrolytic stability and a high heat distortion temperature.

Finally mention may be made of the phenoxy resins. These do not contain the carbonate group but are otherwise similar in structure, and to some extent in properties, to the bis-phenol A polycarbonate. They are dealt with in detail in Chapter 21.

References

1. EINHORN, A., *Ann.*, **300**, 135 (1898)
2. BISCHOFF, C. A. and VON HEDENSTRÖM, H. A., *Ber.*, **35**, 3431 (1902)
3. CAROTHERS, W. H. and NATTA, F. J., *J. Am. Chem. Soc.*, **52**, 314 (1930)
4. SCHNELL, H., *Trans. Plastic Inst.*, **28**, 143 (1960)
5. *U.S. Patent*, 2,468,982
6. *U.S. Patent*, 2,936,272
7. SCHNELL, H., *Angew. Chem.*, **68**, 633 (1956)
8. *German Patent*, 959,497
9. PRIETSCHK, A., *Kolloid-Z.*, **156**, (1), 8, Dr. Dietrich Steinkopff Verlag, Darmstadt (1958)
10. PEILSTÖCKER, G., *Kunststoffe Plastics*, **51**, 509 (September 1961)
11. STANNETT, V. T. and MEYERS, A. W., Unpublished, quoted in reference 12
12. CHRISTOPHER, W. F. and FOX, D. W., *Polycarbonates*, Reinhold, New York (1962)
13. FIEDLER, E. F., CHRISTOPHER, W. F. and CALKINS, T. R., *Mod. Plastics*, **36**, 115 (1959)

Bibliography

- CHRISTOPHER, W. F. and FOX, D. W., *Polycarbonates*, Reinhold, New York (1962)
- JOHNSON, K., *Polycarbonates—Recent Developments* (Patent Review), Noyes Data Corporation, New Jersey (1970)
- SCHNELL, H., *Chemistry and Physics of Polycarbonates*, Interscience, New York (1964)

Reviews

- KIRCHER, K., *Kunststoffe*, **77**, 993 (1987)
- KIRCHER, K., *Kunststoffe*, **80**, 1113 (1990)
- KIRCHER, K., *Kunststoffe*, **86**(10), 1490–1 (1996)
- PAKULL, R., GRIGO, U. and FREITAG, D., *RAPRA Review Report No 40* (Vol 4 No 6 1991)
Polycarbonates

Other Thermoplastics Containing *p*-Phenylene Groups

21.1 INTRODUCTION

The successful development of poly(ethylene terephthalate) fibres such as Dacron and Terylene stimulated extensive research into other polymers containing *p*-phenylene groups in the main chain. This led to not only the now well-established polycarbonates (see Chapter 20) but also to a wide range of other materials. These include the aromatic polyamides (already considered in Chapter 18), the polyphenylene ethers, the polyphenylene sulphides, the polysulphones and a range of linear aromatic polyesters.

The common feature of the *p*-phenylene group stiffens the polymer backbone so that the polymers have higher T_g s than similar polymers which lack the aromatic group. As a consequence the aromatic polymers tend to have high heat deformation temperatures, are rigid at room temperature and frequently require high processing temperatures.

One disadvantage of many of these materials, however, is their rather poor electrical tracking resistance.

Although the first two materials discussed in this chapter, the polyphenylenes and poly-*p*-xylylenes, have remained in the exotic category, most of the other materials have become important engineering materials. In many cases the basic patents have recently expired, leading to several manufacturers now producing a polymer where a few years ago there was only one supplier. Whilst such competition has led in some cases to overcapacity, it has also led to the introduction of new improved variants and materials more able to compete with older established plastics materials.

21.2 POLYPHENYLENES

Poly-*p*-phenylene has been prepared in the laboratory by a variety of methods,¹ including the condensation of *p*-dichlorobenzene using the Wurtz-Fittig reaction. Although the polymer has a good heat resistance, with decomposition

temperatures of the order of 400°C, the polymer (*Figure 21.1*) is brittle, insoluble and infusible.

Several substituted linear polyphenylenes have also been prepared but none appear to have the resistance to thermal decomposition shown by the simple poly-*p*-phenylene.

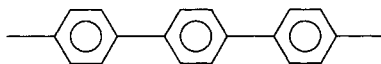


Figure 21.1

In 1968 the Monsanto Company announced the availability of novel soluble low molecular weight 'polyphenylene' resins. These may be used to impregnate asbestos or carbon fibre and then cross-linked to produce heat-resistant laminates. The basic patent (BP 1037111) indicates that these resins are prepared by heating aromatic sulphonyl halides (e.g. benzene-1,3-disulphonyl dichloride) with aromatic compounds having replaceable nuclear hydrogen (e.g. bisphenoxybenzenes, sexiphenyl and diphenyl ether). Copper halides are effective catalysts. The molecular weight is limited initially by a deficiency in one component. This is added later with further catalyst to cure the polymer.

The resultant cross-linked polymer is not always entirely polyphenylene because of the presence of ether oxygen in many of the intermediates. Neither do the polymers have the heat resistance of the ultimate in polyphenylenes, graphite, which has a melting point of 3600°C.

In 1974 another polyphenylene-type material was introduced. This was designated by the manufacturer, Hercules Inc., as H-resin (not to be confused with H-film, a term that has been used by Du Pont to describe a polyimide film). The Hercules materials may be described as thermosetting branched oligophenylenes of schematic structure shown in *Figure 21.2*. The oligomers are soluble in aromatic and chlorinated hydrocarbons, ketones and cyclic ethers. After blending with a cross-linking system, usually of the Zeigler-Natta catalyst type, the compound is shaped, for example by compression moulding, and then cured. Form stability is achieved by heating to 160°C but post-curing to 230–300°C is essential to obtain the best solvent resistance and mechanical properties.

It is claimed that the cured materials may be used continuously in air up to 300°C and in oxygen-free environments to 400°C. The materials are of interest as heat- and corrosion-resistant coatings, for example in geothermal wells, high-temperature sodium and lithium batteries and high-temperature polymer- and metal-processing equipment.

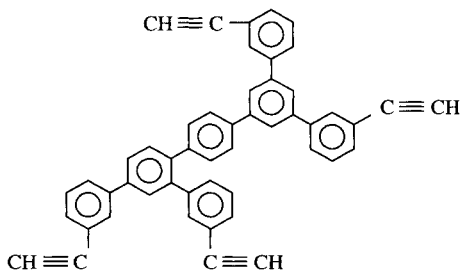


Figure 21.2

21.3 POLY-*p*-XYLYLENE

This polymer first appeared commercially in 1965 (Parylene N Union Carbide). It is prepared by a sequence of reactions initiated by the pyrolysis of *p*-xylene at 950°C in the presence of steam to give the cyclic dimer. This, when pyrolysed at 550°C, yields monomeric *p*-xylylene. When the vapour of the monomer condenses on a cool surface it polymerises and the polymer may be stripped off as a free film. This is claimed to have a service life of 10 years at 220°C, and the main interest in it is as a dielectric film. A monochloro-substituted polymer (Parylene C) is also available. With both Parylene materials the polymers have molecular weights of the order of 500 000.

21.4 POLY(PHENYLENE OXIDES) AND HALOGENATED DERIVATIVES

It is to be expected that a polymer consisting of benzene rings linked at the 1 and 4 positions via one oxygen atom would have a high resistance to heat deformation and heat aging. For this reason there has been considerable research activity in the study of such poly(phenylene oxides) and a number of preparative routes have been established.¹ These include the thermal decomposition of 3,5-dibromobenzene-1,4-diazo-oxide, the oxidation of halogenated phenols, Ullman-type condensations and by refluxing potassium or silver halogenated phenates in benzophenone. Comparison of a number of halogenated poly(phenylene oxides) with the unsubstituted material have in general shown that the latter material has the greatest heat stability. For example, the simple poly(phenylene oxide) will volatilise about 30% to 500°C in 2 hours whilst at the same time and temperature poly-*p*-2,6-dichlorophenylene oxide, one of the more stable halogenated materials, will decompose 65%. Neither the unsubstituted poly(phenylene oxide) nor the halogenated derivatives have become of any commercial importance.

21.5 ALKYL SUBSTITUTED POLY(PHENYLENE OXIDES) INCLUDING PPO

In 1959 Hay^{2,3} *et al.* reported that catalytic oxidation of 2,6-disubstituted phenols with oxygen either led to high molecular weight polyphenylene ethers or to diphenoquinone (*Figure 21.3*). In a typical process, for poly-(2,6-dimethyl-*p*-phenylene ether) the 2,6-dimethylphenol was reacted with oxygen in pyridine in the presence of copper(I) chloride for about 7 minutes at 28–46°C. The reaction mixture was added to methanol, filtered and washed with methanol to give a colourless polymer. This polymer softened at about 240°C but did not melt up to 300°C, similar polymers have been prepared with ethyl and isopropyl side groups. In the case of the dimethyl material this reaction is of interest because of the extreme facility of the reaction, because it was the first time a high molecular weight poly(phenylene ether) had been prepared and also the first example of a polymerisation that occurs by an oxidative coupling using oxygen as the oxidising agent. Of the other materials it is found that polymer formation readily occurs only if the substituent groups are relatively small and not too electronegative. With large bulky substituents tail-to-tail coupling leading to diphenoquinones becomes more probable.

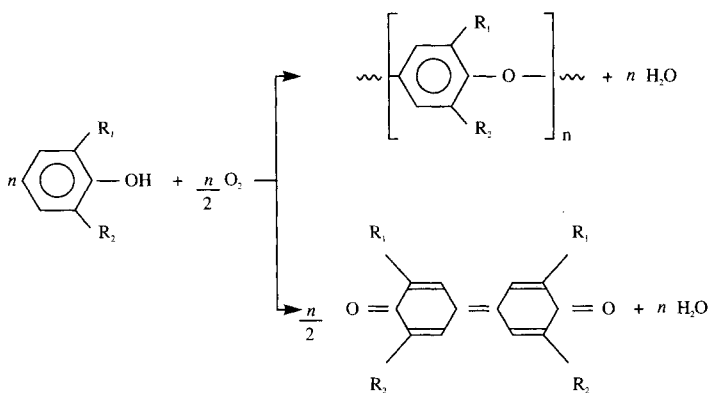


Figure 21.3

In 1965 the poly-(2,6-dimethyl-*p*-phenylene ether) was introduced as poly-phenylene oxide (misleadingly!) and also as PPO by the General Electric Co. in the USA and by AKU in Holland. The commercial materials had a molecular weight of 25 000–60 000.

Using the processes described above, complex products are obtained if a monosubstituted phenol is used instead of a 2,6-substituted material. However, by using as the amine⁴ a 2-disubstituted pyridine such as 2-amylpyridine, more linear and, subsequently, useful polymers may be obtained.

21.5.1 Structure and Properties of Poly-(2,6-dimethyl-*p*-phenylene oxide) (PPO)

The rigid structure of the polymer molecule leads to a material with a high T_g of 208°C. There is also a secondary transition at -116°C and the small molecular motions that this facilitates at room temperature give the polymer in the mass a reasonable degree of toughness.

When polymerised the polymer is crystalline but has a surprisingly low reported melting point (T_m) of 257°C. The ratio T_g/T_m of 0.91 (in terms of K) is uniquely high. Because of the small difference in T_g and T_m there is little time for crystallisation to occur on cooling from the melt and processed polymer is usually amorphous. However, if molecular movements are facilitated by raising the temperature or by the presence of solvents, crystallisation can occur.

The solubility parameter is in the range 18.4–19 MPa^{1/2} and the polymer is predictably dissolved by halogenated and aromatic hydrocarbons of similar solubility parameter. Stress cracking can occur with some liquids.

Being only lightly polar and well below the T_g at common ambient temperatures the polymer is an excellent electrical insulator even at high frequencies.

The commercial polymers are of comparatively low molecular weight ($\bar{M} = 25\,000\text{--}60\,000$) and whilst being essentially linear may contain a few branches or cross-links arising out of thermal oxidation. Exposure to ultraviolet light⁵ causes a rapid increase in gel content, whilst heating in an oven at 125°C causes gelation only after an induction period of about 1000 hours. For outdoor applications it is necessary to incorporate carbon black. The polymers, however, exhibit very good hydrolytic stability.

Table 21.1 Comparison of properties of unfilled grades of thermoplastics containing *p*-phenylene groups

Property	Units	Polycarbonate	Polysulphone ^a			Phenoxy	PPO	PPO-PS Blend	PET	PBT
			Type II	Type III	Type IV					
Transparent	—	Yes	Yes	Yes	Yes	Yes	No	No	In thin film ^b White	In very thin film White
Natural colour	—	Very pale yellow	Light amber	Light amber	Light amber	Pale yellow	—	—		
Specific gravity	—	1.2	1.24	1.37	1.36	1.18–1.3	1.06	1.06	1.37	1.32
Tensile yield stress	lbf/in ² (MPa)	9000 (62)	10 000 (69)	12 200 (84)	13 000 (90)	9500 (65)	10 500 (72)	7–12 000 (48–83)	10 500 (72)	8200 (56)
Elongation at break	%	61–100	50–100	—	10	50–100	80	20	150–300	150
Flexural modulus	lbf/in ² (MPa)	400 000 (2760)	300 000 (2100)	373 000 (2570)	400 000 (2760)	400 000 (2760)	300 000 (2100)	400 000 (2760)	40 000 (2760)	340 000 (2400)
Rockwell hardness	—	118R	120R	88M	110M	123R	119R	78M	106M	85M
Izod impact strength	ft lbf in ⁻¹ notch	2–8	1.3	1.6	2.4	2.5	1.5–1.8	1.7–2.0	0.8	0.8
Tensile impact	ft lbf in ⁻²	275	250	—	—	—	250–450	120	—	—
Coefficient of thermal expansion	cm/cm °C ⁻¹	7.0×10^{-5}	5.6×10^{-5}	5.5×10^{-5}	4.7×10^{-5}	—	5.2×10^{-5}	5.2×10^{-5}	7×10^{-5}	$8.8-23 \times 10^{-5}$
Heat distortion temperature at 264 lbf/in ² load (1.82 MPa)	°C	143	174	203	274	86	190	100–175	85	65
24 h water absorption	%	0.2	0.22	0.43	1.4	1.5	0.1	0.07	0.02	0.08
Volume resistivity	Ω cm	10 ¹⁶	10 ¹⁶	10 ¹⁷ –10 ¹⁸	10 ¹⁶	>10 ¹³	10 ¹⁷	10 ¹⁷	10 ¹⁶	10 ¹⁷ –10 ¹⁸
Power factor 60 Hz	—	0.0009	0.001	0.001	0.003	0.001	0.000 35	0.0004–0.007	—	0.001
10 ⁶ Hz	—	0.01	0.006	0.006	0.013	0.03	0.000 9	0.001–0.002	0.22	—
Permittivity 60 Hz	—	3.17	3.14	3.5	3.94	4.1	2.58	—	—	3.24
10 ⁶ Hz	—	2.16	—	3.5	3.7	3.8	2.58	2.58	3.37	—
Dielectric strength	kV/cm	160	—	—	—	200	180	220	160	203

^a see Table 21.3 ^bTransparent or opaque according to moulding conditions.

One particular feature of PPO is its exceptional dimensional stability amongst the so-called engineering plastics. It has a low coefficient of thermal expansion, low moulding shrinkage and low water absorption, thus enabling moulding to close tolerances.

Typical properties of PPO are given in *Table 21.1*.

21.5.2 Processing and Application of PPO

Since PPO has a high heat distortion temperature (deflection temperature under load) it is not surprising that high processing temperatures are necessary.^{6,7} Typical cylinder temperatures are about 280–330°C and mould temperatures 100–250°C. If overheated the material oxidises, resulting in poor finish and streakiness. Because of this it is advisable to purge machines before they are cooled down after moulding. The melts of PPO are almost Newtonian, viscosity being almost independent of shear rate.

PPO forms one of a group of rigid, heat-resistant, more-or-less self-extinguishing polymers with a good electrical and chemical resistance, low water absorption and very good dimensional stability. This has led to a number of applications in television such as tuner strips, microwave insulation components and transformer housings. The excellent hydrolytic stability has also led to applications in water distribution and water treatment applications such as in pumps, water meters, sprinkler systems and hot water tanks. It is also used in valves of drink vending machines.

Unfortunately for PPO its price is too great to justify more than very restricted application and this led to the introduction of the related and cheaper Noryl materials in 1966 by the General Electric Corporation. These will be discussed in the next section. In recent years the only sources of unmodified PPO have been the USSR (Aryloxa) and Poland (Biapen).

21.5.3 Blends Based in Polyphenylene Oxides (Modified PPOs)

If poly-(2,6-dimethyl-*p*-phenylene oxide) (T_g 208°C) is blended with polystyrene (T_g c. 90°C) in equal quantities a transparent polymer is obtained which by calorimetric and dielectric loss analysis indicates a single T_g of about 150°C. Such results indicate a molecular level of mixing but this view is somewhat disturbed by the observation of two transitions when measured by dynamical methods.⁸ These results lead to the conclusion that although the degree of mixing is good it is not at a segmental level. Since both polystyrene and the poly-(2,6-dimethyl-*p*-phenylene oxide) have similar secondary transitions at about 116°C the blends also show this transition. In the case of the main T_g this tends to vary in rough proportion to the ratio of the two polymers. Since the electrical properties of the two polymers are very similar the blends also have similar electrical characteristics. Since polystyrene has a much lower viscosity than the phenylene oxide polymer at the processing temperatures relevant to the latter the viscosity of the blends is reduced at these temperatures when compared to the polyphenylene oxide resin. Like polystyrene but unlike PPO the blends are highly pseudoplastic, the apparent viscosities falling with increased rates of shear.

Although the first commercial modified PPOs may be considered as derived from such PPO–polystyrene blends, today three distinct classes of material can be recognised:

- (1) Blends of PPO with a styrenic material, usually, but not always, high-impact polystyrene. (Referred to below as Styrenic PPOs.)
- (2) Blends of PPO with polyamides. (Referred to below as polyamide PPOs.)
- (3) Other blends such as with poly(butylene terephthalate) and poly(phenylene sulphide) which are niche materials not further discussed in this chapter.

21.5.4 Styrenic PPOs

By 1994 there were over 60 grades of Noryl and in addition a number of competitive materials. In Japan, Asahi Glass introduced Xyron in the late 1970s and Mitsubishi introduced Diamar in 1983. More recently, BASF have marketed Luranyl and Hüls introduced Vestoran. By 1996 three further Japanese suppliers came on stream. In the late 1990s global capacity was of the order of 320 000 t.p.a. Although this figure probably also includes the more specialised polyamide PPOs discussed later, the Styrenic PPOs are clearly significant materials amongst the so-called engineering polymers.

Like polystyrene these blends have the following useful characteristics:⁹

- (1) Good dimensional stability (and low moulding shrinkage)—thus allowing the production of mouldings with close dimensional tolerances.
- (2) Low water absorption.
- (3) Excellent resistance to hydrolysis.
- (4) Very good dielectric properties over a wide range of temperature.

In addition, unlike polystyrene:

- (5) They have heat distortion temperatures above the boiling point of water, and in some grades this is as high as 160°C.

The range of blends now available comprises a broad spectrum of materials superior in many respects, particularly heat deformation resistance, to the general purpose thermoplastics but at a lower price than the more heat-resistant materials such as the polycarbonates, polyphenylene sulphides and polysulphones. At the present time the materials that come closest to them in properties are the ABS/polycarbonate blends. Some typical properties are given in *Table 21.1*.

In common with other 'engineering thermoplastics' there are four main groups of modified PPOs available. They are:

- (1) Non-self-extinguishing grades with a heat distortion temperature in the range 110–160°C and with a notched Izod impact strength of 200–500 J/m.
- (2) Self-extinguishing grades with slightly lower heat distortion temperatures and impact strengths.
- (3) Non-self-extinguishing glass-reinforced grades (10, 20, 30% glass fibre) with heat distortion temperatures in the range of 120–140°C.
- (4) Self-extinguishing glass-reinforced grades.

Amongst the special grades that should be mentioned are those containing blowing agents for use in the manufacture of structural foams (see Chapter 16).

Modified polyphenylene oxides may be extruded, injection moulded and blow moulded without undue difficulty. Predrying of granules is normally only necessary where they have been stored under damp conditions or where an

optimum finish is required. As with other materials care must be taken to avoid overheating and dead spots, whilst the machines must be sufficiently rugged and/or with sufficiently powered heaters. Processing conditions depend on the grade used but in injection moulding a typical melt temperature would be in the range 250–300°C.

The introduction of self-extinguishing, glass-reinforced and structural foam grades has led to steady increase in the use of these materials in five main application areas. These are:

- (1) The automotive industry.
- (2) The electrical industry.
- (3) Radio and television
- (4) Business machines and computer housings.
- (5) Pumps and other plumbing applications.

Use in the automotive industries largely arises from the availability of high-impact grades with heat distortion temperatures above those of the general purpose thermoplastics. Specific uses include instrument panels, steering column cladding, central consoles, loudspeaker housings, ventilator grilles and nozzles and parcel shelves. In cooling systems glass-reinforced grades have been used for radiator and expansion tanks whilst several components of car heating systems are now also produced from modified PPOs. The goods dimensional stability, excellent dielectric properties and high heat distortion temperatures have also been used in auto-electrical parts including cable connectors and bulb sockets. The materials are also being increasingly used for car exterior trim such as air inlet and outlet grilles and outer mirror housings.

In the electrical industry well-known applications include switch cabinets, fuse boxes and housings for small motors, transformers and protective circuits.

Radio and television uses largely arise from the ability to produce components with a high level of dimensional accuracy coupled with good dielectric properties, high heat distortion temperatures and the availability of self-extinguishing grades. Specific uses include coil formers, picture tube deflection yokes and insert card mountings.

Glass-reinforced grades have widely replaced metals in pumps and other functional parts in washing equipment and central heating systems. In the manufacture of business machine and computer housings structural foam materials have found some use. Mouldings weighing as much as 50 kg have been reported.

21.5.5 Processing of Styrenic PPOs

The processing of blends of an amorphous material (polystyrene) and a crystalline material with a high melting point (PPO) reflects the nature of the constituent materials. The processing is mainly by injection moulding, and the major points to be considered when processing Noryl-type materials are:

- (1) The low water absorption. Moulding can usually be undertaken without the need for predrying the granules.
- (2) The polymer has a good melt thermal stability. It is claimed that up to 100% regrind may be used. Under correct processing conditions the polymers have been shown to produce samples with little change in physical properties even after seven regrinds.

- (3) For such a heat-resisting material, a modest enthalpy requirement to reach the processing temperature of about 434 J. This also means that quite short cooling cycles are possible.
- (4) Melt temperatures depend on the grade of material used. One rule of thumb is to use the formula $(H + 125)^{\circ}\text{C}$, where H is the heat deflection temperature. Typical melt temperatures are in the range 250–290°C.
- (5) The melts, unlike unmodified PPO, are very pseudoplastic. At 280°C one standard grade (Noryl 110) has a viscosity of 675 N s m^{-2} at 100 s^{-1} but a value of only 7 N s m^{-2} at $100\,000 \text{ s}^{-1}$. The flow depends considerably on the grade but flow path ratios tend to be in the same range as for ABS materials
- (6) A low moulding shrinkage (0.005–0.007 cm/cm) in unfilled grades down to about 0.002 cm/cm in 30% glass-fibre-filled grades.
- (7) To reduce strains in mouldings, fairly high mould temperatures are recommended (65–95°C in unfilled and up to 120°C in glass-filled grades).

21.5.6 Polyamide PPOs

The blending of PPO and polyamides requires special grafting techniques to give a good bond between the two polymers, as otherwise the two polymers are incompatible. Whilst these polymers show the good dimensional stability and toughness of styrenic PPOs, they also have

- (1) Better heat resistance (Vicat softening points of 190–225°C).
- (2) Better melt flow characteristics.
- (3) Better resistance to many chemicals associated with the automobile industry. This covers not only commonly used automobile fuels, oils and greases, but detergents, alcohols, aliphatic and aromatic hydrocarbons and alkaline chemicals.

As a consequence of these advantages, these blends are finding particular application for car parts that can be painted on-line side by side with metals at high temperatures.

Disadvantages include the following:

- (1) The higher water absorption (typically 3.5% compared with about 0.3% at saturation for a styrenic PPO).
- (2) At the time of writing (1999) the best available flame retardance is to UL94 V1 rating but the incandescent wire resistance of up to 960°C makes the materials of interest in such electrical applications as plug and socket containers.

Polyamide PPOs are manufactured by General Electric (Noryl GTX), BASF having now withdrawn from marketing their product (Ultranyl). Usage of the blends has so far been mainly in the automobile field for such applications as valance panels, wheel trims, grilles, rear quarter panels, front bumpers and tailgates.

21.5.7 Poly(2,6-Dibromo-1,4-Phenylene Oxide)

The dibromo equivalent of PPO is commercially manufactured by Velsicol Chemical Corporation under the trade name Firemaster. As the trade name

suggests, the material is recommended as a fire retardant; in particular for glass-reinforced nylons, thermoplastic polyesters and other engineering thermoplastics requiring high processing temperatures and thus an additive with a high level of thermal stability, a property shown by this polymer. With a bromine content of 63–65.5%, the commercial product has a high softening range of 200–230°C in spite of a somewhat low molecular weight of about 3150. One consequence of this low molecular weight is that it also appears to act as a flow promoter in blends with engineering thermoplastics. This polymeric fire retardant, which has a specific gravity of 2.07, is incorporated by melt blending.

21.6 POLYPHENYLENE SULPHIDES¹⁰

These materials have been prepared by polymerisation of *p*-halothiophenoxide metal compounds both in the solid state and in solution. They have also been prepared by condensation of *p*-dichlorobenzene with elemental sulphur in the presence of sodium carbonate while the commercial polymers are said to be produced by the reaction of *p*-dichlorobenzene with sodium sulphide in a polar solvent.

The first commercial grades were introduced by Phillips Petroleum in 1968 under the trade name Ryton. These were of two types, a thermoplastic branched polymer of very high viscosity which was processed by PTFE-type processes and an initially linear polymer which could be processed by compression moulding, including laminating with glass fibre, and which was subsequently oxidatively cross-linked.

When introduced in Europe in 1973 the main emphasis was on moderate molecular weight grades which could be injection moulded at 340 to 370°C and then if desired cross-linked by air aging. In the moulding stage mould temperatures of 25–40°C were said to give the greatest impact strength whilst a high surface gloss is obtained at 120°C. Coating grades also became available.

With the expiry of the basic Phillips patents in 1985, other companies entered the market so that in the early 1990s there were six producers. Besides Phillips, these included Bayer (Tedur), Hoechst-Celanese (Fortron) and General Electric (Supec). This has led to some overcapacity but production rose from about 10 000 tonnes in 1985 to about 35 000 tonnes in 1997. Such competition has stimulated the production of improved grades of materials. In particular, many of the newer grades are less branched than the early materials, making possible fibre forming, production of biaxially stretched film and mouldings of improved impact resistance. Newer grades also have a much lower level of ionic contaminants. At the same time that the newer grades of PPS were being introduced, Phillips also produced some interesting related amorphous polymers.

Whilst the properties of poly(phenylene sulphides) vary between grades, particularly because of varying molecular linearity and presence of contaminants, they generally show the following special characteristics:

- (1) Heat resistance (for a thermoplastics material).
- (2) Flame resistance.
- (3) Chemical resistance, although surpassed by some other polymers such as PTFE.
- (4) Electrical insulation characteristics, although also surpassed by some other polymers such as PTFE and polyethylene.

The linear polymers are highly crystalline, with T_m in the range 285–295°C. Quoted values for the T_g range from 85°C to 150°C. Unfilled materials have rather low heat deflection temperatures but filled grades can have values in excess of 260°C. This is in line with common experience that the deflection temperatures of unfilled crystalline polymers are close to the glass transition temperature, whilst the deflection temperatures of fibre-filled polymers are closer to the T_m . The US Underwriters Laboratories have awarded PPS grades temperature indices as high as 240°C—the highest ratings awarded to date to a commercial thermoplastics material. Thermogravimetric analysis shows no noticeable weight loss either in nitrogen or oxygen at temperatures below 500°C.

The resistance to burning is also very good indeed, this being reflected by oxygen indices as high as 53% and Underwriters Laboratories 94 V-0 and 94–5V classifications without the use of additives. The UL94 V-0 ratings are achieved with minimum wall thicknesses as low as 0.4 mm, putting the material into a highly select class that includes the polyethersulphones, the polyester liquid crystal polymers, the polyketones and the polyetherimides.

Outstandingly, all the grades of at least one manufacturer pass the demanding glow wire test at 960°C at 3.2 mm.

In addition to the inherent flame resistance, the polymers are also interesting because of the low smoke generation and low levels of toxic and corrosive emissions when exposed to fire.

The chemical resistance of the linear polymers is also very good. Resistant to most acids, aqueous bases, hydrocarbons, most halogenated hydrocarbons, alcohols and phenols, they are attacked by concentrated sulphuric acid, formic acid, some amines, benzaldehyde, nitromethane and a few other reagents. They will dissolve in 1-chloronaphthalene at elevated temperatures but in general have excellent solvent resistance. The polymer is cross-linked by air oxidation at elevated temperatures.

Typical properties of poly(phenylene sulphides) are shown in *Table 21.2*. Whilst rigidity and tensile strength are similar to those of other engineering

Table 21.2 Typical properties of injection moulded PPS, PAS-1 and PAS-2 thermoplastics

<i>Property</i>	<i>Units</i>	<i>PPS</i>	<i>PPS/GF (60/40)</i>	<i>PAS-1</i>	<i>PAS-2</i>
T_g	°C	85	—	145	215
Heat distortion temp. (Method A)	°C	135	265	170	190
Tensile strength (21°C)	MPa	64–77	150	77	92
(204°C)	MPa	33	33	—	—
Elongation at break	%	3	2	—	>10
Flexural modulus	MPa	3900	10 500	3400	3200
Izod impact (unnotched)	J/m	320	350	223	1200
(notched)	J/m	20	—	21	50
Limiting oxygen index	%	44	47	46	46
Dielectric constant (10^3 – 10^6 Hz)		3.1	3.8	—	—
Dissipation factor (1 kHz)		0.004	0.0037	—	—
Volume resistivity	ohm.cm	2.5×10^{16}	$>10^{13}$	—	—
Water absorption 24 h	%	—	0.01	—	—
Saturation at 23°C	%	—	1.01	—	—

plastics, the poly(phenylene sulphides) do not possess the toughness of amorphous materials such as the polycarbonates and the polysulphones and are indeed somewhat brittle. On the other hand they do show a good level of resistance to environmental stress cracking.

The unfilled grades are of little importance, with the following filled grades being of commercial interest:

- (1) Glass-reinforced grades (at 30 and 40% glass content loading).
- (2) Glass-fibre/particulate-mineral-filled grades. These may offer cost savings and in some cases give the highest temperature ratings. Arc and tracking resistance, somewhat limited as with most aromatic polymers, is greatest with these grades, although with some loss in volume resistivity and dielectric strength.
- (3) Glass-fibre/mineral-filled colour compounds.
- (4) Carbon-fibre-reinforced grades. These are useful because of their high tensile strength and rigidity, improved EMI shielding and static electricity dissipation. They are also more effective than glass fibre in reducing the coefficient of friction against steel.
- (5) Lubricated fibre-filled grades containing, typically, 15% of PTFE and occasionally about 2% of a silicone. These materials yield very high PV values (see Chapter 19), with published data indicating PV values of 30 000 (using the units of Chapter 19) at surface velocities of 1000 fpm. These figures appear to be better than for any other engineering thermoplastic material.

The heat and flame resistance coupled with good electrical insulation characteristics, which includes in some grades good arcing and arc tracking resistance, has led to PPS replacing some of the older thermosets in electrical parts. These include connectors, coil formers, bobbins, terminal blocks, relay components, moulded bulb sockets for electric power station control panels, brush holders, motor housings, thermostat parts and switch components.

In the industrial mechanical field PPS was soon established for use in chemical processing plant such as gear pumps. More recently it has found application in the automotive sector as a result of its ability to resist corrosive engine exhaust gases, ethylene glycol and petrol (gasoline). Specific uses include exhaust gas return valves to control pollution, carburettor parts, ignition plates and flow control valves for heating systems.

The material also finds use in cooking appliances, sterilisable medical, dental and general laboratory equipment, and hair dryer components.

Compared with other glass-reinforced thermoplastics, PPS materials are generally considered as showing good processability. Easy-flow properties at processing temperatures with flow path ratios of the order of 150 allow thin-wall sections to be produced. It is a consequence of such easy-flow behaviour that care has to be taken to minimise mould flashing and this had led to marketing of 'low-flash' grades. Furthermore, as shown in *Table 8.1*, the amount of heat required to be removed before an injection moulding can be extracted from a mould is quite low and this makes possible short cycle times.

Typical melt temperatures are in the range 300–360°C (e.g. 320°C). Mould temperatures are usually about 135°C in order to optimise the amount of crystallinity and hence give mouldings of greatest stiffness, dimensional stability, thermal stability and surface finish. It is, however, possible to use relatively cold

moulds, as low as 30°C, to reduce crystallinity to yield products of higher toughness and durability but with lower heat resistance and with a matt surface finish.

The thermosetting materials are said to be initially linear but are cross-linked by heating in air to a temperature of at least 345°C. It is claimed that they have a useful working range up to 315°C. The materials may be used in compression mouldings powders, as the binder resin in glass cloth laminates and as the polymer base in heat-resistant metal coatings.

21.6.1. Amorphous Polyarylene Sulphides

The Phillips Corporation have recently introduced interesting copolymers related to PPS. In addition to the use of *p*-dichlorobenzene and Na₂S_x, a second aromatic dichloro compound is used. For the marketed material PAS-2 this is 4,4'-dichlorodiphenylsulphone whilst for the developmental products PAS-1 and PAS-B the compounds are 4,4'-dichlorodiphenyl and 4,4'-dichlorodiphenylketone. Each of these copolymers is amorphous, so that a high heat deformation resistance requires a high value for T_g .

PAS-2 is particularly notable for its high level of chemical and hydrolysis resistance in addition to a T_g of 215°C. Some typical properties of the copolymers PAS-1 and PAS-2 are given in *Table 21.2* in comparison with data for PPS.

21.7 POLYSULPHONES

Although it is somewhat of an oversimplification, the polysulphones are best considered as a group of materials similar to the aromatic polycarbonates but which are able to withstand more rigorous conditions of use. Because of their higher price they are only considered when polycarbonates or other cheaper polymers are unsuitable.

The simplest aromatic polysulphone, poly(*p*-phenylene sulphone) (formula I of *Table 21.3*) does not show thermoplastic behaviour, melting with decomposition above 500°C. Hence in order to obtain a material capable of being processed on conventional equipment the polymer chain is made more flexible by incorporating ether links into the backbone.

The first commercial polymer (*Table 21.3*, II) was offered in 1965 by Union Carbide as Bakelite Polysulfone, now renamed Udel. In 1967 Minnesota Mining and Manufacturing introduced Astrel 360 (*Table 21.3*, V), which they referred to as a polyarylsulfone. In 1972 ICI brought a third material onto the market which they called a polyethersulphone (III) and which they then marketed as Victrex. They also introduced a material intermediate between III and V known as Polyethersulphone 720P (IV) but which has now been withdrawn. In the late 1970s Union Carbide introduced Radel (VI), which has a higher level of toughness. Around 1986 Union Carbide sold their interest in polysulphones to Amoco. In addition the Astrel materials were produced by Carborundum under licence from ICI.

In 1992 ICI withdrew from the polysulphone market, with BASF (Ultrason) joining Amoco as manufacturers whilst a small plant operated by Sumitomo was due to come on stream in the mid-1990s.

It will be seen that by varying the degree of spacing between the *p*-phenylene groups a series of polymers may be obtained with a spectrum of T_g s, which

Table 21.3 Aromatic polysulphones

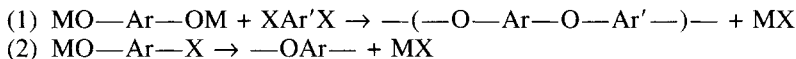
	Tyre	T _g (°C)	Trade name
I		(melts with decomposition above 500°C)	—
II		190	Udel
III		230	Victrex
IV		250	Polyether-sulphone 720P
V		285	Astrel 260
VI			Radel

determine the heat distortion temperature (or deflection temperature under load, since the materials are also amorphous). It is also to be noted that all of the commercial materials mentioned above may be described as polysulphones, polyarylsulphones, polyether sulphones or polyaryl ether sulphones.

In principle there are two main routes to the preparation of polysulphones:

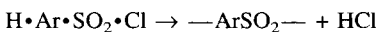
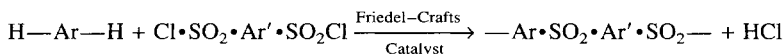
- (1) Polyetherification.
- (2) Polysulphonylation.

In the polyetherification route the condensation reaction proceeds by reactions of types (1) and (2) where M is an alkali metal and X a halide.



The Ar and/or Ar' group(s) will contain sulphone groups and if Ar = Ar' then identical products may be obtained by the two routes. Polyetherification processes form the basis of current commercial polysulphone production methods. These will be discussed further below.

Polysulphonylation reactions are of the following general types:



In this case the Ar and/or Ar' group(s) will contain an ether oxygen. As before if Ar = Ar' then basically identical products may be made by the two polysulphonylation routes (see e.g. Figure 21.4). Where a diether and a disulphonyl chloride are co-condensed there may be some reaction at *o*- and *m*-positions in addition to the desired reaction at the *para*-position. It has been found that *o*- and *m*-linked polymers are more brittle, at least in the above example. It is of interest to note that self-condensation of the monosulphonyl chloride of diphenyl ether, on the other hand, can proceed so as to give a virtually all-*para* and hence tough material. Whilst the self-condensation polysulphonylation route has been used commercially it is understood not to be in current commercial use.

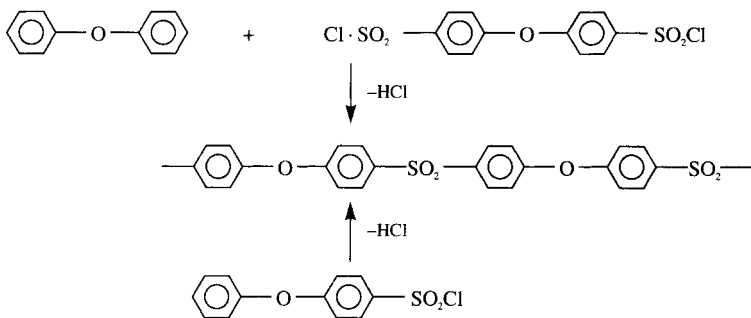


Figure 21.4

In the polyetherification route the sulphone group plays an active role in the synthesis. When metal phenates are reacted with certain activated aromatic halides in suitable solvents, high yields of the corresponding aryl ethers are obtainable under the appropriate conditions. The equation for the reaction is shown in Figure 21.5 when M is Na, K, etc., X is *ortho*- or *para*- halogen and W is a negative group such as ---NO_2 , SO_2R , etc.

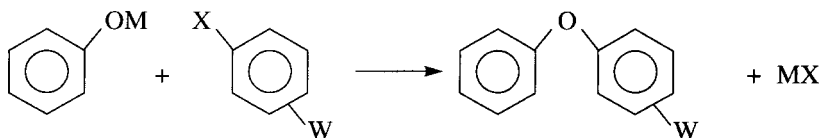


Figure 21.5

A consequence of the reaction is that it is possible to produce a range of polymers by reacting bisphenates with appropriately activated aromatic dihalides. In the case when the dihalide is activated by the presence of a sulphone $\text{---SO}_2\text{---}$ group the polymers may be referred to as polysulphones. The Amoco materials are prepared in this way.

The laboratory preparation of the Udel-type polymer has been described.¹¹ Bis-phenol A is mixed with chlorobenzene (solvent) and dimethyl sulphoxide (active solvent) and heated to 60°C to obtain a clear solution. Air is displaced from the system by nitrogen or argon and an aqueous solution of caustic soda added. This results in a two-phase system, one predominantly chlorobenzene the

other the disodium salt dissolved in aqueous dimethyl sulphoxide. This mixture is brought to reflux and continually heated until the temperature reaches 150–160°C. A solution of di-(4-chlorophenyl) sulphone is slowly added to the mixture and the whole reacted for about one hour.

If the temperature is below 150°C low molecular weight, sodium-ended, polymer is precipitated and is difficult to redissolve on subsequently raising the temperature. Above 160°C the reaction is extremely rapid and solvent decomposition and/or discolouration and even gelation of the mass can occur. Methyl chloride may be added, forming unreactive methyl ether and groups preventing further polymerisation. The addition of the methyl chloride also causes the vivid orange–yellow product formed initially to fade to a light amber colour.

The condensation reaction is promoted by certain polar solvents and of the many which have been tested dimethyl sulphoxide appears to be the most effective. As usual with linear condensation polymers molecular equivalence and near-absence of monofunctional material is necessary to ensure a high molecular weight. Moisture and alcohols can also have a devastating effect on the molecular weight. In the case of water it is believed that 4-chlorophenyl 4-hydroxyphenyl sulphone¹² is formed which functions as an effective chain terminator. Gross contamination with air is also believed to reduce the maximum attainable molecular weight as well as causing intense discolouration.

A range of polysulphones has been prepared with a variety of bis-phenols other than bis-phenol A.¹¹ As might be expected from the discussion in Chapter 4 and from experience with the range of polycarbonates (Chapter 20), replacement of the isopropylidene link with a methylene, sulphide or oxygen link depresses the T_g whilst $-\text{C}(\text{C}_6\text{H}_5)_2-$ and sulphone links raise it. The bis-phenol derived from norcamphor leads to a polysulphone with a T_g of 250°C (195°C for a Udel-type polymer).

Not surprisingly a number of other poly(aryl ethers) have been prepared from aromatic dihalides not containing sulphone links. For example, a number have been prepared from difluorobenzophenone and, in general, it is found that such materials have T_g s about 30–40°C lower than the corresponding sulphone polyether. In fact it is generally found that the higher T_g values are obtained with the sulphone polyethers.

21.7.1 Properties and Structure of Polysulphones

All of the commercial polymers are linear and although most have regular structures they are all, at least for practical intents and purposes, amorphous. The high in-chain aromaticity leads to high values of the T_g , the Amoco product Udel having a T_g of about 190°C whilst the ICI polymer has an even higher value of about 230°C. The Amoco materials have a secondary transition at -100°C and that of the ICI polymer is -70°C .¹³ Typical \bar{M}_n values are about 23 000.

Within these temperature ranges the polymers are, like the polycarbonates, tough. Because of the stiff chain and the resultant high T_g , processing temperatures need to be above 300°C.

It is interesting that all the commercial polysulphones are unable to crystallise in spite of their regular structure. It might be expected that the stiff chain with its high T_g and T_m would only crystallise with difficulty but in itself this would not be expected to inhibit it completely. One suggestion¹⁴ is that whereas the ether link has a bond angle of 120° the C—S—C bond angle is 105° and that it is difficult to fit these bond angles into a crystal lattice.

Although the structure is polar much of the polarity is frozen in at normal service temperatures. In such conditions electrical insulation properties are quite good even at high frequencies. As with many aromatic polymers, tracking resistance leaves something to be desired.

In addition to the heat deformation resistance the polymers are also resistant to chemical change on heating. This has been ascribed to the high degree of resonance which gives an enhanced bond strength. It is therefore capable of absorbing a high degree of thermal and ionising radiation without cross-linking. It has also been suggested that since the sulphur is in its highest oxidation state electrons are withdrawn from the benzene rings so that the structure is less susceptible to oxidation.

The commercial polymers are generally resistant to aqueous acids and alkalis although they are attacked by concentrated sulphuric acid. As might be expected of a highly polar polymer it is not dissolved by aliphatic hydrocarbons but solvents include dimethyl formamide and dimethyl acetamide.

21.7.2 General Properties of Polysulphones

The principal features of the commercial polysulphones are their exceptional resistance to creep, good high-temperature resistance, rigidity, transparency and self-extinguishing characteristics. These characteristics also figure prominently in a consideration of polycarbonates and a comparison is given in *Table 21.1*. In brief the polysulphones are more heat resistant and have greater resistance to creep whilst the polycarbonates have a somewhat higher Izod and tensile impact strength as well as being less expensive. The polysulphones are tough but as with the polycarbonates they are notch sensitive.

The differences between the main types of polysulphone are quite small. The polyethersulphones (Type III in *Table 21.3*) have markedly better creep resistance at elevated temperatures, e.g. 150°C, significantly higher heat distortion temperatures and marginally superior room temperature mechanical properties than the Type II materials. They also exhibit higher water absorption, dielectric constant and specific gravity.

This difference should be borne in mind when comparing relative costs of the polymers.

Table 21.4 Comparison of glass-filled with unfilled polysulphone¹⁵

<i>Property</i>	<i>Units</i>	<i>Unfilled</i>	<i>40% Glass-filled</i>
Specific gravity	—	1.24	1.54
Tensile strength	lbf/in ²	10 200	18 000
	MPa	70	124
Tensile modulus	lbf/in ²	370 000	1 500 000
	MPa	2600	11 000
Tensile impact strength	ft lb in ⁻²	400–500	60–100
Creep resistance. Deflection after 500 cycles at 2000 lbf in ⁻² at 22.2°C	%	1.05	0.29
Heat distortion temperature (264 lb in ⁻²)	°C	174	187
Coefficient of linear expansion	cm cm ⁻¹ °C ⁻¹	5.58 × 10 ⁻⁵	1.98 × 10 ⁻⁵
Moulding shrinkage	cm/cm	0.007	0.002

Higher molecular weight grades show somewhat greater resistance to stress cracking, have better long-term strength under load and, in some cases, have better impact strength.

Glass-fibre-filled polysulphones are also available. These show significantly increased creep resistance and lower coefficients of thermal expansion (*Table 21.4*).

21.7.3 Processing of Polysulphones

When processing polysulphones there are four main points to bear in mind:

- (1) The polymers absorb some moisture and at the high moulding temperatures employed this can be very troublesome, leading to streaks and splash marks.
- (2) The polymers have high softening points and hence processing temperatures in the range 320–415°C may be required.
- (3) Even at these temperatures the melts are very viscous, necessitating robust equipment.
- (4) The rather rigid molecules and high setting temperatures are conducive to molecules freezing in an oriented position with consequent high frozen-in stresses.

In injection moulding a screw preplasticiser is preferred with melt temperatures in the usual range 335–400°C. Mould temperatures are in the range 100–160°C, the higher temperatures giving the more stress-free mouldings. Because of the high melt viscosity generous cross-section runners and gates are required. With time a black layer of degraded polymer may build up on the cylinder wall and eventually pull away, giving black marks to the moulding. This necessitates periodic purging. Purging should also be carried out if the machine to be used has been employed for moulding other polymers. Highly stabilised polypropylene and (more expensive) polycarbonates can be employed for this purpose.

The amount of frozen-in stress may be reduced not only by high mould temperatures, which increase the moulding cycle, but by annealing in air or, preferably, glycerine at about 160°C. A qualitative idea of the degree of frozen-in stress can be obtained by immersing mouldings into ethyl acetate. If the moulding does not show cracks within 3 seconds the moulding is often considered to be satisfactory. Liquids cause different degrees of stress cracking. It has been suggested that for acetone and ethyl acetate the critical stress is less than 200 lbf/in² (1.4 MPa), for cellulose 1200 lbf/in² (8.5 MPa) and for carbon tetrachloride 2400–2600 lbf/in² (17–19 MPa).

For extrusion and blow moulding the polysulphones used are of higher molecular weight. Melt temperatures for blow moulding are of the order of 300–360°C with mould temperatures about 70–95°C.

21.7.4 Applications

The polysulphones tend to be used in applications when requirements cannot quite be met by the much cheaper polycarbonates and possibly aromatic polyethers. In many of the fields of use they have replaced or are replacing ceramics, metals and thermosetting plastics rather than other thermoplastics.

The generally very good electrical insulation properties coupled with heat resistance and non-burning behaviour indicate usage in coil bobbins, printed circuit boards (which resist heat of soldering), lamp bulb bases and TV

components. The chemical resistance to petrol, mineral oils and acids together with heat resistance are important considerations when selecting car 'under-the-bonnet' components. Several hair dryer, oven, iron and fan-heater components may also be made from the polymers.

Other, more recently developed, uses include microwave oven parts, transparent pipelines, chemical plant pumps and coffee machine hot water dispensers. One exceptional use has been to produce, by an extrusion moulding process, very large rollers for textile finishing for use where cast nylons cannot meet the specification. Also of growing interest are medical equipment applications that may be repeatedly steam-sterilised at 134°C, filtration membranes and cartridges for ink-jet printers.

There has also been particular interest in a rigid foam material for use in aerospace, shipbuilding and medical appliances.

There has been a high growth rate in global production capacity from about 9500 t.p.a. in the early 1990s to about 30000 by the turn of the century the bulk of this being for the cheaper Udel-type materials. It is still however less than 3% of the market for polycarbonates. The polysulphone market is split approximately into 46% North America, 27% Western Europe, and 27% Japan. Reviews published at the beginning of the 1990s estimated that about 30% of the market was for glass-filled materials which are often less expensive than filled grades. It was also estimated that 45% of total polysulphone production found use in electronics applications, 25% for end user products, 10% in transport and 10% in medical applications.

21.7.5 Blends Based on Polysulphones

Several blends based on polysulphone materials have been marketed. Probably the most well known is Mindel, originally produced by Uniroyal, acquired by Union Carbide, but now marketed by Amoco. Whilst not exhibiting the heat resistance of the unblended homopolymer, Mindel materials, which are blends of polysulphone and ABS, are lower in cost, easier to process and have higher notched impact strengths. The Mindel A materials are unreinforced, the Mindel B grades contain glass fibre, and the Mindel M grades contain other mineral fillers. A related polysulphone/SAN blend has been marketed as Ucardel.

A 50/50 blend of Udel and ABS based on α -methylstyrene was introduced by Uniroyal but is now marketed by USS Chemicals as Arylon T. This material has a heat deflection temperature almost identical to that of the unfilled Mindel materials (150°C).

21.8 POLYARYLEETHER KETONES

The chemistry and technology of this class of polymer may be considered as an extension to those of the polysulphones, particularly insofar as there are strong parallels in preparative methods. The two polymer classes also have strong structural similarities with polysulphones containing the structure (I) and the polyetherketones the structure (II) of *Figure 21.6*.

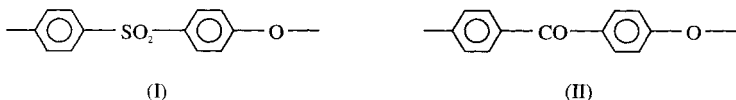


Figure 21.6

The first preparations reported, analogous to the polysulphonylation reaction with the polysulphones, were by self-condensation of acid chlorides under Friedel–Crafts conditions (Bonner¹⁶; Goodman *et al.*¹⁷) but the products had a low average molecular weight (*Figure 21.7*). The difficulty in obtaining larger molecules was in due course found to be due to the ready ability of these materials to crystallise (unlike the polysulphones) and hence not remain in solution in organic solvents. It was, however, found that hydrofluoric acid was a solvent for the polymer at 20°C. Dahl and his colleagues¹⁸ at Raychem developed a route to high molecular mass polymer by reacting in HF with BF₃ as a catalyst. This product was marketed during the period 1972 to 1976 as Stilan.

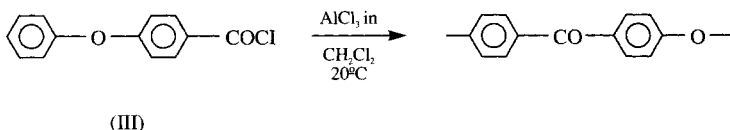


Figure 21.7

Alternative approaches were developed by Rose and his colleagues at ICI^{19,20} involving polyetherification reactions, in principle very similar to the polyetherification processes that they had developed earlier for the manufacture of polysulphones (*Table 21.3*), either by self-condensation of products such as IV or reaction between intermediates V and VI (*Figure 21.8*).

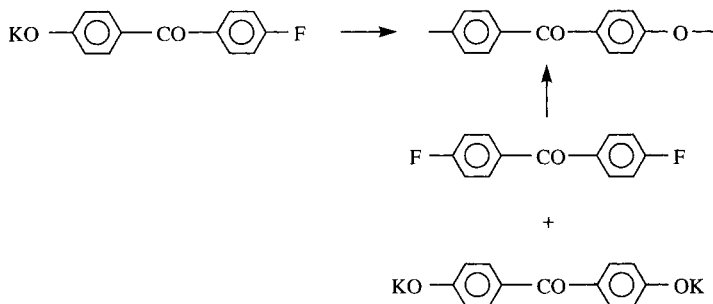


Figure 21.8

Once again there are problems due to crystallisation as the polymer is being formed. One way of avoiding this, with the consequent throwing out of the growing polymer from the reactant mixture, is to react in a high boiling solvent at a temperature close to the T_m of the polymer.

Several polyaryl ether ketones, generically given the abbreviation PAEK, have been reported in the literature, including those shown in *Table 21.5*. Of these, three have been in commercial production. They are:

- (1) Polyether ether ketone (PEEK) (structure B of *Table 21.5*). This material was first prepared in the laboratories of ICI in 1977 and test marketed in 1978. The material is now marketed by Victrex as Victrex PEEK.

Table 21.5

	Polymer	T_g (°C)	T_m (°C)
A	(PEK)	154	367
B	(PEEK)	144	335
C	(PEKK)	—	384
D	—	—	416
E	(PEEKK)	160	—

- (2) Polyether ketone (PEK) (structure A). In 1986 three European companies (BASF, Hoechst and ICI) announced they were developing the material (to be marketed under the trade names of Ultrapek, Hostatec and Victrex PEK respectively).
- (3) Polyether ether ketone ketone (PEEKK), the latest material to be introduced (Hostatec X—Hoechst).

By 1998 only PEEK was still commercially available.

The polyaryl ether ketones quickly became established as outstanding heat-resistant thermoplastics materials for the following reasons:

- (1) As with the polysulphones, the deactivated aromatic nature of the polymer leads to a high degree of oxidative stability, with an indicated UL Temperature Index in excess of 250°C for PEEKK. The only other melt-processable polymers in the same league are poly(phenylene sulphides) and certain liquid crystal polyesters (see Chapter 25).
- (2) PAEK materials show extremely low flammability, achieving UL V-0 classifications with a wall thickness as low as 0.8 mm without the need for fillers or other additives. It is reported that at least one PAEK (PEEKK) is able to meet the OSU Test for heat release which has been required by the Federal Aviation Administration since 1990—a requirement no longer satisfied by many of the materials used in aircraft construction.
- (3) Extremely low smoke emission. PEEK has been claimed to have the lowest toxic gas and smoke emissions of any plastics material.
- (4) A high softening point. Data for softening points (heat distortion temperatures, deflection temperatures under load etc.) follow the usual predictions for crystalline plastics (as discussed in Section 9.2). Thus unfilled grades have softening points close to the T_g , whilst glass-filled grades have values close to the T_m . Thus a glass-filled grade of PEEK has a deflection temperature of 315°C compared to a T_m of 315°C.

Other notable features of PAEKs are:

- (1) Excellent toughness and wear resistance. For example, the resistance to 'cut through' of wire coverings is far superior to that of most other heat-resisting plastics. It is interesting to note that in 1994, 50% of applications of PEEK were related to the excellent wear behaviour.
- (2) Excellent fatigue resistance.
- (3) Excellent hydrolytic stability. (For example, PEK has very good resistance to hot water at 125°C, under which conditions other heat-resisting plastics such as the polyimides are liable to fail.)
- (4) Good radiation resistance with no significant degradation below 1100 Mrad.
- (5) Very good low-friction properties of bearing grades (usually containing 10–20% of PTFE). Thus a bearing grade of PEEKK has been reported to have a coefficient of friction as low as 0.06 (similar to that of PTFE), whilst at elevated temperatures it has been noted that for PEEK the static and dynamic coefficients of friction tend to converge, thus reducing slip-stick effects.

The main differences between the commercial types of PAEK arise largely from the differences in the T_m . Whilst the higher T_m may lead to a higher heat deformation temperature, there is also a corresponding higher processing temperature required and this can have an adverse effect on the thermal stability. Some typical properties are given in *Table 21.6* but it should be pointed out that the data have been acquired from different sources and are therefore not closely comparable.

Polyaryl ether ketones may be processed on conventional injection moulding and extrusion equipment, providing sufficiently high temperatures can be achieved. Melt temperatures required are typically 370°C for unreinforced PEEK, 390°C for reinforced PEEK and both unreinforced and reinforced PEK and unreinforced PEEKK, and 410°C for reinforced PEEKK. For the latter material a temperature profile from feed zone to nozzle would be

Table 21.6 Some typical properties of PAEK materials

Property	Unfilled polymer			30% GF polymer			30% CF Polymer PEEKK
	PEEK	PEK	PEEKK	PEEK	PEK	PEEKK	
Specific gravity	1.32*	1.32	1.3	—	—	1.55	1.45
Melting point (°C)	334	365	365	—	—	—	—
Heat deflection temp. (°C)	150	165	160	315	340	>320	>320
Tensile strength (MPa)	92	110	86	157	180	168	218
Modulus (MPa)	3900	—	4000	8700	—	13 500	22 500
Izod impact KJ/m ²	8	8	—	10	10	—	—
J/m	—	—	51	—	—	71	60
Water absorption (%) (24 h)	0.51	—	—	0.10	—	—	—
Volume resistivity (Ωcm)	10 ¹⁶	—	10 ¹⁷	—	—	—	—
Permittivity	3.2	—	3.6	—	—	—	—
Dissipation factor	0.001	—	0.001	—	—	—	—

* Data are for fully crystalline material apart from electrical data for PEEKK. It may be noted that the amorphous SG of PEEK is 1.265. The modulus data is flexural for PEEK and tensile for PEEKK.

380/390/400/410°C. Typical mould temperatures can be as high as 165°C. At these temperatures small amounts of moisture can be serious, so that drying of granules is essential (e.g. 3 h at 150°C).

Although total usage of PAEK materials was estimated as being as high as 5000 t.p.a. in 1995 the withdrawal of all suppliers except Victrex reduced capacity to about 1600 t.p.a. by the end of 1996. In 1998 however Victrex announced a capacity expansion to 2000 t.p.a.

The polymers have been used in such aggressive environments as nuclear plant, oil and geothermal wells, chemical plant and high-pressure steam valves. One specific example announced in 1998 was for gas compressor line valve plates used in the collection, pressurisation and transportation of gases in chemical, petroleum and industrial process uses. Factors leading to the selection of PEEK as a replacement for metal in this application were the excellent corrosion resistance, strength, durability including wear resistance, high temperature stability, light weight and superior sealing characteristics. For similar reasons PEEK has replaced stainless steel in pumps for handling chemicals. In the car industry the combination of excellent thermal properties and excellent low-friction properties of bearing grades have led to use in such applications as bearing cages, gear support bearings, thrust washers, clutch seals, transmission parts, housings for tyre pressure sensors and valve spring discs. In the aircraft industry there is great interest as a result of the excellent fire properties and resistance to rain erosion of composites, whilst in general machinery and processing equipment the materials are used for rollers, guides, gears and reciprocating components. Parts for domestic irons and microwave ovens have been produced from PEEK. Wire coverings are of interest because of the excellent fire properties, including absence of halogens, the resistance to radiation and the resistance to 'cut through' round sharp corners, which helps miniaturisation. Filaments are used in filter cloths. Recent Japanese studies have indicated that PEEK is very suitable as a piping material for transporting ultra-pure material in microchip manufacture.

In 1998 it was also announced that PEEK had obtained FDA approval for food contact applications. This raises the possibility of the material being used for such purposes as food containers, bearings and seals for processing equipment and as a coating for metals in non-stick cookware.

There has been considerable interest in PEEK/carbon fibre composites. These are fabricated using techniques based on those developed for glass-reinforced thermosetting plastics but using high temperatures. Temperature control during the cooling stage is particularly important in order to control the crystallinity and morphology. Fabricated parts are claimed to have a 30% weight saving over aluminium, high impact toughness and excellent damage tolerance, good creep and fatigue resistance and outstanding fire resistance. Tensile strengths as high as 2700 MPa in the direction of fibre orientation have been reported. The composites have been primarily of interest to the aircraft industry, one well-publicised application being in the manufacture of a helicopter tailplane.

In 1997 it was reported that carbon-fibre reinforced PEEK had replaced aluminium in the fuel pump suction manifold of the Airbus. For this application the product has to withstand pressure thrusts of up to 30 bar and resist kerosene at operating temperatures in the range 40–200°C. The ventilation wheel for cooling the electric motor in the same application has also been converted from aluminium to PEEK.

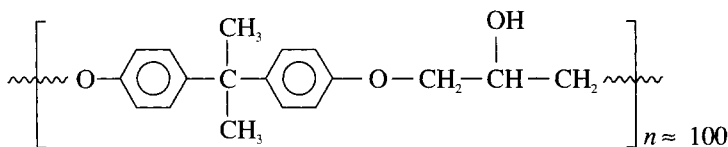


Figure 21.9

21.9 PHENOXY RESINS²¹

The so-called phenoxy resins were a development of epoxide resin technology which had hitherto been used exclusively in the thermosetting resin field (see Chapter 26). As with the most important epoxide resins they are prepared by reacting bis-phenol A with epichlorohydrin to give the following structure (Figure 21.9):

Their main point of difference is that the phenoxies are of much higher molecular weight (~25 000). The phenoxies are also said to be slightly branched. Like the epoxide resins they are capable of cross-linking via the pendant hydroxyl groups, in this instance by di-isocyanates and other agents.

The polymer structure bears a clear resemblance to that of the polycarbonate of bis-phenol A and of the polysulphones so that there are a number of similarities between the materials. The greatest difference arises from the substantial aliphatic segment, which enhances chain flexibility and hence leads to comparatively low softening points. This has placed severe restrictions on the value of these materials and they have found difficulty in competing with the more successful polycarbonates.

The solubility parameter is about $19.2 \text{ MPa}^{1/2}$ and being amorphous they dissolve in such solvents as tetrahydrofuran, mesityl oxide, diacetone alcohol and dioxane. Since the main chain is composed of stable C—C and C—O—C linkages the polymer is relatively stable to chemical attack, particularly from acids and alkalis. As already mentioned, the pendant hydroxyl groups are reactive and provide a site for cross-linking.

The important properties of the phenoxies are their high rigidity, ductility, impact strength and creep resistance, properties for which the polycarbonates are also outstanding. The phenoxies also show very good resistance to alkalis and low gas permeability and it is these two properties which have been important considerations in their applications as plastics. Since the phenoxy resins are notch sensitive, Izod-type impact strengths only yield moderate values. On the other hand dart impact tests on flat unnotched sheets indicate a very high order of toughness.

Dried granules may be injection moulded, blow moulded and extruded without undue difficulty with melt temperatures of 220–260°C. The moulding shrinkage (0.003–0.004 cm/cm) is very low and a somewhat greater than normal draft may be required in deep draw moulds.

The resins found some use as coating, structural adhesives and for bottles to contain alkaline solutions but are no longer marketed.

21.10 LINEAR AROMATIC POLYESTERS

Polyesters form the subject of Chapter 25 but since certain linear aromatic

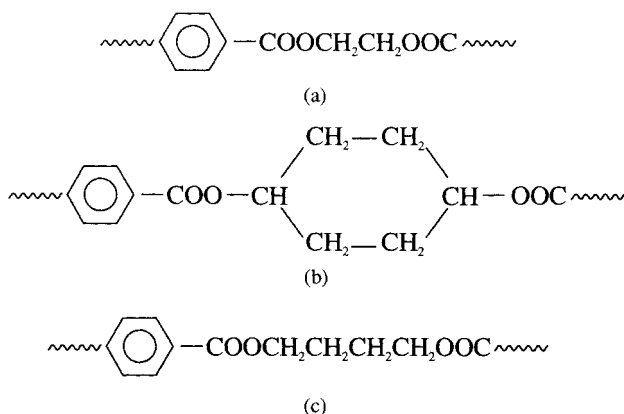


Figure 21.10

thermoplastic polyesters have become available during the past decade to become competitive with the polycarbonates, polyamides and the polymers considered in this chapter they will be given brief treatment here.

The first commercial polymer was poly(ethylene terephthalate) (Figure 21.10(a)) prepared by Whinfield and Dickson in 1941 and which found great success as a fibre (e.g. Terylene, Dacron) and in turn as a film material (e.g. Melinex, Mylar). Because of its sensitivity to traces of moisture at high temperatures and the difficulty of achieving much crystallisation during cooling from the melt it was not generally considered suitable as a moulding material until the introduction of Arnite (AKU-Holland) in the mid-1960s. This material necessitated high moulding temperatures (ca 140°C) in order to control the crystallinity.

In the late 1970s several developments occurred causing renewed interest in poly(ethylene terephthalate) as a plastics material. These included the development of a new mouldable grade by ICI (Melinar) and the development of a blow moulding technique to produce biaxially oriented PET bottles. In addition there appeared a glass-fibre filled, ionomer nucleated, dibenzoate plasticised material by Du Pont (Rynite) (see Chapter 26).

In the early 1960s other terephthalates became available, particularly poly(1,4-cyclohexylene terephthalate) (Figure 21.10 (b)), with slightly higher T_m and superior water and weathering stability to poly(ethylene terephthalate). Fibre and film forms became available.

In the early 1970s a spate of poly(butylene terephthalate) (Figure 21.10 (c)) plastics were introduced primarily as moulding materials. These included Deretron (ICI), Celanix (American Celanese), Valox (General Electric) and Tenite Polyterephthalate (Eastman). The key features of these materials are their good resistance to chemical stress cracking coupled with excellent dimensional stability. They have low T_g s (22–43°C) and melting points of about 224°C. Crystallisation during moulding is rapid even with moulds at temperatures as low as 35°C. The materials clearly do not have the rigidity at elevated temperatures enjoyed by the polycarbonates and other plastics material discussed in this chapter. For this reason the bulk of these materials are of the glass-fibre-filled type, with the fibres giving the polymer a rigidity it retains up to near the

crystalline melting point (T_m). By the end of the 1970s it had become appreciated that there were too many suppliers of this material and many companies withdrew from this market.

There has also been considerable interest in more highly aromatic polyesters. The US company Carborundum for some years offered a range of polyhydroxybenzoates under the trade name Ekkcel which may be used for short periods up to 350°C. Whilst these materials were difficult to process, modifications have given rise to an important class of *liquid crystal polymers* which, besides being self-reinforcing, have many other characteristics of high-performance heat-resisting engineering thermoplastics. In Japan Unitika have offered a copolyester (U-Polymer) which is the reaction product of a mixture of isophthalic acid and terephthalic acid with bis-phenol A. These polymers are also now being offered by the Belgian company Solvay as Arylef and which they referred to as polyarylates. They are amorphous. A similar material made by Eastman (Tenite PCDT) is a copolyester of phthalic acid and terephthalic acid with the hydrogenation product of terephthalic acid. These materials may all be considered as alternatives to the polycarbonates, polysulphones, polyketones and similar materials discussed in this chapter but for consistency in presentation are discussed in greater detail in the chapter on polyesters (Chapter 25).

Another amorphous terephthalate has also been introduced commercially. This is a copolymer based on 1,4-cyclohexylene glycol with a combination of terephthalic acid and isophthalic acid. The copolymer is claimed to have excellent optical properties, have low moulding shrinkage and be relatively easy to vacuum form. As with other terephthalates it is considered in more detail in Chapter 25.

21.11 POLYHYDANTOIN RESINS

These resins have a structure of the form shown in *Figure 21.11*.

Available as wire enamels for some years, they also became available from Bayer as electrical insulating films in 1970.

With a T_g of 273°C and excellent resistance to hydrolysis these films may be used continually at temperatures up to 160°C and for short periods up to 260°C. Their excellent electrical insulation characteristics are well maintained up to temperatures quite close to the T_g as illustrated in *Figure 21.12*. Some other typical properties are given in *Table 21.7*.

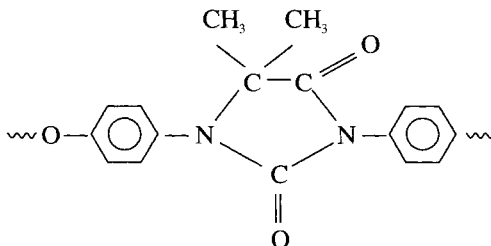


Figure 21.11

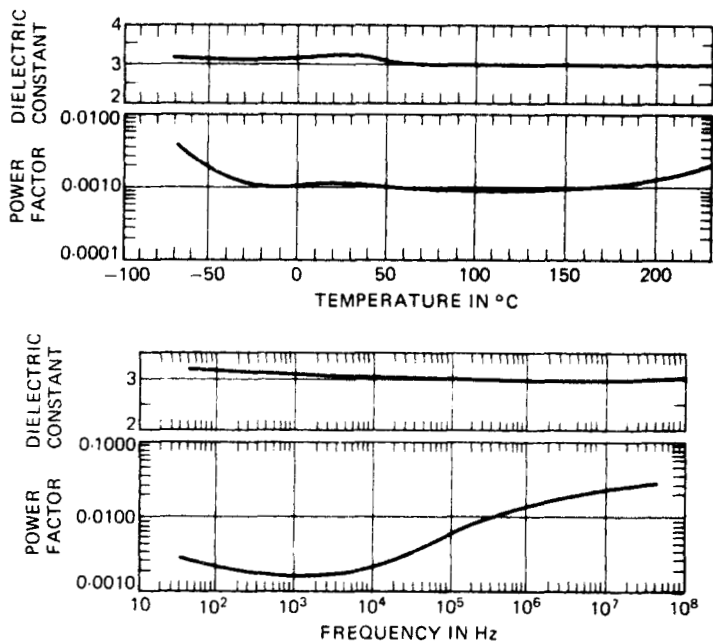


Figure 21.12. Dependence of temperature (at 50 Hz) and frequency (at 23°C) on the dielectric constant and power factor of polyhydantoin film

The resins are resistant to aqueous solutions of acids and alkalis and have a wide range of resistance to solvents. Amongst suitable solvents are methylene dichloride, dimethylformamide and phenol. The films bond well to polyesterimide resins.

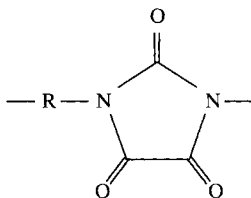
Films have been used for insulating electric motors, in capacitors requiring a heat resistance not met by conventional polyester and polycarbonate dielectrics and as a soldering-resistant base for flexible printed circuits.

Table 21.7 Some properties of polyhydantoin film

Property	Units	Value	Test method
Specific gravity	—	1.27	DIN 53479
Tensile strength	MPa	100	DIN 53455
Elongation at break	%	100	DIN 53455
24 h water absorption	%	4.5	DIN 53475
Breakdown voltage (40 μ m film/50 Hz in air, ball/plate)	kV/mm	200	VDE 0303 Pt2

21.12 POLY(PARABANIC ACIDS)

Closely related to the polyhydantoin are the 2,4,5-triketimidazolidine polymers, known as poly(parabanic acids)²² and produced by Exxon (Tradlon) and Hoechst. They contain the basic structure



where R is typically $-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-$ or $-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-$.

Materials of these types have T_g s of some 290–300°C and some grades are claimed to be stable to about 400°C. Whilst resistant to hydrocarbons, halogenated hydrocarbons, ethers and acids the polymers are soluble in such materials as dimethylformamide, *N*-methylpyrrolidone and pyridine. Bases can cause stress cracking. These non-crystalline polymers are tough at temperatures as low as –46°C whilst at 260°C they have the strength shown by PTFE at room temperature. The polymers also exhibit excellent electrical insulation properties.

Fabrication is most conveniently carried from solution to produce insulating film, wire lacquers and even fibres. The polymers have also been compression moulded. Some properties of two experimental Exxon grades are given in *Table 21.8*.

Table 21.8 Some properties of compression moulded poly(parabanic acid) materials at 23°C²²

Property	Units	Type PPA-M	Type PPA-E
Specific gravity		1.30	1.38
T_g	°C	290	299
Tensile yield strength	MPa	99	106
Tensile modulus	MPa	2500	2700
Volume resistivity	Ωcm	10^{17}	10^{17}
Dielectric constant		3.82	3.60
Dissipation factor		0.0040	0.0027

21.13 SUMMARY

The polymers considered in this chapter have the common feature of possessing in-chain rings which give them higher T_g s than their aliphatic counterparts and even their *ortho*- and *meta*-analogues. In themselves they divide into three groups:

- (1) Polymers with no pretence of high heat resistance but which complement the existing range of thermoplastics used mainly in light engineering application, e.g. phenoxies and aromatic polyesters.
- (2) Polymers with very good heat resistance (both in terms of deformation and of heat aging resistance) but which may be processed by conventional techniques, e.g. polysulphones and poly(phenylene oxides).

- (3) Polymers with exceptional heat stability which require special fabrication techniques such as the polyphenylenes. These materials form part of a group of exceptionally heat-stable materials which will be considered further in Chapter 29.

References

1. WRIGHT, W. W., and LEE, W. A., 'The Search for Thermally Stable Polymers', Chapter in *Progress in High Polymers* Vol. II (Eds. ROBB and PEAKER, Heywood, London (1968))
2. HAY, A. S., BLANCHARD, H. S., ENDRES, G. F., and EUSTANCE, J. W., *J. Am. Chem. Soc.*, **81**, 6335 (1959)
3. *Fr. Patent* 1,234,336 (May 16, 1960)
4. HAY, A. S. and ENDRES, G. F., *Polymer Lett.*, **3**, 887 (1965)
5. KELLEHER, P. G., JASSIE, L. B., and GESNER, B. D., *J. Appl. Pol. Sci.*, **11**, 137 (1967)
6. CIZEK, E. P., *SPEJ.*, **20**, 1295 (1964)
7. HAYCOCK, S. M., *Plast. Technol.*, **12**, 35 (1966)
8. MACKNIGHT, W. J., STOELTING, J., and KARASZ, F. E., Chapter in *Multicomponent Polymer Systems*, Advances in Chemistry Series No. 99, American Chem. Soc., Washington (1971)
9. KRAMER, M., Chapter in *Polyblends and Composites* (Ed. BRUINS, P. F.), Interscience, New York (1970)
10. SMITH, H. A., 'Poly(arylene Sulphides)', Contribution to the *Encyclopaedia of Polymer Science and Technology*, **10**, Interscience, New York (1969)
11. JOHNSON, R. M., FARNHAM, A. G., GLENDINNING, R. A., HALE, W. F., and MERRIAM, C. N., *Journal of Polymer Sci.*, A1, **5**, 2375 (1967)
12. JOHNSON, R. N., and FARNHAM, A. G., *J. Poly. Sci.*, A1, **5**, 2415 (1967)
13. LESLIE, V. J., Private communication
14. ATTWOOD, T. E., KING, T., LESLIE, V. J., and ROSE, J. B., *Polymer*, **18**, 369 (1977)
15. CLAYTON, H. M., and THORNTON, A. E., *Plastics*, **33** (363), 76; (346), 187; and (365), 310 (1968)
16. BONNER, W. H., *U.S. Patent*, 3,065,205 (1962)
17. GOODMAN, I., MCINTYRE, J. E., and RUSSELL, W., *British Patent* 971,227 (1964)
18. DAHL, K. J., *British Patent* 1,387,303 (1975)
19. ROSE, J. B., *British Patent* 1,414,421 (1975)
20. ATTWOOD, T. E., DAWSON, P. C., FREEMAN, J. L., HOY, L. R. J., ROSE, J. B., and STANILAND, P. A., *Polymer Preprints*, **20** (1), ACS Honolulu Meeting, April 1979
21. *Mod. Plastics*, **40** (3), 169 (1962)
22. HENDERSON, D. J., JOHNSON, B. H., and PATTON, T. L., *S.P.E. 30th Ann. Tech. Conf. Papers*, **18** (Pt 2), 669 (1972)

Reviews

- BEHLE, U. and MERMANS, B., *Kunststoffe*, **86**(10), 1549–50 (1996) (PPS)
- DÖRING, E., *Kunststoffe*, **80**, 1149–54 (1990)
- ELIAS, H.-G., and VOHWINKEL, F., *New Commercial Polymers 2* (English edition), Gordon and Breach, New York, London (1986) (see in particular Chapters 6 and 8)
- FELDMANN, H. and STEINERT, P., *Kunststoffe*, **80**, 1123–7 (1990)
- KOCH, E. M. and WALTER, H.-M., *Kunststoffe*, **80**, 1146–9 (1990)
- LÜCKE, A., *Kunststoffe*, **80**, 1154–8 (1990)
- MARGOLIS, J. M. (Ed.), *Engineering Thermoplastics*, Marcel Dekker, New York and Basel (1985) (Chapter 7, J. E. Harris; Chapter 8, D. G. Brady and H. W. Hill; Chapter 9, R. B. Rigby; Chapter 12, R. B. Rigby)
- REIMER, W., *Kunststoffe*, **86**(10), 1540–44 (1996) (PEEK)
- REINKING, K., *Kunststoffe*, **80**, 1141–9 (1990)
- STAHL, P. O., *Kunststoffe* **86**(10), 1552–54 (1996) (Modified polyphenylene ethers)
- TICKTIN, A. and AHLERS, J., *Kunststoffe*, **86**(10), 1534 (1996) (Polysulphonates)

Cellulose Plastics

22.1 NATURE AND OCCURRENCE OF CELLULOSE

Cellulose is the most abundant of naturally occurring organic compounds for, as the chief constituent of the cell walls of higher plants, it comprises at least one-third of the vegetable matter of the world. The cellulose content of such vegetable matter varies from plant to plant. For example, oven-dried cotton contains about 90% cellulose, while an average wood has about 50%. The balance is composed of lignin, polysaccharides other than cellulose and minor amounts of resins, proteins and mineral matter. In spite of its wide distribution in nature, cellulose for chemical purposes is derived commercially from only two sources, cotton linters and wood pulp.

Cotton linters are the short fibres removed from cotton seeds after the long fibres for use in textiles have been taken off by the process of ginning. Digestion under pressure at temperatures in the range 130–180°C with a 2–5% aqueous solution of sodium hydroxide will remove the bulk of the impurities and after a bleaching operation to remove coloured bodies the residual cotton contains about 99% alpha-cellulose, the term given to pure cellulose of high molecular weight. The viscosity average molecular weight of native cellulose is in excess of 500 000 but the purification stage is accompanied by some degradation so that the resultant material usually has a molecular weight in the range 100 000–500 000 (600–3000 repeating glucose units).

Alternatively cellulose is produced from wood via wood pulp. A number of processes are used in which the overall effect is the removal of the bulk of the non-cellulosic matter. The most widely used are the sulphite process, which uses a solution of calcium bisulphite and sulphur dioxide, the soda process using sodium hydroxide and the sulphate process using a solution of sodium hydroxide and sodium sulphide. (The term sulphate process is used since sodium sulphate is the source of the sulphide.) For chemical purposes the sulphite process is most commonly used. As normally prepared these pulps contain about 88–90% alpha-cellulose but this may be increased by alkaline purification and bleaching.

Analysis of pure cellulose indicates an empirical formula $C_6H_{10}O_5$ corresponding to a glucose anhydride. There is ample evidence to indicate that in fact cellulose is a high molecular weight polyanhydroglucose. In particular it may be

mentioned that controlled hydrolysis of cellulose yields cellobiose, cellotriose and cellotetraose which contain respectively two, three and four anhydroglucose units. Complete hydrolysis will give yields of glucose as high as 95–96%.

The fact that, whereas glucose is a strongly reducing sugar, cellulose is almost non-reducing indicates that the linkage between the anhydroglucose units occurs at the reducing carbon atom. As cellobiose, known to consist of two glucose units joined by β -linkage, rather than maltose with the α -linkage, is one of the stepwise degradation products the evidence is that cellulose molecules are made up of many anhydroglucose units joined together by beta-glucosidic linkages (*Figure 22.1*).

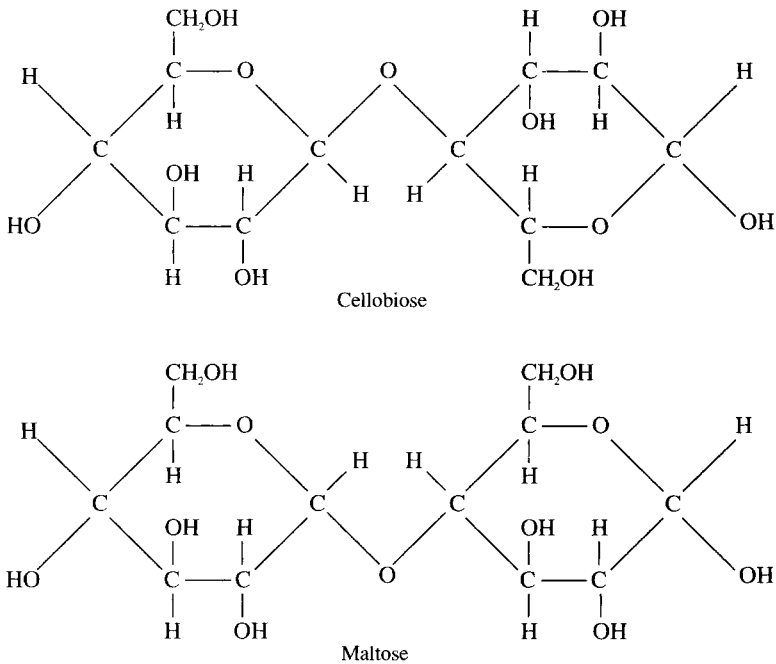


Figure 22.1

Study of the structure of cellulose (*Figure 22.2*) leads one to expect that the molecules would be essentially extended and linear and capable of existing in the crystalline state. This is confirmed by X-ray data which indicate that the cell repeating unit (10.25 Å) corresponds to the cellobiose repeating unit of the molecule.

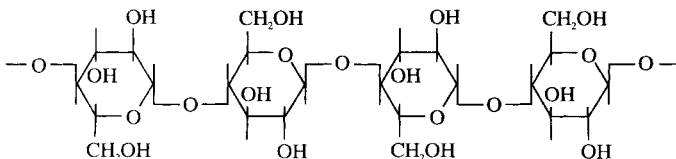


Figure 22.2

Although it might be anticipated that, because of the abundance of hydroxyl groups, cellulose would be water soluble this is not the case. This is because the regular spacing of hydroxyl groups, particularly in the crystalline zones, facilitates extensive hydrogen bonding. Thus although cellulose is somewhat hygroscopic, intermolecular bonds are too great for solution to occur.

Cellulose may be degraded by a number of environments. For example, acid-catalysed hydrolytic degradation will eventually lead to glucose by rupture of the 1,4- β -glucosidic linkages. Intermediate products may also be obtained for which the general term hydrocellulose has been given.

A wide variety of oxidation products, oxycelluloses, may also be produced. Oxidation may occur at a number of points but does not necessarily lead to chain scission.

Of somewhat greater technical interest are the addition compounds and the cellulose esters and ethers. Of the apparent addition compounds the most important is alkali cellulose produced by steeping cellulose in caustic soda and considered to be of general form $(C_6H_{10}O_5)_x (NaOH)_y$ rather than a sodium alcoholate compound. Alkali cellulose is a particularly important starting point in the manufacture of cellulose ethers. The ability of aqueous cuprammonium hydroxide solutions to dissolve cellulose appears to be dependent on addition compound formation.

Many cellulose derivatives have been prepared of which the esters and ethers are important. In these materials the hydroxyl groups are replaced by other substituent groups. The *degree of substitution* is the term given to the average number of hydroxyl groups per anhydroglucose unit that have been replaced.

Therefore a fully substituted derivative would have a degree of substitution of 3.0 whilst a cellulosic material in which on average 1.8 hydroxyl groups per glucose unit had been replaced would have a degree of substitution of 1.8. Commercial derivatives usually have a degree of substitution of less than 3.0, the actual value chosen being determined by the end-use.

The likelihood of any given hydroxyl group reacting will be determined largely by its position in the molecule and the position of the molecule in the fibrous structure. The reaction rate is largely determined by the rate of diffusion of the reagent and this is much greater in amorphous regions than in the crystalline areas. It is desirable in the preparation of derivatives that uniform substitution should occur, or at least that the hydroxyl groups in one molecule should have the same chance of reaction as those in another molecule. If this is not the case molecules on the surface of a cellulose fibre may well be fully substituted while molecules disposed in the centre of the fibre will be completely unreacted.

When reaction is carried out homogeneously in solution this state of affairs more or less exists and it is possible to achieve a statistically random degree of substitution. (It is to be noted that the primary hydroxyl groups will be more reactive than the secondary hydroxyl groups.)

The nitration of cellulose is unusual in that uniform reaction takes place even though the fibrous structure is retained. This is explained by the fact that nitration is an equilibrium reaction unaffected by fibre structure, the extent of nitration being determined by the strength of the nitrating acid.

Because of the insolubility of cellulose it is not possible to carry out uniform esterification with the lower organic acids (acetic acid, propionic acid etc.) and in those cases where incompletely substituted derivatives are required a two-stage reaction is employed. This involves total esterification in a medium in

which the ester dissolves, followed by the uniform removal of some of the substituent groups (this now being possible in solution) by hydrolysis.

22.2 CELLULOSE ESTERS

The cellulose esters are useful polymers for the manufacture of plastics. Until about 1950 they did in fact form the most important group of thermoplastics materials. The historical importance and significance of these materials have been discussed more fully in the first chapter of this book.

The most important of the esters is cellulose acetate. This material has been extensively used in the manufacture of films, moulding and extrusion compounds, fibres and lacquers. As with all the other cellulose polymers it has, however, become of small importance to the plastics industry compared with the polyolefins, PVC and polystyrene. In spite of their higher cost cellulose acetate–butyrate and cellulose propionate appear to have retained their smaller market because of their excellent appearance and toughness.

The early 1990s have also seen much interest in biodegradable cellulose acetate compounds.

The doyen of the ester polymers is cellulose nitrate. Camphor-modified cellulose nitrate has been known for over 120 years and still retains its use in a few specialised applications.

22.2.1 Cellulose Nitrate

Preparation

The reaction between cellulose and nitric acid is one of esterification. It is possible to achieve varying degrees of esterification according to the number of hydroxyl groups that have been replaced by the nitrate group. Complete substitution at all three hydroxyl groups on the repeating anhydroglucose units will give the explosive cellulose trinitrate, containing 14.14% nitrogen. This material is not made commercially but esters with lower degrees of nitrate are of importance, as indicated in *Table 22.1*.

Table 22.1

<i>Degree of nitration</i>	<i>Nitrogen content (%)</i>	<i>Typical usage</i>
Cellulose mononitrate	6.76% (theor.)	—
Cellulose dinitrate	11.11 (theor.) 10.7–11.1 11.2–12.3 12.4–13.5	plastics, lacquers films, lacquers cordite
Cellulose trinitrate	14.14 (theor.)	

It will be observed from *Table 22.1* that industrial cellulose nitrates or ‘nitrocellulose’ (as they are often erroneously called) have a degree of substitution somewhere between 1.9 and 2.7 and that materials with lower degrees of substitution are used for plastics applications.

The nitration process involves the steeping of cotton linters into a mixture of nitric and sulphuric acids and subsequent removal, stabilisation, bleaching and washing of the product. Subsequent conversion into plastics materials involves displacing residual water by alcohol, mixing the alcohol-wet nitrate with camphor and other ingredients, seasoning the rolled hides, pressing and finally cutting to shape.

Before nitration the moisture content of the purified linters is reduced to well below 5% since the presence of water will modify the progress of the reaction and tends to produce undesirable products. The drying operation is carried out by breaking open the cotton linters and passing along a hot air drier.

The nitration bath normally contains sulphuric acid as a condensing agent and a typical bath for producing a cellulose nitrate with a nitrogen content of 11% would be

Nitric acid	25%
Sulphuric acid	55%
Water	20%

In a typical process 1200 lb (545 kg) of the mixed acids are run into the reaction vessel and 30 lb (13.5 kg) of the dried cotton linters are added. The mixture is agitated by a pair of contra-rotating stirrers and nitration is allowed to proceed at about 35–40°C for 20 minutes. It is interesting to note that the cellulosic material retains its fibrous form throughout the nitration process.

On the completion of nitration the batch is dropped from the reaction vessel into a centrifuge and the acid mixture spun off and recovered. The nitrated linters, which still contain appreciable quantities of acid, are then plunged into a drowning tank, where the nitric acid is diluted with a large volume of water. The resultant ester is then pumped, as a slurry, into storage vats which may hold the products of several nitrations.

The product at this stage is unstable. It has been shown that some of the sulphuric acid reacts with the cellulose hydroxyl group to form sulphates. These tend to split off, re-forming sulphuric acid to initiate an autocatalytic decomposition which can lead, and has in the past led, to disastrous explosions. The remedy lies in removing the sulphate groups in a stabilisation process by boiling the cellulose ester with water that contains a controlled trace of acid for several hours. Side effects of this process are a reduction in molecular weight and in the nitrogen content.

The stabilised nitrate may then be bleached with sodium hypochlorite, centrifuged to remove much of the water in which the polymer has been slurried and dehydrated by displacement with alcohol while under pressure in a press. It is interesting to note that in these processes approximately 35 000 gallons (160 000 litres) of water are used for every ton of cellulose nitrate produced. Control of purity of the water is important; in particular the iron content should be as low as 0.03 parts per million since iron can adversely affect both the colour and heat stability of the polymer.

Manufacture of celluloid sheets

Although originally a trade name the term celluloid has come into general use to describe camphor-plasticised cellulose nitrate compositions.

The rather unexpected plasticising effect of camphor was first appreciated by Hyatt over a hundred years ago and, in spite of all that has been learned about polymers since then, no superior plasticiser has yet been discovered.

Camphor was originally obtained from the camphor tree *Laurus camphora* in which it appeared in the optically active dextro-rotary form. Since about 1920 the racemic (\pm) mixture derived from oil of turpentine has been more generally used. By fractional distillation of oil of turpentine the product pinene is obtained. By treating this with hydrochloric acid, pinene hydrochloride (also known as bornyl chloride) may be produced. This is then boiled with acetic acid to hydrolyse the material to the racemic borneol, which on oxidation yields camphor. Camphor is a white crystalline solid (m.p. 175°C) with the structure shown in *Figure 22.3*.

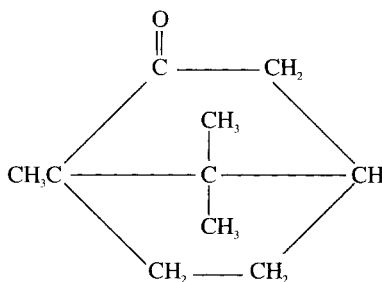


Figure 22.3

It has a low solubility parameter ($15.3 \text{ MPa}^{1/2}$) which differs considerably from that of the cellulose dinitrate ($21.8 \text{ MPa}^{1/2}$). This indicates that compatibility is not simply due to similarities of cohesive forces but also to some form of interaction probably involving the carbonyl group.

Mixing of the ingredients is carried out in steam-heated dough mixers fitted with solvent extraction hoods. A typical charge would consist of 240 lb (10.9 kg) of cellulose nitrate and 80 lb (3.6 kg) of camphor. The residual alcohol in the nitrate develops a powerful solvent action and the cellulose nitrate loses its fibrous form and the whole mix becomes a gelatinous mass. Typically mixing temperatures are of the order of 40°C and mixing times are approximately 1 hour.

Pigments or dyes may be added at this stage and where clear water-white sheet is required a small amount of a soluble violet dye is added to offset the faintly yellow colour of the natural mix. Stabilisers such as zinc oxide, zinc acetate or urea may be added to prevent the composition from developing acidity.

The celluloid dough is then filtered by forcing through a pad of calico and brass gauze backed by a heavy brass plate at a press of about 1.5 tons per square inch. Any undesirable foreign matter is thus separated from the dough.

The filtered dough is then returned to a mixer and the alcohol content reduced to 25% by kneading under vacuum. Further reduction in the alcohol content is brought about by rolling the compound on a hooded two-roll mill. The milled product is then consolidated on a two-bowl calender and sheeted off in hides about $\frac{1}{2}$ in thick. At this stage the solvent content is between 12 and 16%.

A number of hides are then laid up in a box mould with a grooved base. The mould is then loaded into a press and heated with hot water to consolidate the

mass. Great care must be taken to avoid overheating since this can cause disastrous explosions. It is not unknown for the head of a hydraulic press to have been blown through the roof of the press shop as a result of overheating the celluloid. Press temperatures are typically about 75°C and pressure about 500 lbf/in² (3.5 MPa).

After pressing, the moulded slab is allowed to cool and then sliced using a horizontally reciprocating knife. The thickness of the sliced sheet may range from 0.005 in to 1 in (0.012–2.5 cm). Attractive mottled effects may be produced by plying sliced sheets, repressing and then subsequently reslicing on the bias. Bias-cut sheets of different patterns may then again be pressed and the process repeated indefinitely. In this way complex but reproducible patterns may be built up.

The sliced sheet will still contain large quantities of alcohol and it is necessary to 'season' the sheet at elevated temperatures. This may only take three days at 49°C for 0.010 in (0.025 cm) thick sheet but will take about 56 days for 1 in (2.5 cm) thick blocks. The removal of alcohol, as might be expected, is accompanied by considerable shrinkage. Fully seasoned sheet has a volatile content of 2%, the bulk of which is water but there is some residual alcohol. The sheet may be fully polished by heating in a press between glazed plates under pressure for a few minutes. Because the material is thermoplastic it is necessary to cool it before removal from the press.

It is also possible to extrude alcohol-containing celluloid compositions through either ram or screw extruders under carefully controlled conditions. The process is now believed to be universally obsolete.

Sheet and block may be machined with little difficulty providing care is taken to avoid overheating and to collect the inflammable swarf.

Structure and properties of celluloid

Nitration of cellulose followed by plasticisation of the product with camphor has the effect of reducing the orderly close packing of the cellulose molecules. Hence whereas cellulose is insoluble in solvents, except in certain cases where there is chemical reaction, celluloid is soluble in solvents such as acetone and amyl acetate. In addition the camphor present may be dissolved out by chloroform and similar solvents which do not dissolve the cellulose nitrate.

The solvation by plasticiser also gives celluloid thermoplastic properties owing to the reduction in interchain forces. On the other hand since the cellulose molecule is somewhat rigid the product itself is stiff and does not show rubbery properties at room temperature, cf. plasticised PVC.

As may be expected from such a polar material it is not a particularly good electrical insulator, particularly at high frequencies. The high dielectric constant is particularly noteworthy.

The chemical resistance of celluloid is not particularly good. It is affected by acids and alkalis, discolours on exposure to sunlight and tends to harden on aging. More seriously it is extremely inflammable, this being by far the greatest limitation of the material.

Typical physical properties of celluloid are compared with other cellulose plastics in *Table 22.2*.

The high inflammability and relatively poor chemical properties of celluloid severely restrict its use in industrial applications. Consequently, the material is used because of the following desirable characteristics.

Table 22.2 Typical physical properties of cellulosic plastics. (It is necessary to quote a range of figures in most instances since the value of a particular property is very dependent on formulation)

	<i>Cellulose nitrate</i>	<i>Cellulose acetate</i>	<i>Cellulose acetate–butyrate</i>	<i>Cellulose acetate–propionate</i>	<i>Cellulose propionate</i>	<i>Ethyl cellulose</i>
Specific gravity	1.35–1.40	1.27–1.32	1.15–1.22	1.19–1.23	1.18–1.24	1.12–1.15
Refractive index (25°C)	1.5	1.47–1.5	1.47–1.48	1.46–1.49	1.46–1.49	1.47
Tensile strength (10^3 lbf/in ²)	5–10	3.5–11	2.5–7.5	3.5–7.3	2–6	6–9
(MPa)	35–70	24–76	17–52	24–50	14–42	42–62
Elongation at break (%)	10–40	5–55	8–80	30–100	45–65	10–40
Izod impact ft lbf in ⁻¹ notch	2.0–8.0	0.5–5.0	0.4–5.0	0.9–5.0	1.2–11.0	1.0–6.5
Rockwell M hardness 70°F (ASTM D.229–39)	25–50	-30 to +75	0–80	60–120 (R-scale)	-15 to +106	-25 to +80
Flow temperature (°C) (ASTM D.569–40T)	145–152	115–165	115–165	150–180	145–180	100–150
Heat distortion temperature (°C)	—	50–100	56–94	45–110	51–70	50–66
Volume resistivity (Ω m) 50% RH, 25°C	$\sim 10^{13}$	$\sim 10^{14}$	$\sim 10^{14}$	$\sim 10^{14}$ – 10^{16}	$\sim 10^{14}$ – 10^{17}	10^{17}
Dielectric constant 60 Hz	6.7–7.3	3.5–7.5	3.7–4.5	3.7–4.0	3.0–3.5 (10^6 Hz)	2.7
Power factor 60 Hz	0.06–0.15	0.01–0.07	0.008–0.012	0.01–0.04	0.017–0.02 (10^6 Hz)	0.007
% Water absorption 2 in \times $\frac{1}{8}$ in disc 24 h immersion (ASTM D.570–40T)	0.6–2.0	1.0–3.0	0.9–2.4	1.5–2.8	1.6–2.0	0.5–1.5

- (1) Water-white transparency of basic composition but capable of forming highly attractive multi-coloured sheeting.
- (2) Rigidity.
- (3) Reasonable toughness.
- (4) Capable of after-shrinkage around inserts.

Applications

The annual production of celluloid is now negligible compared with the total world production of plastics.

The one-time important applications in photographic film, in bicycle parts (pump covers and mudguards) and in toys manufactured by a blowing process from flat sheet are no longer of importance.

Today the principal outlets are knife handles, table-tennis balls and spectacle frames. The continued use in knife handles is due to the pleasant appearance and the ability of the material to after-shrink around the extension of the blade. Table-tennis balls continue to be made from celluloid since it has been difficult to match the 'bounce' and handle of the celluloid ball, the type originally used, with balls fabricated from newer polymers. Even here celluloid is now meeting the challenge of synthetic polymers. Spectacle frames are still of interest because of the attractive colour. There are, however, restrictions to their use for this application in certain countries and cellulose acetate is often preferred.

22.2.2 Cellulose Acetate

Preparation

The earliest preparation of cellulose acetate is credited to Schützenberger in 1865. The method used was to heat the cotton with acetic anhydride in sealed tubes at 130–140°C. The severe reaction conditions led to a white amorphous polymer but the product would have been severely degraded and the process difficult to control. Subsequent studies made by Liebermann, Francimont, Miles, the Bayer Company and by other workers led to techniques for controlled acetylation under less severe conditions.

The methods available today may be considered under two headings, homogeneous acetylation, in which the acetylated cellulose dissolves into a solvent as it is formed, and the heterogeneous technique, in which the fibre structure is retained.

As mentioned in Section 22.1 the probability of acetylation of any one cellulosic group is strongly dependent on its position in the fibre. Since they cannot be dissolved before acetylation it will be realised that some molecules will be completely acetylated whilst others may be untouched. It is thus necessary first to acetylate completely the cellulose and the resultant triacetate material, which is soluble in certain solvents, may then be back-hydrolysed in solution. Under these conditions the probabilities of hydrolysis of any acetyl groups in one molecule will be similar to the reaction probabilities of these groups in another molecule and products with a reasonably even degree of substitution less than three may be obtained.

The preparation of the acetate by homogeneous acetylation may be considered in three stages:

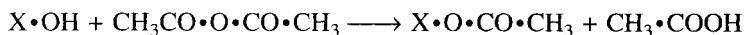
- (1) Pretreatment of the cellulose.
- (2) Acetylation.
- (3) Hydrolysis.

The aim of pretreatment is to open up the cellulosic matter in order to achieve more even substitution and to accelerate the main acetylation reaction. A large number of pretreatments have been described in the patent literature but in practice exposure to glacial acetic acid is that most commonly employed.

The acetylation is usually carried out in bronze stirred mixers. The acetylating mixture normally contains three components, an acetylating agent, a catalyst and a diluent.

Although acetyl chloride and ketene ($\text{CH}_2 = \text{C} = \text{O}$) have been described in the literature, acetic anhydride has been the commonly employed acetylating agent.

The reaction between one of the hydroxyl groups of the cellulose molecule ($\text{X}\cdot\text{OH}$) and the anhydride is:



Similarly, a number of catalysts have been suggested but concentrated sulphuric acid, first suggested by Francimont in 1879, is almost universally employed today.

The diluent, which is usually a solvent for the acetate, facilitates the reaction, particularly in respect of temperature control. Acetic acid is generally employed either alone or in conjunction with other materials for this purpose. It may be added initially but is also formed during the acetylation of the cellulose. A mild acetylating agent in itself it is not merely a diluent but influences the course of the reaction. The low boiling solvent methylene dichloride (b.p. 40°C) is now commonly used in conjunction with acetic acid. An advantage in using methylene dichloride is that excessive exothermic heat may be removed as latent heat of evaporation as the methylene chloride boils. Bubbles formed during boiling or 'simmering' may also assist in mixing of the reaction blend.

In the so-called Dormagen process developed by IG Farben the cotton was first preheated with 30–40% of its own weight with glacial acetic acid for 1–2 hours. The pretreated material was then fed to the acetylisers, which consisted of horizontal bronze cylinders. For every 100 parts of pretreated cellulose there was added the following acetylating mixture, previously cooled to $15\text{--}20^\circ\text{C}$:

300 parts	acetic anhydride
400 parts	methylene dichloride
1 part	sulphuric acid

Cooling water was passed through jackets surrounding the reactor in order to prevent the temperature from exceeding 50°C .

Esterification is complete in 5–6 hours and the product at this stage is known as *primary cellulose acetate*.

Current acetylation techniques may be based on continuous production similar to that employed in the Dormagen process or batchwise in dough-type mixers.

Whatever acetylating technique is used, this is then followed by the ripening operation. The 'ripening' is carried out without isolating the triacetate. Dilute acetic acid or water is added to the acetylising mixture, about 20–25% based on

Table 22.3 Influence of degree of substitution on the properties and uses of cellulose acetate

Degree of substitution	Acetyl content (%—COCH ₃)	Acetic acid yield (%)	Solubility	Uses
2.2–2.3	36.5–38.0	52.1–54.3	soluble in acetone	injection moulding film
2.3–2.4	38.0–39.5	54.3–56.4		
2.4–2.6	39.5–41.5	56.4–59.3		
2.8–3.0	42.5–44	60.7–62.8	insoluble in acetone, soluble in chloroform	lacquers triacetate film and fibre

the weight of the cellulose. Hydrolysis is allowed to proceed for a number of days, typically for about 72 hours. The progress of hydrolysis is followed by checking the solubility of the acetate in alcohol–benzene and acetone solutions. When the required degree of substitution has been reached the cellulose acetate is precipitated by judicious addition of water to the stirred mixture. It is then washed thoroughly and dried in an electric or vacuum oven. Care must be taken in the operation of the precipitation stage since otherwise lumps are likely to be formed. For certain applications, such as for photographic film, further purification operations may be carried out.

The product at this stage is referred to as *secondary cellulose acetate*. Different degrees of acetylation are required for different end-products and these are indicated in *Table 22.3*.

Compounding of cellulose acetate

The cellulose molecule is rigid and forms strong hydrogen bonds with adjacent molecules. It is thus insoluble and decomposes before softening on heating. Partial replacement of hydroxyl groups by acetyl groups has a number of effects:

- (1) It reduces interchain hydrogen bonding.
- (2) It increases interchain separation.
- (3) It makes the polymer less polar—the polarity depending on the degree of acetylation.

Because of these influences cellulose acetate can be dissolved in a variety of media, although a liquid suitable as a solvent for cellulose acetate with a degree of substitution of two would be unlikely to be a solvent for acetates with degrees of substitution of either one or three.

Although acetylation thus renders the cellulosic structure soluble, cellulose acetate will still decompose below its softening point. It is thus necessary to compound cellulose acetate with plasticisers in order to obtain plastics materials of suitable flow properties. Other ingredients are also added at the same time.

Although the prime function of plasticisers in cellulose acetate is to bring the processing temperature of the compound below the polymer decomposition temperature, it has additional values. An increase in the plasticiser content will reduce the melt viscosity at a given temperature and simplify processing. The physical properties of the finished product will be modified, increasing toughness

but reducing the heat distortion temperature, the latter not being an important property in most cellulose acetate applications.

Although many plasticisers have been suggested for cellulose acetate very few have been used in practice. The most important of these are dimethyl phthalate ($\delta = 21.4$), triacetin ($\delta = 20.3$) and triphenyl phosphate ($\delta = 20.0$), each of which have a solubility parameter within one unit of that of cellulose diacetate (~ 22.0). (All in units of $\text{MPa}^{1/2}$.)

Of these *dimethyl phthalate* (DMP) is used in most compositions. It is cheap, has a high compatibility with secondary cellulose acetate and is efficient in increasing flexibility, toughness and the ease of flow at a given temperature. Its principal disadvantages are its high volatility and the fact that it increases the flammability of the compound. Similar in compatibility but rather less volatile is *diethyl phthalate*. This material has less of an influence on flexibility and flow properties than the methyl ester.

Triphenyl phosphate is a crystalline solid which has less compatibility with the polymer. This may be expected from solubility parameter data. It is often used in conjunction with dimethyl phthalate and has the added virtues of imparting flame resistance and improved water resistance. It is more permanent than DMP. *Triacetin* is less important now than at one time since, although it is compatible, it is also highly volatile and lowers the water resistance of the compound. Today it is essential to prepare low-cost compounds to allow cellulose acetate to compete with the synthetic polymers, and plasticisers such as *ethyl phthalyl ethyl glycollate*, which are superior in some respects, are now rarely used.

Small amounts of stabiliser (1–5%) are normally added to improve weather resistance. These materials are the usual ultraviolet light absorbers such as phenyl salicylate and various benzoates. Triphenyl phosphate also has a beneficial influence.

Other ingredients may include cheapening extenders such as castor oil, colouring agents, lubricants and, rarely, fillers.

Compounding may be carried out by either a wet or a dry process. In the wet process, now obsolescent, the ingredients are mixed as a viscous solution in acetone in a dough mixer. The resulting dough is then rolled on a hot two-roll mill to evaporate the bulk of the solvent. It is then necessary to 'season' the resulting hides until the solvent content is reduced to a tolerably low level.

Dry processes which obviate solvent difficulties are now preferred^{1,2} and are similar to those employed with the major thermoplastics. They include the use of two-roll mills, internal mixers, extruders and extrusion compounders. The use of dry blend techniques similar to that used more recently with PVC have also been used.²

Properties of cellulose acetate plastics

Cellulose acetate plastics have no really outstanding properties. Their continued use for mouldings and extrusions depends on their toughness and good appearance at a reasonable cost, although somewhat above the prices ruling for the major vinyl plastics, PVC, polyethylene and polystyrene. In common with most other plastic materials they are capable of unlimited colour variations, including water-white transparency. Processing is quite straightforward provided the granules are dry.

Compared with the major vinyls cellulose acetate plastics have a high water absorption, poor electrical insulation characteristics, limited aging resistance and

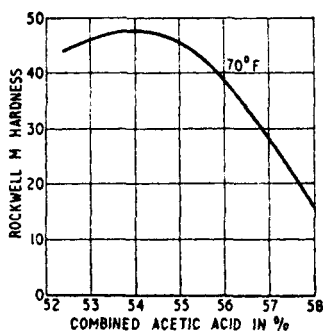
limited heat resistance and are attacked or dissolved by a wide variety of reagents.

A wide range of cellulose acetate compounds are commercially available. The properties of these compounds depend on three major factors:

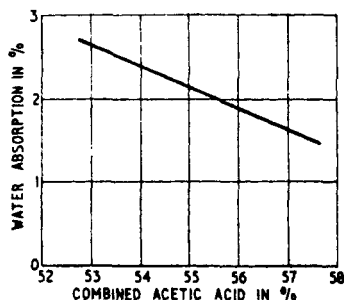
- (1) The chain length of the cellulose molecule.
- (2) The degree of acetylation.
- (3) The type and amount of plasticiser(s).

During production of cellulose acetate from cellulose a certain amount of chain degradation takes place. As a result the degree of polymerisation of commercial acetate esters is usually within the range 175–360. It is convenient to assess the chain length by solution viscosity methods. Products differing in viscosity will be produced by varying the source of the original cellulose and by modifying reaction conditions. Since marked batch-to-batch variations in the viscosity of the finished product occur in practice, products of specified viscosity are obtained by blending.

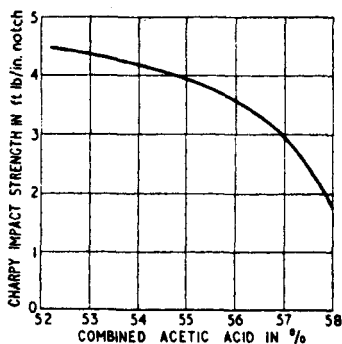
The greater the molecular weight the higher is the flow temperature and the heat distortion temperature. Variations in molecular weight, in the normal range, however, have less effect than do variations in the degree of acetylation and in the plasticiser used.



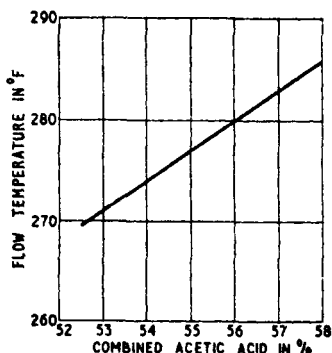
(a)



(b)



(c)



(d)

Figure 22.4. Effect of degree of acetylation on (a) hardness, (b) water absorption, (c) impact strength and (d) flow temperature. (31% plasticiser content) (Hercules Powder Co. literature)

Increasing the degree of acetylation from that corresponding to a diacetate will obviously reduce the hydroxyl content and this will increase the water resistance. The polymer also becomes less polar and the solvent properties correspondingly alter. It is also observed that an increase in the degree of acetylation reduces the hardness, impact strength and water absorption but increases the 'flow temperature'. The influence of the degree of acetylation on these properties is shown clearly in *Figure 22.4* (a)–(d).

Cellulose acetate plastics are generally produced using polymers from a fairly narrow range of molecular weights and degrees of acetylation. In practice the greatest variation in properties is achieved by modifying the type and amount of plasticiser. *Table 22.4*³ shows the influence of varying the amount of plasticiser on several important properties of cellulose acetate.

Table 22.4 Influence of amount of plasticiser (dimethyl phthalate) on some physical properties of cellulose acetate compositions

Parts DMP per 100 pts polymer	37.8	30.0	22.6
Flow temperature (°C)	130	140	152
Elongation (%)	8.0	6.5	5.0
Tensile strength (lbf/in ²)	6630	8100	9930
(MPa)	45	56	68
Flexural strength (lbf/in ²)	11 140	14 200	17 000
(MPa)	77	98	120
Rockwell hardness (<i>M</i>)	79.5	90.5	101.1
Water absorption (%)	2.13	2.47	3.24
Leaching (48 h)%	0.58	0.52	0.45
Loss in weight (1 week 150°C)%	2.40	0.86	0.53

The so-called flow temperature cannot be considered to be either the processing temperature or the maximum service temperature. It is obtained using the highly arbitrary Rossi–Peakes flow test (BS 1524) and is the temperature at which the compound is forced down a capillary of fixed dimensions by a fixed load at a specified rate. It is thus of use only for comparison and for quality control purposes. Since the rates of shear and temperatures used in processing are vastly different from those used in this test, extreme caution should be taken when assessing the result of flow temperature tests.

Typical values for the principal properties of cellulose acetate compounds are tabulated in *Table 22.2* in comparison with other cellulosic plastics. Since cellulose acetate is seldom used today in applications where detailed knowledge of physical properties are required these are given without further comment.

Applications

As already indicated, cellulose acetate is used because of its reasonable toughness, transparency and wide colour range. It is not suitable when good electrical insulation properties, heat resistance, weathering resistance, chemical resistance and dimensional stability are important.

The main outlets are for films and sheeting. Because of its clarity the film is used extensively for photographic purposes and for packaging. Sheeting is used

for a variety of purposes. Thin sheet is useful for high-quality display boxes whilst thicker sheet is used for spectacle frames.

Triacetate film is used in the graphic arts, for greetings cards, and for specialised electrical applications such as non-conducting separators.

The use of cellulose acetate for moulding and extrusion is now becoming small owing largely to the competition of the styrene polymers and polyolefins. The major outlets at the present time are in the fancy goods trade as toothbrushes, combs, hair slides etc. Processing provides no major problem provided care is taken to avoid overheating and the granules are dry. The temperatures and pressure used vary, from 160 to 250°C and 7 to 15 ton/in² respectively, according to grade. The best injection mouldings are obtained using a warm mould.

Secondary cellulose acetate has also been used for fibres and lacquers whilst cellulose triacetate fibre has been extensively marketed in Great Britain under the trade name Tricel.

Biodegradable Cellulose Acetate Compounds

As a result of development work between the Battelle Institute in Frankfurt and a German candle-making company, Aeterna, biodegradable cellulose acetate compounds have been available since 1991 from the Rhône-Poulenc subsidiary Tubize Plastics. They are marketed under the trade names Bioceta and Biocellat. The system is centred round the use of an additive which acts both as a plasticiser and a biodegrading agent, causing the cellulose ester to decompose within 6–24 months.

The initial use was as a blow moulded vessel for vegetable oil candles. However, because of its biodegradability it is of interest for applications where paper and plastics materials are used together and which can, after use, be sent into a standard paper recycling process. Instances include blister packaging (the compound is transparent up to 3 mm in thickness), envelopes with transparent windows and clothes point-of-sale packaging.

Compared with more common plastics used as packaging materials, the compound does have some disadvantages, such as a high water vapour permeability and limited heat resistance, losing dimensional stability at about 70°C. It is also substantially more expensive than the high-tonnage polyolefins. Last but not least its biodegradability means that it must be used in applications that will have completed their function within a few months of the manufacture of the polymer compound.

22.2.3 Other Cellulose Esters

Homologues of acetic acid have been employed to make other cellulose esters and of these cellulose propionate, cellulose acetate–propionate and cellulose acetate–butyrate are produced on a commercial scale. These materials have larger side chains than cellulose acetate and with equal degrees of esterification, molecular weights and incorporated plasticiser, they are slightly softer, of lower density, have slightly lower heat distortion temperatures and flow a little more easily. The somewhat greater hydrocarbon nature of the polymer results in slightly lower water-absorption values (see *Table 22.2*).

It should, however, be realised that some grades of cellulose acetate may be softer, be easier to process and have lower softening points than some grades of

cellulose acetate–butyrate, cellulose acetate–propionate and cellulose propionate since the properties of all four materials may be considerably modified by chain length, degree of substitution and in particular the type and amount of plasticiser.

Cellulose acetate–butyrate (CAB) has been manufactured for a number of years in the United States (Tenite Butyrate–Kodak) and in Germany (Cellidor B–Bayer).

In a typical process for manufacture on a commercial scale bleached wood pulp or cotton linters are pretreated for 12 hours with 40–50% sulphuric acid and then, after drying, with acetic acid. Esterification of the treated cellulose is then carried out using a mixture of butyric acid and acetic anhydride, with a trace of sulphuric acid as catalyst. Commercial products vary extensively in the acetate/butyrate ratios employed.

The lower water absorption, better flow properties and lower density of CAB compared with cellulose acetate are not in themselves clear justification for their continued use. There are other completely synthetic thermoplastics which have an even greater superiority at a lower price and do not emit the slight odour of butyric acid as does CAB. Its principal virtues which enable it to compete with other materials are its toughness, excellent appearance and comparative ease of mouldability (providing the granules are dry). The material also lends itself to use in fluidised bed dip-coating techniques, giving a coating with a hard glossy finish which can be matched only with more expensive alternatives. CAB is easy to vacuum form.

A number of injection mouldings have been prepared from CAB with about 19% combined acetic acid and 44% combined butyric acid. Their principal end products have been for tabulator keys, automobile parts, toys and tool handles. In the United States CAB has been used for telephone housings. Extruded CAB piping has been extensively used in America for conveying water, oil and natural gas, while CAB sheet has been able to offer some competition to acrylic sheet for outdoor display signs.

In the mid-1950s *cellulose propionate* became commercially available (Forticel–Celanese). This material is very similar in both cost and properties to CAB. Like CAB it may take on an excellent finish, provided a suitable mould is used, it is less hygroscopic than cellulose acetate, and is easily moulded.

As with the other esters a number of grades are available differing in the degree of esterification and in type and amount of plasticiser. Thus the differences in properties between the grades are generally greater than any differences between ‘medium’ grades of cellulose propionate and CAB. Whereas a soft grade of the propionate may have a tensile strength of 2000 lbf/in² (14 MPa) and a heat distortion temperature of 51°C, a hard grade may have tensile strength as high as 6000 lbf/in² (42 MPa) and a heat distortion temperature of 70°C.

Cellulose acetate–propionate (Tenite Propionate–Kodak) is similar to cellulose propionate. With the shorter side chains, cellulose propionate and cellulose acetate propionate tend to be harder, stiffer and of higher tensile strength than CAB. Like CAB they are easy to vacuum form and also tend to be used for similar applications such as steering wheels, tool handles, safety goggles and blister packs.

Many other cellulose esters have been prepared in the laboratory and some have reached pilot plant status. Of these the only one believed to be of current importance is *cellulose caprate* (decoate). According to the literature, degraded

wood pulp is activated by treating with chloroacetic acid and the product is esterified by treating with capric anhydride, capric acid and perchloric acid. The material is said to be useful as optical cement.¹

22.3 CELLULOSE ETHERS

By use of a modification of the well-known Williamson synthesis it is possible to prepare a number of cellulose ethers. Of these materials ethyl cellulose has found a small limited application as a moulding material and somewhat greater use for surface coatings. The now obsolete benzyl cellulose was used prior to World War II as a moulding material whilst methyl cellulose, hydroxyethyl cellulose and sodium carboxymethyl cellulose are useful water-soluble polymers.

With each of these materials the first step is the manufacture of alkali cellulose (soda cellulose). This is made by treating cellulose (either bleached wood pulp or cotton linters) with concentrated aqueous sodium hydroxide in a nickel vessel at elevated temperature. After reaction excess alkali is pressed out, and the resultant 'cake' is then broken up and vacuum dried until the moisture content is in the range 10–25%. The moisture and combined alkali contents must be carefully controlled as variations in them will lead to variations in the properties of the resultant ethers.

22.3.1 Ethyl Cellulose

Ethyl cellulose is prepared by agitating the alkali cellulose with ethyl chloride in the presence of alkali at about 60°C for several hours. Towards the end of the reaction the temperature is raised to about 130–140°C. The total reaction time is approximately 12 hours. The reaction is carried out under pressure.

If the etherification were taken to completion the product would be the compound shown in *Figure 22.5*.

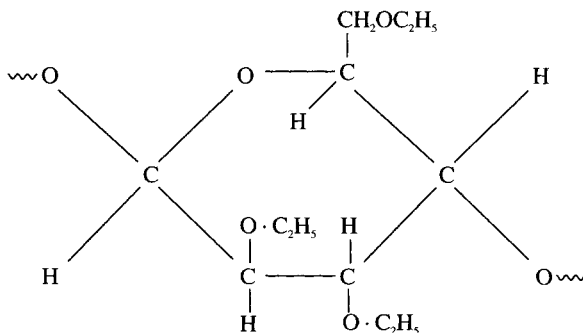


Figure 22.5

It is essential that there be sufficient alkali present, either combined with the cellulose, or free, to neutralise the acid formed by both the main reaction and in a side reaction which involves the hydrolysis of ethyl chloride.

Ethyl ether and ethyl alcohol which are formed as by-products are removed by distillation and the ethyl cellulose is precipitated by hot water. The polymer is then carefully washed to remove sodium hydroxide and sodium chloride and dried.

The properties of the ethyl cellulose will depend on:

- (1) The molecular weight.
- (2) The degree of substitution.
- (3) Molecular uniformity.

The molecular weight may be regulated by controlled degradation of the alkali cellulose in the presence of air. This can be done either before or during etherification. The molecular weight of commercial grades is usually expressed indirectly as viscosity of a 5% solution in an 80:20 toluene-ethanol mixture.

The completely etherified material with a degree of substitution of 3 has an ethoxyl content of 54.88%. This material has little strength and flexibility, is not thermoplastic, has limited compatibility and solubility and is of no commercial value. A range of commercial products are, however, available with a degree of substitution between 2.15 and 2.60, corresponding to a range of ethoxyl contents from 43 to 50%.

The ethoxyl content is controlled by the ratio of reactants and to a lesser degree by the reaction temperature.

Whereas mechanical properties are largely determined by chain length, the softening point, hardness, water absorption and solubility are rather more determined by the degree of substitution (see *Figure 22.6*).

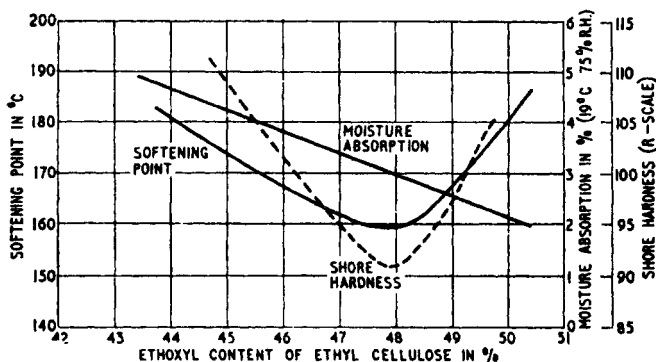


Figure 22.6. Influence of the ethoxyl content of ethyl cellulose on softening point, moisture absorption and hardness. (Hercules Powder Co. literature)

Typical physical properties of ethyl cellulose are compared with those of the cellulose ethers in *Table 22.2*.

The solubility of ethyl cellulose depends on the degree of substitution. At low degrees of substitution (0.8-1.3) the replacement of some of the hydroxyl groups by ethoxyl groups reduces the hydrogen bonding across the cellulosic chains to such an extent that the material is soluble in water. Further replacement of hydroxyl groups by the less polar and more hydrocarbon ethoxyl groups

increases the water resistance. Fully etherified ethyl cellulose is soluble only in non-polar solvents.

The relationship between degree of substitution and solubility characteristics is predictable from theory and is summarised in *Table 22.5*.

Table 22.5 Solubility of ethyl cellulose

<i>Average number of ethoxyl groups per glucose unit</i>	<i>Solubility</i>
~0.5	soluble in 4–8% sodium hydroxide
0.8–1.3	soluble in water
1.4–1.8	swelling in polar–non-polar solvent mixtures
1.8–2.2	increasing solubility in above mixtures
2.2–2.4	increasing solubility in alcohol and less polar solvents
2.4–2.5	widest range of solubilities
2.5–2.8	soluble only in non-polar solvents

Ethyl cellulose is subject to oxidative degradation when exposed to sunlight and elevated temperatures. It is therefore necessary to stabilise the material against degrading influences during processing or service. In practice three types of stabiliser are incorporated, an antioxidant such as the phenolic compound 2,2'-methylenebis-(4-methyl-6-tert-butylphenol), an acid acceptor such as an epoxy resin for use where plasticisers may give rise to acidic degradation products and an ultraviolet absorber such as 2,4-dihydroxybenzophenone for outdoor use. Plasticisers such as tritolyl phosphate and diamylphenol have a beneficial stabilising effect.

Ethyl cellulose has never become well known in Europe and apart from one or two specific applications has not been able to capture any significant proportion of the market held by the cellulose esters. Although it has the greatest water resistance and the best electrical insulating properties amongst the celluloses this is of little significance since when these properties are important there are many superior non-cellulosic alternatives. The principal uses for ethyl cellulose injection mouldings are in those applications where good impact strength at low temperatures is required, such as refrigerator bases and flip lids and ice-crusher parts.

Ethyl cellulose is often employed in the form of a 'hot melt' for strippable coatings. Such strippable coatings first became prominent during World War II for packaging military equipment. Since then they have been extensively used for protecting metal parts against corrosion and marring during shipment and storage. A typical composition consists of 25% ethyl cellulose, 60% mineral oil, 10% resins and the rest stabilisers and waxes. Coating is performed by dipping the cleaned metal part into the molten compound. The metal part is withdrawn and an adhering layer of the composition is allowed to harden by cooling. Hot melts have also been used for casting and paper coating.

The ether is also used in paint, varnish and lacquer formulations. A recent development is the use of ethyl cellulose gel lacquers. These are permanent coatings applied in a similar way to the strippable coatings. They have been used in the United States for coating tool handles, door knobs and bowling pins.

22.3.2 Miscellaneous Ethers

Only one other cellulose ether has been marketed for moulding and extrusion applications, *benzyl cellulose*. This material provides a rare example of a polymer which although available in the past is no longer commercially marketed. The material had a low softening point and was unstable to both heat and light and has thus been unable to compete with the many alternative materials now available.

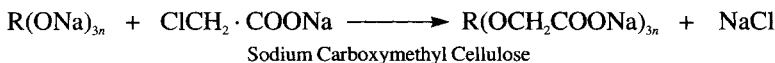
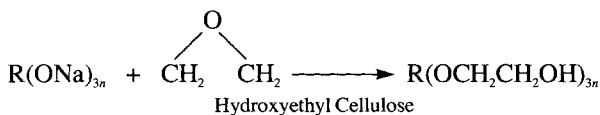
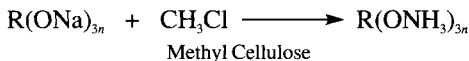
A number of water-soluble cellulose ethers are marketed.⁴ *Methyl cellulose* is prepared by a method similar to that used for ethyl cellulose. A degree of substitution of 1.6–1.8 is usual since the resultant ether is soluble in cold water but not in hot. It is used as a thickening agent and emulsifier in cosmetics, as a paper size, in pharmaceuticals, in ceramics and in leather tanning operations.

Hydroxyethyl cellulose, produced by reacting alkali cellulose with ethylene oxide, is employed for similar purposes.

Hydroxypropyl cellulose, like methyl cellulose, is soluble in cold water but not in hot, precipitating above 38°C. It was introduced by Hercules in 1968 (Klucel) for such uses as adhesive thickeners, binders, cosmetics and as protective colloids for suspension polymerisation. The Dow company market the related *hydroxypropylmethyl cellulose* (Methocel) and also produce in small quantities a *hydroxyethylmethyl cellulose*.

Reaction of alkali cellulose with the sodium salt of chloroacetic acid yields *sodium carboxymethyl cellulose*, (SCMC). Commercial grades usually have a degree of substitution between 0.50 and 0.85. The material, which appears to be physiologically inert, is very widely used. Its principal application is as a soil-suspending agent in synthetic detergents. It is also the basis of a well-known proprietary wallpaper adhesive. Miscellaneous uses include fabric sizing and as a surface active agent and viscosity modifier in emulsions and suspensions. Purified grades of SCMC are employed in ice cream to provide a smooth texture and in a number of pharmaceutical and cosmetic products.

Schematic equations for the production of fully substituted varieties of the above three ethers are given below (R represents the cellulose skeleton).



22.4 REGENERATED CELLULOSE

Because of high interchain bonding, cellulose is insoluble in solvents and is incapable of flow on heating, the degradation temperature being reached before the material starts to flow. It is thus somewhat intractable in its native form. Cellulose, however, may be chemically treated so that the modified products may

be dissolved and the solution may then either be cast into film or spun into fibre. By treatment of the film or fibre the cellulose derivative may be converted back (regenerated) into cellulose although the processing involves reduction in molecular weight.

In the case of fibres three techniques have been employed:

- (1) Dissolution of the cellulose in cuprammonium solution followed by acid coagulation of extruded fibre ('cuprammonium rayon'—no longer of commercial importance). In this case the acid converts the cuprammonium complex back into cellulose.
- (2) Formation of cellulose acetate, spinning into fibre and subsequent hydrolysis into cellulose.
- (3) Reaction of alkali cellulose with carbon disulphide to produce a cellulose xanthate which forms a lyophilic sol with caustic soda. This may be extruded into a coagulating bath containing sulphate ions which hydrolyses the xanthate back to cellulose. This process is known as the viscose process and is that used in the manufacture of rayon.

By modification of the viscose process a regenerated cellulose foil may be produced which is known under the familiar trade name Cellophane.

The first step in the manufacture of the foil involves the production of alkali cellulose. This is then shredded and allowed to age in order that oxidation will degrade the polymer to the desired extent. The alkali cellulose is then treated with carbon disulphide in xanthating churns at 20–28°C for about three hours.

The xanthated cellulose contains about one xanthate group per two glucose units. The reaction may be indicated schematically as



The resultant yellow sodium cellulose xanthate is dispersed in an aqueous caustic soda solution, where some hydrolysis occurs. This process is referred to as 'ripening' and the solution as 'viscose'. When the hydrolysis has proceeded sufficiently the solution is transferred to a hopper from which it emerges through a small slit on to a roller immersed in a tank of 10–15% sulphuric acid and 10–20% sodium sulphate at 35–40°C. The viscose is coagulated and by completion of the hydrolysis the cellulose is regenerated. The foil is subsequently washed, bleached, plasticised with ethylene glycol or glycerol and then dried.

The product at this stage is 'plain' foil and has a high moisture vapour transmission rate. Foil which is more moisture proof may be obtained by coating with pyroxylin (cellulose nitrate solution) containing dibutyl phthalate as plasticiser or with vinylidene chloride–acrylonitrile copolymers. A range of foils are available differing largely in their moisture impermeability and in heat sealing characteristics.

Regenerated cellulose foil has been extensively and successfully used as a wrapping material, particularly in the food and tobacco industries. Like other cellulose materials it is now having to face the challenge of the completely synthetic polymers. Although the foil has been able to compete in the past, the

advent of the polypropylene film in the early 1960s produced a serious competitor which led to a marked reduction in the use of the cellulosic materials.

Regenerated cellulose does, however, have the advantage that it biodegrades well aerobically in composting (rather more slowly anaerobically).

22.5 VULCANISED FIBRE

This material has been known for many years, being used originally in the making of electric lamp filaments. In principle vulcanised fibre is produced by the action of zinc chloride on absorbent paper. The zinc chloride causes the cellulosic fibres to swell and be covered with a gelatinous layer. Separate layers of paper may be plied together and the zinc chloride subsequently removed to leave a regenerated cellulose laminate.

The removal of zinc chloride involves an extremely lengthy procedure. The plied sheets are passed through a series of progressively more dilute zinc chloride solutions and finally pure water in order to leach out the gelatinising agent. This may take several months. The sheets are then dried and consolidated under light pressure.

The sheets may be formed to some extent by first softening in hot water or steam and then pressing in moulds at pressures of 200–500 lbf/in² (1.5–3.5 MPa). Machining, using high-speed tools, may be carried out on conventional metal-working machinery.

A number of grades have been available according to the desired end use. The principal applications of vulcanised fibre are in electrical insulation, luggage, protective guards and various types of materials-handling equipment. The major limitations are dimensional instability caused by changes in humidity, lack of flexibility and the long processing times necessary to extract the zinc chloride.

References

1. PAIST, W. D., *Cellulosics*, Reinhold, New York (1958)
2. STANNETT, V., *Cellulose Acetate Plastics*, Temple Press, London (1950)
3. FORDYCE, C. R., and MEYER, L. W. A., *Ind. Eng. Chem.*, **33**, 597 (1940)
4. DAVIDSON, R. L., and SITTING, M., *Water Soluble Resins*, Reinhold, New York (1962)

Bibliography

- DAVIDSON, R. L., and SITTING, M., *Water Soluble Resins*, Reinhold, New York (1962)
- MILES, F. D., *Cellulose Nitrate*, Oliver and Boyd, London (1955)
- OTT, G., SPURLIN, H. M., and GRAFFLIN, M. W., *Cellulose and its Derivatives* (3 vols), Interscience, New York, 2nd Edn (1954)
- PAIST, W. D., *Cellulosics*, Reinhold, New York (1958)
- ROWELL, R. M. and YOUNG, R. A. (Eds.), *Modified Cellulosics*, Academic Press, New York–San Francisco–London (1978)
- STANNETT, V., *Cellulose Acetate Plastics*, Temple Press, London (1950)
- YARSLEY, V. E., FLAVELL, W., ADAMSON, P. S., and PERKINS, N. G., *Cellulosic Plastics*, Iliffe, London (1964)

Phenolic Resins

23.1 INTRODUCTION

The phenolic resins may be considered to be the first polymeric products produced commercially from simple compounds of low molecular weight, i.e. they were the first truly synthetic resins to be exploited. Their early development has been dealt with briefly in Chapter 1 and more fully elsewhere.¹

Although they are now approaching their centenary, phenolic resins continue to be used for a wide variety of applications, such as moulding powders, laminating resins, adhesives, binders, surface coatings and impregnants. Until very recently the market has continued to grow but not at the same rate as for plastics materials in general. For example, in 1957 production of phenolic resins was of the same order as for PVC and for polyethylene and about twice that of polystyrene. Today it is less than a tenth that of polyethylene and about one-third that of polystyrene. In the early 1990s it was estimated that production in the USA was about 1 200 000 t.p.a., in Western Europe 580 000 t.p.a. and in Japan 380 000 t.p.a. With most markets for phenolic resins being long-established but at the same time subject to increased competition from high-performance thermoplastics the overall situation had not greatly changed by the end of the 1990s.

Phenolic moulding powders, which before World War II dominated the plastics moulding materials market, only consumed about 10% of the total phenolic resin production by the early 1990s.

In recent years there have been comparatively few developments in phenolic resin technology apart from the so-called Friedel–Crafts polymers introduced in the 1960s and the polybenzoxazines announced in 1998 which are discussed briefly at the end of the chapter.

Phenolic resins are also widely known as phenol–formaldehyde resins, PF resins and phenoplasts. The trade name Bakelite has in the past been widely and erroneously used as a common noun and indeed is noted as such in many English dictionaries.

23.2 RAW MATERIALS

The phenolics are resinous materials produced by condensation of a phenol, or mixture of phenols, with an aldehyde. Phenol itself and the cresols are the most widely used phenols whilst formaldehyde and, to a much less extent, furfural are almost exclusively used as the aldehydes.

23.2.1 Phenol

At one time the requirement for phenol (melting point 41°C), could be met by distillation of coal tar and subsequent treatment of the middle oil with caustic soda to extract the phenols. Such tar acid distillation products, sometimes containing up to 20% *o*-cresol, are still used in resin manufacture but the bulk of phenol available today is obtained synthetically from benzene or other chemicals by such processes as the sulphonation process, the Raschig process and the cumene process. Synthetic phenol is a purer product and thus has the advantage of giving rise to less variability in the condensation reactions.

In the sulphonation process vaporised benzene is forced through a mist of sulphuric acid at $100\text{--}120^{\circ}\text{C}$ and the benzene sulphonic acid formed is neutralised with soda ash to produce benzene sodium sulphonate. This is fused with a 25–30% excess of caustic soda at $300\text{--}400^{\circ}\text{C}$. The sodium phenate obtained is treated with sulphuric acid and the phenol produced is distilled with steam (Figure 23.1).

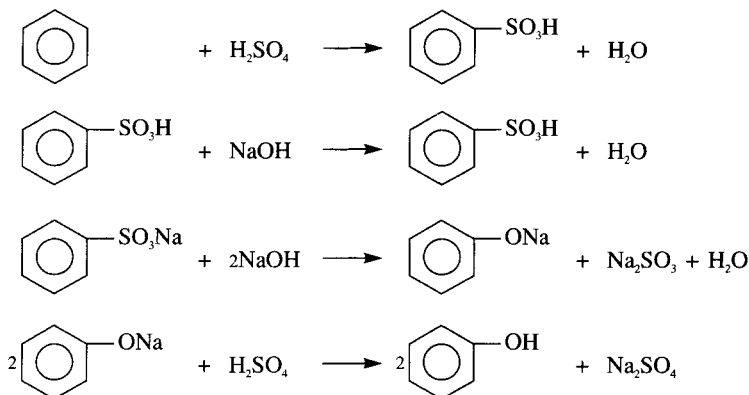


Figure 23.1

Today the sulphonation route is somewhat uneconomic and largely replaced by newer routes. Processes involving chlorination, such as the Raschig process, are used on a large scale commercially. A vapour phase reaction between benzene and hydrochloric acid is carried out in the presence of catalysts such as an aluminium hydroxide–copper salt complex. Monochlorobenzene is formed and this is hydrolysed to phenol with water in the presence of catalysts at about 450°C , at the same time regenerating the hydrochloric acid. The phenol formed is extracted from benzene, separated from the latter by fractional distillation and purified by vacuum distillation. In recent years developments in this process have reduced the amount of by-product dichlorobenzene formed and also considerably increased the output rates.

A third process, now the principal synthetic process in use in Europe, is the cumene process.

In this process liquid propylene, containing some propane, is mixed with benzene and passed through a reaction tower containing phosphoric acid on kieselguhr as catalyst. The reaction is exothermic and the propane present acts as a quench medium. A small quantity of water is injected into the reactor to

maintain catalyst activity. The effluent from the reactor is then passed through distillation columns. The propane is partly recycled, the unreacted benzene returned to feed and the cumene taken off (*Figure 23.2*). The cumene is then oxidised in the presence of alkali at about 130°C (*Figure 27.3*). The hydroperoxide formed is decomposed in a stirred vessel by addition of dilute sulphuric acid. The mixture is passed to a separator and the resulting organic layer fractionated (*Figure 23.4*). Some benzophenone is also produced in a side reaction.

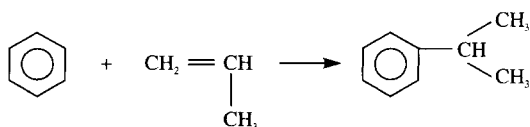


Figure 23.2

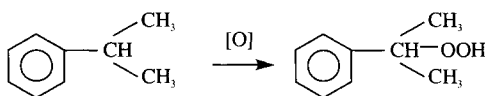


Figure 23.3

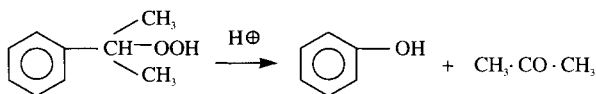


Figure 23.4

The economics of this process are to some extent dependent on the value of the acetone which is formed with the phenol. The process is, however, generally considered to be competitive with the modified Raschig process in which there is no by-product of reaction. In all of the above processes benzene is an essential starting ingredient. At one time this was obtained exclusively by distillation of coal tar but today it is commonly produced from petroleum.

A route to phenol has been developed starting from cyclohexane, which is first oxidised to a mixture of cyclohexanol and cyclohexanone. In one process the oxidation is carried out in the liquid phase using cobalt naphthenate as catalyst. The cyclohexanone present may be converted to cyclohexanol, in this case the desired intermediate, by catalytic hydrogenation. The cyclohexanol is converted to phenol by a catalytic process using selenium or with palladium on charcoal. The hydrogen produced in this process may be used in the conversion of cyclohexanone to cyclohexanol. It also may be used in the conversion of benzene to cyclohexane in processes where benzene is used as the precursor of the cyclohexane.

Other routes for the preparation of phenol are under development and include the Dow process based on toluene. In this process a mixture of toluene, air and catalyst are reacted at moderate temperature and pressure to give benzoic acid. This is then purified and decarboxylated, in the presence of air, to phenol (*Figure 23.5*).

Pure phenol crystallises in long colourless needles which melt at 41°C. It causes severe burns on the skin and care should be taken in handling the material.

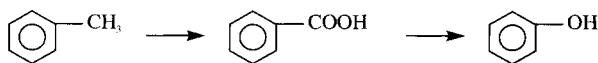


Figure 23.5

Phenol is supplied commercially either in the solid (crystalline) state or as a 'solution' in water (water content 8–20%). Where supplied as a solid it is usually handled by heating the phenol, and the molten material is pumped into the resin kettles or into a preblending tank. If the 'solution' is used care must be taken to avoid the phenol crystallising out.

23.2.2 Other Phenols

A number of other phenols obtained from coal tar distillates are used in the manufacture of phenolic resins. Of these the cresols are the most important (Figure 23.6).

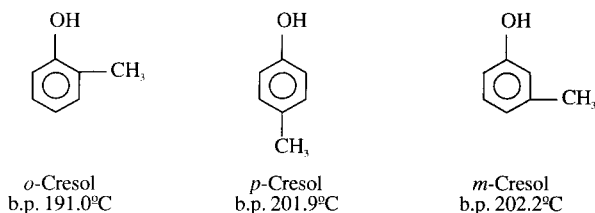


Figure 23.6

The cresols occur in cresylic acid, a mixture of the three cresols together with some xylenols and neutral oils, obtained from coal tar distillates. Only the *m*-cresol has the three reactive positions necessary to give cross-linked resins and so this is normally the desired material. The *o*-isomer is easily removed by distillation but separation of the close-boiling *m*- and *p*-isomers is difficult and so mixtures of these two isomers are used in practice.

Xylenols, also obtained from coal tar, are sometimes used in oil-soluble resins. Of the six isomers (Figure 23.7) only 3,5-xyleneol has the three reactive positions

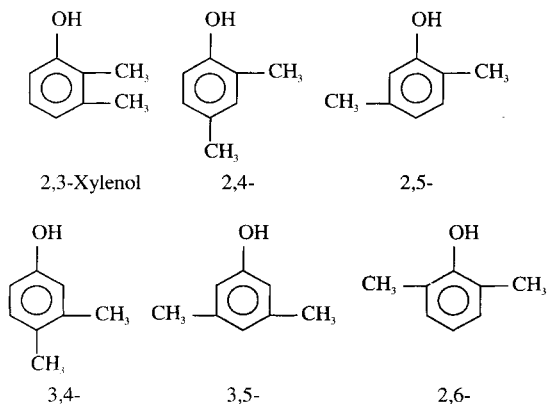


Figure 23.7

necessary for cross-linking and thus mixtures with a high proportion of this isomer are generally used.

Other higher boiling phenolic bodies obtainable from coal tar distillates are sometimes used in the manufacture of oil-soluble resins. Mention may also be made of cashew nut shell liquid which contains phenolic bodies and which is used in certain specialised applications.

A few synthetic substituted phenols are also used in the manufacture of oil-soluble resins. They include *p*-tert-butylphenol, *p*-tert-amylphenol, *p*-tert-octylphenol, *p*-phenylphenol and dihydroxyphenylpropane (bis-phenol A).

23.2.3 Aldehydes

Formaldehyde (methanal) is by far the most commonly employed aldehyde in the manufacture of phenolic resins. Its preparation has been described in Chapter 19. It is normally used as an aqueous solution, known as formalin, containing about 37% by weight of formaldehyde. From 0.5–10% of methanol may be present to stabilise the solution and retard the formation of polymers. When the formalin is used soon after manufacture, only low methanol contents are employed since the formalin has a higher reactivity. Where a greater storage life is required the formalin employed has a higher methanol content, but the resulting increasing stability is at the expense of reduced reactivity.

Furfural (see Chapter 28) is occasionally used to produce resins with good flow properties for use in moulding powders.

23.3 CHEMICAL ASPECTS

Although phenolic resins have been known and widely utilised for over 60 years their detailed chemical structure remains to be established. It is now known that the resins are very complex and that the various structures present will depend on the ratio of phenol to formaldehyde employed, the pH of the reaction mixture and the temperature of the reaction. Phenolic resin chemistry has been discussed in detail elsewhere²⁻⁷ and will be discussed only briefly here.

Reaction of phenol with formaldehyde involves a condensation reaction which leads, under appropriate conditions, to a cross-linked polymer structure. For commercial application it is necessary first to produce a tractable fusible low molecular weight polymer which may, when desired, be transformed into the cross-linked polymer. For example, in the manufacture of a phenolic (phenol-formaldehyde, P-F) moulding a low molecular weight resin is made by condensation of phenol and formaldehyde. This resin is then compounded with other ingredients, the mixture ground to a powder and the product heated under pressure in a mould. On heating, the resin melts and under pressure flows in the mould. At the same time further chemical reaction occurs, leading to cross-linking. It is obviously desirable to process under such conditions that the required amount of flow has occurred before the resin hardens.

The initial phenol-formaldehyde reaction products may be of two types, *novolaks* and *resols*.

23.3.1 Novolaks

The novolaks are prepared by reacting phenol with formaldehyde in a molar ratio of approximately 1:0.8 under acidic conditions. Under these conditions there is

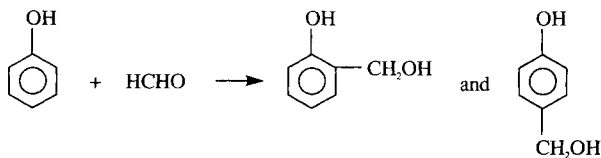


Figure 23.8

a slow reaction of the two reactants to form the *o*- and *p*-hydroxymethylphenols (Figure 23.8).

These then condensate rapidly to form products of the bis(hydroxyphenyl)-methane (HPM) type (e.g. Figure 23.9).

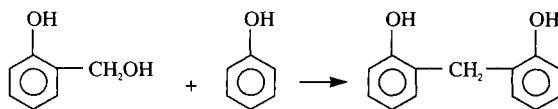


Figure 23.9

There are three possible isomers and the proportions in which they are formed will depend on the pH of the reaction medium. Under the acid conditions normally employed in novolak manufacture the 2,4'- and 4,4'-HPM compounds are the main products (Figure 23.10).

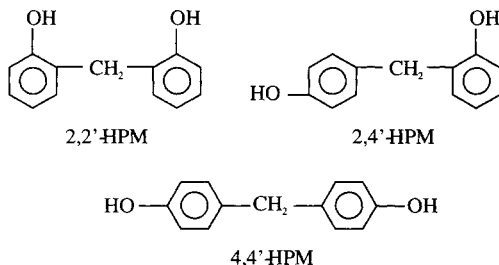


Figure 23.10

These materials will then slowly react with further formaldehyde to form their own methylol derivatives which in turn rapidly react with further phenol to produce higher polynuclear phenols. Because of the excess of phenol there is a limit to the molecular weight of the product produced, but on average there are 5–6 benzene rings per molecule. A typical example of the many possible structures is shown in Figure 23.11.

The novolak resins themselves contain no reactive methylol groups and do not form cross-linked structures on heating. If, however, they are mixed with compounds capable of forming methylene bridges, e.g. hexamethylenetetramine or paraformaldehyde, they cross-link on heating to form infusible, 'thermoset' structures.

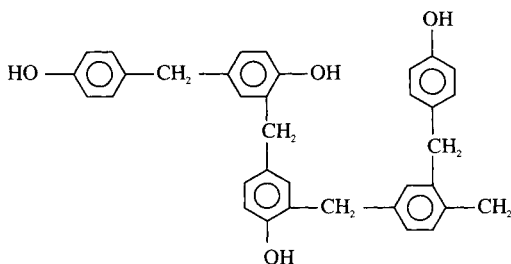


Figure 23.11

In general it is considered essential that the bulk of the phenol used initially should not be substituted, i.e. should be reactive, at the *o*- and *p*-positions and is thus trifunctional with respect to the reaction with formaldehyde.

23.3.2 Resols

A resol is produced by reacting a phenol with an excess of aldehyde under basic conditions.

In this case the formation of phenol-alcohols is rapid but their subsequent condensation is slow. Thus there is a tendency for polyalcohols, as well as monoalcohols, to be formed. The resulting polynuclear polyalcohols are of low molecular weight. Liquid resols have an average of less than two benzene rings per molecule, while a solid resol may have only three to four. A typical resol would have the structure shown in *Figure 23.12*.

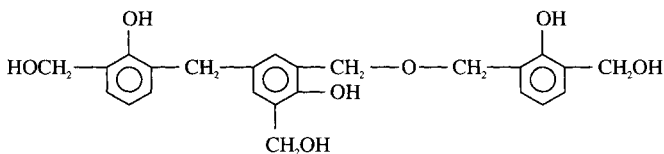


Figure 23.12

Heating of these resins will result in cross-linking via the uncondensed methylol groups or by more complex mechanisms. The resols are sometimes referred to as *one-stage resins* since cross-linked products may be made from the initial reaction mixture solely by adjusting the pH. On the other hand the novolaks are sometimes referred to as *two-stage resins* as here it is necessary to add some agent which will enable additional methylene bridges to be formed.

23.3.3 Hardening

The novolaks and resols are soluble and fusible low molecular weight products. They were referred to by Baekeland as A-stage resins. On hardening, these resins pass through a rubbery stage in which they are swollen, but not dissolved, by a variety of solvents. This is referred to as the B-stage. Further reaction leads to rigid, insoluble, infusible, hard products known as C-stage resins. When prepared from resols the B-stage resin is sometimes known as a *resitol* and the C-stage

product a *resit*. The terms A-, B- and C-stage resins are also sometimes used to describe analogous states in other thermosetting resins.

The mechanism of the hardening processes has been investigated by Zinke in Austria, von Euler in Sweden and Hultsch in Germany using blocked methylol phenols so that only small isolable products would be obtained.

In general their work indicates that at temperatures below 160°C cross-linking occurs by phenol methylol–phenol methylol and phenol methylol–phenol condensations, viz *Figure 23.13*.

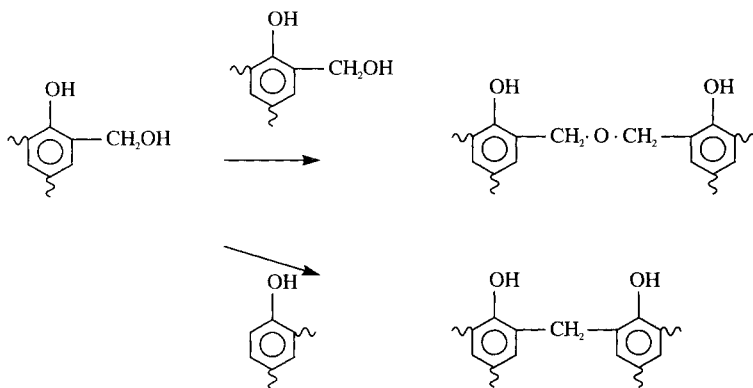


Figure 23.13

As these condensation reactions can occur at the two *ortho* and the *para* positions in phenol, *m*-cresol and 3,5-xyleneol, cross-linked structures will be formed. It has been pointed out by Megson⁵ that because of steric hindrance the amount of cross-linking that can take place is much less than would involve the three reactive groups of all the phenolic molecules. It is now generally considered that the amount of cross-linking that actually takes place is less than was at one time believed to be the case.

Above 160°C it is believed that additional cross-linking reactions take place involving the formation and reaction of quinone methides by condensation of the ether linkages with the phenolic hydroxyl groups (*Figure 23.14*).

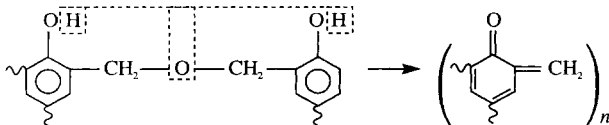


Figure 23.14

These quinone methide structures are capable of polymerisation and of other chemical reactions.

It is likely that the quinone methide and related structures formed at these temperatures account for the dark colour of phenolic compression mouldings. It is to be noted that cast phenol–formaldehyde resins, which are hardened at much

lower temperatures, are water-white in colour. If, however, these castings are heated to about 180°C they darken considerably.

In addition to the above possible mechanisms the possibility of reaction at *m*-positions should not be excluded. For example, it has been shown by Koebner that *o*- and *p*-cresols, ostensibly difunctional, can, under certain conditions, react with formaldehyde to give insoluble and infusible resins. Furthermore, Megson has shown that 2,4,6-trimethylphenol, in which the two *ortho*- and the one *para*-positions are blocked, can condense with formaldehyde under strongly acidic conditions. It is of interest to note that Redfarm produced an infusible resin from 3,4,5,-trimethylphenol under alkaline conditions. Here the two *m*- and the *p*-positions were blocked and this experimental observation provides supplementary evidence that additional functionalities are developed during reaction, for example in the formation of quinone methides.

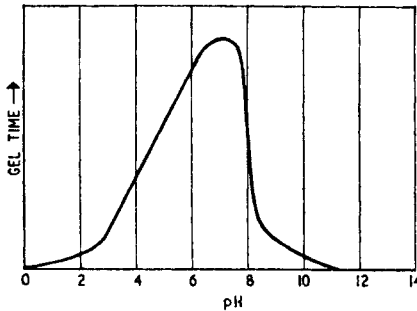


Figure 23.15. Effect of pH on the gel time of a P-F cast resin. (After Apley⁸)

The importance of the nature of the catalyst on the hardening reaction must also be stressed. Strong acids will sufficiently catalyse a resol to cure thin films at room temperature, but as the pH rises there will be a reduction in activity which passes through a minimum at about pH 7. Under alkaline conditions the rate of reaction is related to the type of catalyst and to its concentration. The effect of pH value on the gelling time of a casting resin (phenol-formaldehyde ratio ~1:2.25) is shown in *Figure 23.15*.

23.4 RESIN MANUFACTURE

Both novolaks and resols are prepared in similar equipment, shown diagrammatically in *Figure 23.16*. The resin kettle may be constructed from copper, nickel or stainless steel where novolaks are being manufactured. Stainless steel may also be used for resols but where colour formation is unimportant the cheaper mild steel may be used.

In the manufacture of novolaks, 1 mole of phenol is reacted with about 0.8 mole of formaldehyde (added as 37% w/w formalin) in the presence of some acid as catalyst. A typical charge ratio would be:

Phenol	100 parts by weight
Formalin (37% w/w)	70 parts by weight
Oxalic acid	1.5 parts by weight

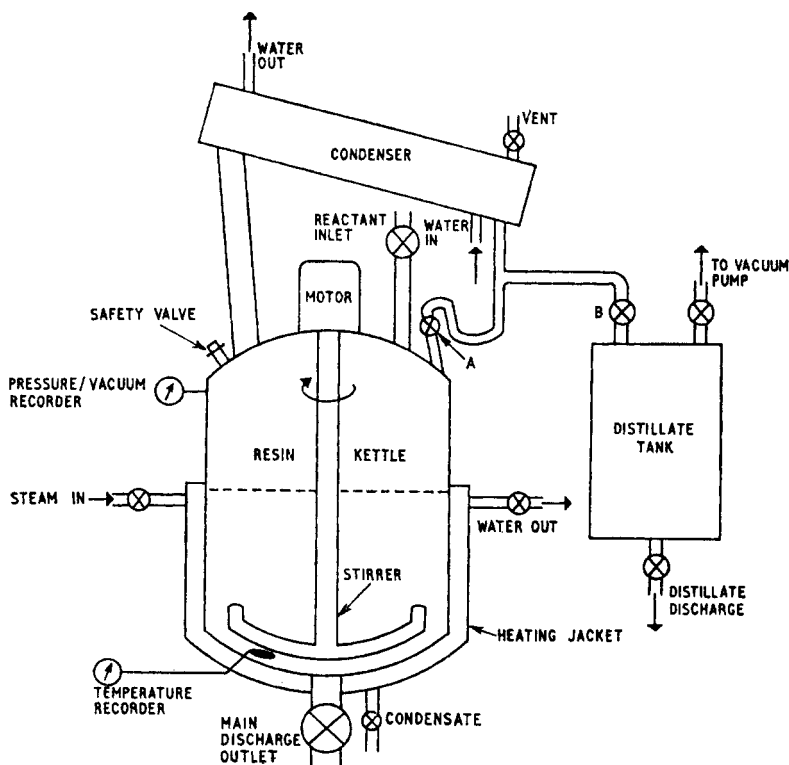


Figure 23.16. Diagrammatic representation of resin kettle and associated equipment used for the preparation of phenolic resins. (After Whitehouse, Pritchett and Barnett²)

The reaction mixture is heated and allowed to reflux, under atmospheric pressure at about 100°C. At this stage valve A is open and valve B is closed. Because the reaction is strongly exothermic initially it may be necessary to use cooling water in the jacket at this stage. The condensation reaction will take a number of hours, e.g. 2–4 hours, since under the acidic conditions the formation of phenol–alcohols is rather slow. When the resin separates from the aqueous phase and the resin reaches the requisite degree of condensation, as indicated by refractive index measurements, the valves are changed over (i.e. valve A is closed and valve B opened) and water present is distilled off.

In the case of novolak resins the distillation is normally carried out without the application of vacuum. Thus, as the reaction proceeds and the water is driven off, there is a rise in the temperature of the resin which may reach as high as 160°C at the end of the reaction. At these temperatures the fluid is less viscous and more easily stirred. In cases where it is important to remove the volatiles present, a vacuum may be employed after the reaction has been completed, but for fast-curing systems some of the volatile matter (mainly low molecular weight phenolic bodies) may be retained.

The end point may be checked by noting the extent of flow of a heated pellet down a given slope or by melting point measurements. Other control tests include alcohol solubility, free phenol content and gelation time with 10% hexa.

In the manufacture of resols a molar excess of formaldehyde (1.5–2.0:1) is reacted with the phenol in alkaline conditions. In these conditions the formation of the phenol alcohols is quite rapid and the condensation to a resol may take less than an hour. A typical charge for a laboratory-scale preparation would be:

Phenol	94 g (1 mole)
Formalin (40%)	112 cm ³ (1.5 moles formaldehyde)
0.88 ammonia	4 cm ³

The mixture is refluxed until the reaction has proceeded sufficiently. It may then be neutralised and the water formed distilled off, usually under reduced pressure to prevent heat-hardening of the resin. Because of the presence of hydroxymethyl groups the resol has a greater water-tolerance than the novolak.

The reaction may be followed by such tests as melting point, acetone or alcohol solubility, free phenol content or loss in weight on stoving at 135°C.

Two classes of resol are generally distinguished, water-soluble resins prepared using caustic soda as catalyst, and spirit-soluble resins which are catalysed by addition of ammonia. The water-soluble resins are usually only partially dehydrated during manufacture to give an aqueous resin solution with a solids content of about 70%. The solution viscosity can critically affect the success in a given application. Water-soluble resols are used mainly for mechanical grade paper and cloth laminates and in decorative laminates.

In contrast to the caustic soda-catalysed resols the spirit-soluble resins have good electrical insulation properties. In order to obtain superior insulation characteristics a cresol-based resol is generally used. In a typical reaction the refluxing time is about 30 minutes followed by dehydration under vacuum for periods up to 4 hours.

23.5 MOULDING POWDERS

Novolaks are most commonly used in the manufacture of moulding powders although resols may be used for special purposes such as in minimum odour grades and for improved alkali resistance. The resins are generally based on phenol since they give products with the greatest mechanical strength and speed of cure, but cresols may be used in acid-resisting compounds and phenol–cresol mixtures in cheaper compositions. Xylenols are occasionally used for improved alkali resistance.

The resols may be hardened by heating and/or by addition of catalysts. Hardening of the novolaks may be brought about by addition of hexamethylenetetramine (hexa, hexamine). Because of the exothermic reaction on hardening (cure) and the accompanying shrinkage, it is necessary to incorporate inert materials (fillers) to reduce the resin content. Fillers are thus generally necessary to produce useful mouldings and are not incorporated simply to reduce cost. Fillers may give additional benefits such as improving the shock resistance.

Other ingredients may be added to prevent sticking to moulds (lubricants), to promote the curing reaction (accelerators), to improve the flow properties (plasticisers) and to colour the product (pigments).

23.5.1 Compounding Ingredients

It is thus seen that a phenol-formaldehyde moulding powder will contain the following ingredients:

- (1) Resin.
- (2) Hardener (with Novolaks).
- (3) Accelerator.
- (4) Filler.
- (5) Lubricant.
- (6) Pigment.
- (7) Plasticiser (not always used).

In addition to the selection of phenol used and the choice between novolak and resol there is a number of further variations possible in the resin used. For example, in the manufacture of a novolak resin slight adjustment of phenol/formaldehyde ratio will affect the size of novolak molecule produced. Higher molecular weight novolaks give a stiff-flow moulding powder but the resin being of lower reactivity, the powders have a longer cure time. A second variable is the residual volatile content. The greater the residual volatiles (phenolic bodies) the faster the cure. Thus a fast-curing, stiff-flow resin may be obtained by using a phenol/formaldehyde ratio leading to larger molecules and leaving some of the low molecular weight constituents in the reaction mixture. Yet another modification may be achieved by changing the catalyst used. Thus whereas in the normal processes, using oxalic acid catalysts, the initial products are *p-p*- and *o-p*-diphenylmethanes, under other conditions it is possible to achieve products which have reacted more commonly in the *ortho*-position. Such resins thus have the *p*-position free and, since this is very reactive to hexa, a fast-curing resin is obtained.

Hexa is used almost universally as the hardener. It is made by passing a slight excess of ammonia through a lightly stabilised aqueous solution of formaldehyde, concentrating the liquor formed and crystallising out the hexa (Figure 23.17).

Between 10 and 15 parts of hexa are used in typical moulding compositions. The mechanism by which it cross-links novolak resins is not fully understood but it appears capable of supplying the requisite methylene bridges required for cross-linking. It also functions as a promoter for the hardening reaction.

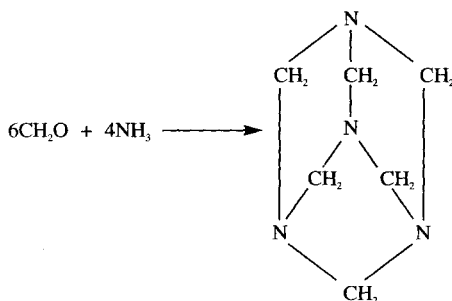


Figure 23.17

Basic materials such as lime or magnesium oxide increase the hardening rate of novolak-hexa compositions and are sometimes referred to as accelerators. They also function as neutralising agents for free phenols and other acidic bodies which cause sticking to, and staining of, moulds and compounding equipment. Such basic substances also act as hardeners for resol-based compositions.

Woodflour, a fine sawdust preferably obtained from softwoods such as pine, spruce and poplar, is the most commonly used filler. Somewhat fibrous in nature, it is not only an effective diluent for the resin to reduce exotherm and shrinkage, but it is also cheap and improves the impact strength of the mouldings. There is a good adhesion between phenol-formaldehyde resin and the woodflour and it is possible that some chemical bonding may occur.

Another commonly employed low-cost organic filler is coconut shell flour. This can be incorporated into the moulding composition in large quantities and this results in cheaper mixes than when woodflour is used. The mouldings also have a good finish. However, coconut shell flour-filled mouldings have poor mechanical properties and hence the filler is generally used in conjunction with woodflour.

For better impact strength cotton flock, chopped fabric or even twisted cord and strings may be incorporated. The cotton flock-filled compounds have the greatest mouldability but the lowest shock resistance whilst the twisted cords and strings have the opposite effect. Nylon fibres and fabrics are sometimes used to confer strength and flexibility and glass fibres may be used for strength and rigidity.

Asbestos may be used for improved heat and chemical resistance and silica, mica and china clay for low water absorption grades. Iron-free mica powder is particularly useful where the best possible electrical insulation characteristics are required but because of the poor adhesion of resin to the mica it is usually used in conjunction with a fibrous material such as asbestos. Organic fillers are commonly used in a weight ratio of 1:1 with the resin and mineral fillers in the ratio 1.5:1.

In some countries the extensive use of asbestos as a filler is somewhat discouraged because of the hazards associated with its use. In other parts of the world moulding compositions of enhanced heat resistance have been developed by the use of especially heat-resisting polymers used in conjunction with asbestos and other mineral fillers.

Stearic acid and metal stearates such as calcium stearate are generally used as lubricants at a rate of about 1–3% on the total compound. Waxes such as carnauba and ceresin or oils such as castor oil may also be used for this purpose.

In order that the rate of cure of phenolic moulding compositions is sufficiently rapid to be economically attractive, curing is carried out at a temperature which leads to the formation of quinone methides and their derivatives which impart a dark colour to the resin. Thus the range of pigments available is limited to blacks, browns and relatively dark blues, greens, reds and oranges.

In some moulding compositions other special purpose ingredients may be incorporated. For example, naphthalene, furfural and dibutyl phthalate are occasionally used as plasticisers or more strictly as flow promoters. They are particularly useful where powders with a low moulding shrinkage are required. In such formulations a highly condensed resin is used so that there will be less reaction, and hence less shrinkage, during cure. The plasticiser is incorporated to

Table 23.1

	<i>GP grade</i>	<i>Electrical grade</i>	<i>Medium shock-resisting grade</i>	<i>High shock-resisting grade</i>
Novolak resin	100	100	100	100
Hexa	12.5	14	12.5	17
Magnesium oxide	3	2	2	2
Magnesium stearate	2	2	2	3.3
Nigrosine dye	4	3	3	3
Woodflour	100	—	—	—
Mica	—	120	—	—
Cotton flock	—	—	110	—
Textile shreds	—	—	—	150
Asbestos	—	40	—	—

the extent of about 1% to give these somewhat intractable materials adequate flow properties.

Some typical formulations are given in *Table 23.1*.

23.5.2 Compounding of Phenol-Formaldehyde Moulding Compositions

Although there are many variants in the process used for manufacturing moulding powders, they may conveniently be classified into dry processes and wet processes.

In a typical dry process, finely ground resin is mixed with the other ingredients for about 15 minutes in a powder blender. This blend is then fed on to a heated two-roll mill. The resin melts and the powdery mix is fluxed into a leathery hide which bands round the front roll. The temperatures chosen are such that the front roll is sufficiently hot to make the resin tacky and the rear roll somewhat hotter so that the resin will melt and be less tacky. Typical temperatures are 70–100°C for the front roll and 100–120°C for the back. As some further reaction takes place on the mill, resulting in a change of melting characteristics, the roll temperatures should be carefully selected for the resin used. In some processes two mills may be used in series with different roll temperatures to allow greater flexibility in operation. To achieve consistency in the end-product a fixed mixing schedule must be closely followed. Milling times vary from 10 minutes down to a straight pass through the mill.

The hide from the mill is then cooled, pulverised with a hammer-mill and the resulting granules are sieved. In a typical general purpose composition the granules should pass a 14 × 26 sieve. For powders to be used in automatic moulding plant fine particles are undesirable and so particles passing a 100 × 41 sieve (in a typical process) are removed. In addition to being more suitable for automatic moulding machines these powders are also more dust-free and thus more pleasant to use. For ease of pelleting, however, a proportion of ‘fines’ is valuable.

For the manufacture of medium-shock-resisting grades the preblend of resin, filler and other ingredients does not readily form a hide on the mill rolls. In this case the composition is preblended in an internal mixer before passing on to the mills.

Extrusion compounders such as the Buss Ko-Kneader have been used for mixing phenolic resins. It is claimed that they produce in some respects a better product and are more economical to use than mill-mixers.

High-shock grades cannot be processed on mills or other intensive mixers without destroying the essential fibrous structure of the filler. In these cases a wet process is used in which the resin is dissolved in a suitable solvent, such as industrial methylated spirits, and blended with the filler and other ingredients in a dough mixer. The resulting wet mix is then laid out on trays and dried in an oven.

23.5.3 Processing Characteristics

As it is a thermosetting material, the bulk of phenol-formaldehyde moulding compositions has in the past been largely processed on compression and transfer moulding plant, with a very small amount being extruded. The injection moulding process as modified for thermosetting plastic is now being used significantly but still on a smaller scale than the traditional processes.

Moulding compositions are available in a number of forms, largely determined by the nature of the fillers used. Thus mineral-filled and woodflour-filled grades are generally powders whilst fibre-filled grades may be of a soft-lumpy texture. Fabric-filled grades are sold in the form of shredded impregnated 'rag'. The powder grades are available in differing granulations. Very fine grades are preferred where there is a limited flow in moulds and where a high-gloss finish is required. Fine powders are, however, dusty and a compromise may be sought. For mouldings in which extensive flow will occur, comparatively coarse (and thus dust-free) powders can be used and a reasonable finish still obtained. For the best pelleting properties it would appear that some 'fines' are desirable for good packing whilst 'fines' are generally undesirable in powders employed in automatic compression moulding.

Since the resins cure with evolution of volatiles, compression moulding is carried out using moulding pressures of 1–2 ton/in² (15–30 MPa) at 155–170°C. In the case of transfer moulding, moulding pressures are usually somewhat higher, at 2–8 ton/in² (30–120 MPa). As with other thermosetting materials an increase in temperature has two effects. Firstly, it reduces the viscosity of the molten resin and, secondly, it increases the rate of cure. As a result of these two effects it is found that in a graph of extent of flow plotted against temperature there is a temperature of maximum flow (*Figure 23.18*).

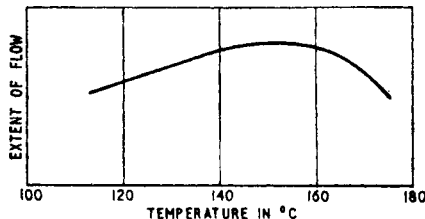


Figure 23.18. Dependence of the extent of flow on temperature for a general purpose phenolic resin. Curves of this type may be obtained from measurements made on widely different pieces of equipment, e.g. the Rossi-Peakes flow tester and the flow disc. Thus no scale has been given for the vertical axis

There is no entirely satisfactory way of measuring flow. In the BS 2782 flow cup test an amount of moulding powder is added to the mould to provide between 2 and 2.5 g of flash. The press is closed at a fixed initial rate and at a fixed temperature and pressure. The time between the onset of recorded pressure and the cessation of flash (i.e. the time at which the mould has closed) is noted. This time is thus the time required to move a given mass of material a fixed distance and is thus a measure of viscosity. It is not a measure of the time available for flow. This property, or rather the more important 'length of flow' or extent of flow, must be measured by some other device such as the flow disc or by the Rossi–Peakes flow test, neither of which are entirely satisfactory. Cup flow times are normally of the order of 10–25 seconds if measured by the BS specification. Moulding powders are frequently classified as being of 'stiff flow' if the cup flow time exceeds 20 seconds, 'medium flow' for times of 13–19 seconds and 'soft flow' or 'free flow' if under 12 seconds.

The bulk factor (i.e. ratio of the density of the moulding to the apparent powder density) of powder is usually about 2–3 but the high-shock grades may have bulk factors of 10–14 when loose, and still as high as 4–6 when packed in the mould. Powder grades are quite easy to pellet, but this is difficult with the fabric-filled grades.

Phenol–formaldehyde moulding compositions may be preheated by high-frequency methods without difficulty. Preheating, by this or other techniques, will reduce cure time, shrinkage and required moulding pressures. Furthermore, preheating will enhance the ease of flow, with consequent reduction in mould wear and danger of damage to inserts.

Moulding shrinkage of general purpose grades is in the order of 0.005–0.08 in/in. Highly loaded mineral-filled grades have a lower shrinkage whilst certain grades based on modified resins, e.g. acid-resistant and minimum odour grades, may have somewhat higher shrinkage values.

Cure times will depend on the type of moulding powder used, the moulding temperature, the degree of preheating employed and, most important, on the end-use envisaged for the moulding. The time required to give the best electrical insulation properties may not coincide with the time required, say, for greatest hardness. However, one useful comparative test is the minimum time required to mould a blister-free flow cup under the BS 771 test conditions. For general purpose material this is normally about 60 seconds but may be over twice this time with special purpose grades.

One of the disadvantages of thermosetting plastics which existed for many years was that whilst the common moulding processes for thermoplastics were easily automated this was much more difficult with thermoset compression moulding. With the development of the reciprocating single-screw injection moulding machines, equipment became available which facilitated the adoption of injection moulding to thermosets. In this adapted process the thermosetting granules are carefully heated in the barrel so that they soften but do not cross-link before entering the mould cavity. The moulds are, however, heated to curing temperatures so that once the mould is filled cure is as fast as possible consistent with obtaining the best balance of properties in the end-product.

As a result of these considerations, typical injection moulding conditions are:

Melt temperature	110–140°C
Cylinder temperature	65–90°C
Nozzle temperature	85–120°C

Mould temperature	165–195°C
Injection pressure	85–250 MPa
Screw back pressure	<7 (typically 1) MPa
Screw speed	65–85 rev/min
Curing time	15–80 s

In order to obtain a good control of cylinder temperature, a fluid heat transfer system is desirable. Such fluid may be heated in an adjacent temperature controller or perhaps more commonly be circulated in channels which are built in between electrical heaters and the barrel chamber. Special temperature-controlled nozzles are employed to avoid setting up either by cooling or cross-linking whilst moulds are usually electrically heated. Many machines are now available which may be changed from thermoplastics to thermosetting moulding and vice versa by a change of the nozzle end-cap and change of screw. For thermosetting plastics screws often have a low compression ratio and are water cooled.

There is a slowly resolving but intensive controversy over the relative merits of compression, transfer and injection moulding. Compared with compression methods both injection and transfer moulding are advantageous in that they are more easily automated, mouldings are flash free and have a good surface finish, it is easier to mould thick and/or void free sections and it is possible to increase cure rates by frictional heat. It is probably also true that in all these instances injection moulding has a slight advantage over transfer. Injection moulding can be very fast and claim has been made that sometimes cycles may be reduced to one-sixth of the compression moulding time. Pelleting and preheating are also unnecessary. Yet another advantage is that the thermoplastics moulder may, by small machine changes, be able to handle a range of materials without the purchase of compression presses. The increased versatility of the machines can also give greater flexibility in planning and potentially increase the loading factor of the equipment.

There are, however, disadvantages to the injection moulding process. Injection moulding machines are very much more expensive than compression presses and with the larger sizes injection machines may be several times the price of compression machines of similar mould size capacities. There may also be possible technical disadvantages. If not moulded carefully the mouldings may exhibit inferior and anisotropic mechanical properties, particularly with thin-walled mouldings. The dimensional stability on heating may be worse and the shrinkage more variable than occurs with compression moulding. The selection between compression and injection moulding must therefore be made with care, with perhaps a tendency for injection moulding to be preferred with fairly small, thick-section long-run mouldings.

Injection moulding compositions have a number of requirements with regard to granule flow and cure characteristics not always met by conventional formulations. For example, granules should be free-flowing (i.e. of a narrow particle size distribution and not too irregular in shape). There are also certain requirements in terms of viscosity.

The viscosity should quickly reach a suitable value on heating in the barrel. It should not be too high since it may be difficult to fill the mould. At the same time it should not be so low that little heat is generated by friction. At the injection melt temperature of 100–130°C the compound should have a good stability but should cure rapidly at the high curing temperatures as exist within the mould.

23.5.4 Properties of Phenolic Mouldings

Since the polymer in phenolic mouldings is cross-linked and highly interlocked, phenolic mouldings are hard, heat-resistant insoluble materials.

The chemical resistance of the mouldings depends on the type of filler and resin used. Simple phenol-formaldehyde materials are readily attacked by aqueous sodium hydroxide solution but cresol- and xylenol-based resins are more resistant. Provided the filler used is also resistant, phenolic mouldings are resistant to acids except 50% sulphuric acid, formic acid and oxidising acids. The resins are stable up to 200°C. Some recently developed grades of moulding compounds are claimed to be capable of exposure to 300°C for short periods.

The mechanical properties are strongly dependent on the type of filler used and typical figures are given in *Table 23.2*

As the mouldings are polar, the electrical insulation properties are not outstanding but are adequate for many purposes. At 100°C a typical woodflour-phenolic moulding has a dielectric constant of 18 and a power factor of 0.7 at 800 Hz.

One disadvantage of phenolics compared with the aminoplastics and the alkyd resins is their poor tracking resistance under conditions of high humidity. This means that phenolics have a tendency to form a conductive path through carbonisation along a surface between two metal electrodes at differing potential. Whether tracking will occur depends on the separation of the electrodes, the humidity of the atmosphere, the potential difference and the presence and nature of surface contaminants. For many applications the poor tracking resistance is not a serious problem and the wide use of phenolic laminates and mouldings for electrical insulation applications is evidence of this.

23.5.5 Applications

Since the advent of Bakelite some 90 years ago phenol-formaldehyde moulding compositions have been used for a great variety of purposes. Perhaps the most well-known applications are in domestic plugs and switches. It should, however, be pointed out that since World War II, in Britain at least, urea-formaldehyde plastics have largely replaced phenol-formaldehyde for these purposes because of their better anti-tracking properties and wider colour range. There are, nevertheless, many applications where the phenolics have proved quite adequate and continue to be used as insulators. In general it may be said that the phenolics have better heat and moisture resistance than the urea-formaldehyde mouldings (see Chapter 24). Phenol-formaldehyde mouldings have also found many other applications in the electrical industry, in some instances where high electrical insulation properties are not so important. These include instrument cases, knobs, handles and telephones. In some of these applications they have now been replaced by urea-formaldehydes, melamine-formaldehydes, alkyds or the newer thermoplastics because of the need for bright colours or in some cases in an attempt to produce tougher products. In the car industry phenol-formaldehyde mouldings are used in fuse-box covers, distributor heads and in other applications where good electrical insulation together with good heat resistance are required.

The newer improved heat-resistant grades are finding use in saucepan handles, saucepan lid knobs, lamp housings, cooker handles, welding tongs and electric iron parts.

Table 23.2 Properties of phenol mouldings

<i>Property</i>	<i>Units</i>	<i>General purpose</i>	<i>Medium shock</i>	<i>High shock</i>	<i>Electrical low loss</i>	<i>Acid resistant</i>	<i>Minimum odour</i>	<i>Heat resistant</i>	<i>BS 2782 test method</i>
BS 771 classification	—	GX	MS	HS	L	—	—	HR	
Specific gravity	—	1.35	1.37	1.40	1.85	1.42	1.38	1.94	509 A
Shrinkage	cm/cm	0.006	0.005	0.002	0.002	0.009	0.007	0.002	106A
Impact strength	ft lbf	0.16	0.29	0.8–1.4	0.14	0.14	0.17	0.10	305A
	J	0.22	0.39	1.08–1.9	0.18	0.18	0.23	0.13	
Cross-breaking strength	lbf/in ²	11 500	11 000	12 000	11 000	8750	11 250	8750	304A
	MPa	80	76	83	76	60	78	60	
Tensile strength	lbf/in ²	8000	7000	6500	8500	6250	7250	5000	301A
	MPa	55	48	45	58	43	50	34	
Blister temperature	°C	175	170	175	190	185	190	195	—
Power factor 800 Hz	—	0.1–0.4	0.1–0.35	0.1–0.5	0.03–0.05	0.03–0.14	0.15–0.3	0.1–0.3	—
10 ⁶ Hz	—	0.03–0.05	—	—	0.01–0.02	—	—	—	207A
Dielectric constant 800 Hz	—	6.0–10.0	5.5–5.7	6.0–10.0	4.0–6.0	5.0–6.0	7.0–9.0	8.0–16.0	—
10 ⁶ Hz	—	4.5–5.5	—	—	4.3–5.4	—	—	—	207A
Dielectric strength (20°C)	V/0.001 in	150–300	200–275	150–250	275–350	225–300	175–225	250–350	—
	kV/cm	58–116	78–106	58–97	106–135	87–116	68–87	97–135	
(90°C)	V/0.001 in	100–250	75–175	50–150	250–350	200–275	75–150	200–300	201A
	kV/cm	39–97	29–68	19–58	97–135	87–106	29–58	78–116	
Water absorption 24h 23°C	mg	45–65	30–50	50–100	2–6	15–25	45–70	3–8	502F
Volume resistivity	Ωm	10 ¹² –10 ¹⁴	10 ¹² –10 ¹⁴	10 ^{11.5} –10 ^{13.5}	10 ^{13.5} –10 ¹⁶	10 ^{13.5} –10 ¹⁵	10 ¹² –10 ^{13.5}	10 ¹¹ –10 ¹⁴	202A

Because of its hardness and ability to be electroplated, together with good dimensional stability, phenolic mouldings are used in the manufacture of 'golf ball' heads for typewriters.

Phenol-formaldehyde mouldings continue to be used in many industrial applications where heat resistance, low cost and adequate shock resistance (varying of course with the type of powder used) are important features. Bottle caps and closures also continue to be made from phenolics in large quantities. For some applications minimum odour grades based on resols are used. The development of automatic compression presses and machines suitable for the injection moulding of thermosetting plastics together with the advent of fast-curing grades has stimulated the use of phenol-formaldehydes for many small applications in spite of the competition from the major thermoplastics.

Today the phenol-formaldehyde moulding compositions do not have the eminent position they held until about 1950. In some important applications they have been replaced by other materials, thermosetting and thermoplastic, whilst they have in the past two decades found use in few new outlets. However, the general increase in standards of living for much of this period has increased the sales of many products which use phenolics and consequently the overall use of phenol-formaldehyde moulding powders has been well maintained.

Recent estimates suggest that in the early 1990s the percentage breakdown of consumption of phenolic moulding materials in Western Europe was approximately:

Electrical engineering, including wiring devices, and electronics	40%
Domestic appliances: pot and pan handles and tableware	33%
Automotive industry	12%
Sanitary sector (toilet seats, bathroom equipment)	3%
Closures	2%
Other	10%

23.6 PHENOLIC LAMINATES

There are now commercially available a large range of laminated plastics materials. Resins used include the phenolics, the aminoplastics, polyesters, epoxies, silicones and the furane resins, whilst reinforcements may be of paper, cotton fibre, other organic fibres, asbestos, carbon fibre or glass fibre. Of these the phenolics were the first to achieve commercial significance and they are still of considerable importance.

One-stage resins (resols) in which there are sufficient methylol groups to enable cross-linking to occur without the need for formaldehyde donors are invariably used. Resins based on phenol, or phenol-cresol mixtures, are used in fabric laminates where the greatest mechanical strength is required, whereas cresylic acid (*m*-cresol content 50–55%) is generally used for electrical grade laminating resins because of the better electrical properties which result. Caustic soda is commonly used as the catalyst for mechanical laminates but is not used in electrical laminates because it affects the electrical insulation properties adversely, and ammonia is the usual catalyst in this instance.

For laminating, the ammonia-catalysed resins are usually dissolved in industrial methylated spirits (IMS) or, less commonly, isopropyl alcohol. Resins which have a high hydroxymethyl content (i.e. made by using a high ratio of

formaldehyde to phenol) and in which caustic soda is used as the catalyst are water-soluble and the aqueous solutions are useful where a high degree of impregnation is desirable. They are commonly used in mechanical and decorative laminates.

The reinforcement may be a paper or a fabric. Many different papers are used, being selected according to the end-use of the laminate. For example, the Kraft papers are strong and produce laminates of high mechanical strength, the relatively non-porous sulphite wood pulp papers are used for electrical tubes whilst cotton paper and α -cellulose paper, which are highly absorbent and of good colour, are used in conjunction with phenolic resins. They include cotton, linen, rayon, glass fabrics and asbestos mat cloth.

Although certain solventless processes have been used the resin is usually applied to the reinforcement by passing the latter through a varnish (40–50% solids content) of the resin in solvent. To ensure consistency of impregnation it is important to control the solids content, the viscosity and the specific gravity of the resin. At the same time the thickness, absorbency and density of the reinforcement, or base material, should also be kept within narrow limits. *Figure 23.19* shows a typical arrangement for applying the resin to the reinforcement. The reinforcement is led into a tank of varnish and the resulting wet base is led through pressure rollers to squeeze out the excess varnish. The coated base material is then passed through either a vertical or horizontal drying oven. In a typical arrangement the temperature at the inlet end of the oven is at about 50–90°C and at the outlet about 145°C. The evaporating solvent is recovered and the resin taken to the required degree of polymerisation before emerging from the oven. The oven temperature must thus be dependent on the curing characteristics of the resin, the length of the oven and the coating rate employed. The impregnated paper is commonly checked for resin content and degree of cure. Control of degree of cure is important, as the resin must have precise flow properties. If the viscosity is too high it will not

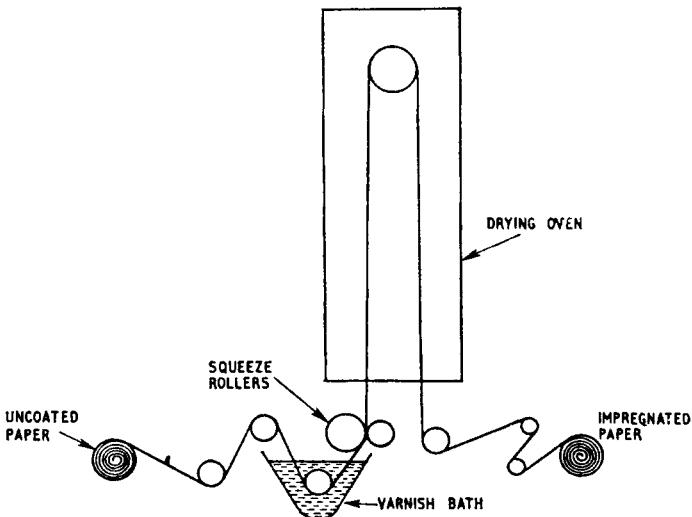


Figure 23.19. Impregnation plant fitted with vertical drying oven. (After Brown⁹)

flow sufficiently to consolidate the resin; conversely if it is too low the resin will spew out and leave a dry and inferior laminate. The degree of cure is perhaps most conveniently assessed by the practical test of preparing a small laminate in the laboratory by pressing at some controlled temperature and pressure. The weight of resin which spews out of the laminate is thus inversely related to the degree of cure, whilst more directly it will give an assessment of the laminating behaviour of the paper.

Flat laminates are prepared by plying up pieces of impregnated paper and pressing in a multi-daylight press between metal plates under pressure of 1000–2000 lbf/in² (7–14 MPa) and a temperature of 150–160°C. After curing, which may take about 30 minutes for $\frac{1}{4}$ in thick sheet, the platens are partially cooled before removal of the laminates in order to reduce blistering and warping. Where the impregnated paper has a high volatile content it may also be necessary to heat the press after loading in order to control the rate of volatilisation and thus reduce blistering.

By the use of carefully tailored pieces of impregnated reinforcement, it is possible to produce laminated mouldings. Such mouldings are tough and have a high mechanical strength but take considerably longer to cure than corresponding products prepared from moulding powders.

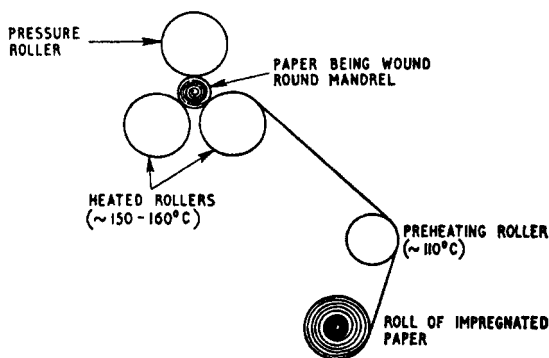


Figure 23.20. Three-roller tube winding machine. (After Brown⁹)

Tubes and bushings are prepared by winding coated or impregnated paper around a mandrel and in pressure contact with heated rollers. A typical three-roller tube winding machine is shown in Figure 23.20. A number of other simple shapes may be prepared by laminating under low pressure using hand-clamped tools or rubber bags.

23.6.1 The Properties of Phenolic Laminates

The properties of a phenolic laminate will obviously depend on a great many factors. Of these the following are perhaps the most important:

- (1) The type of resin used, including the nature of the catalyst, the concentration of methylol groups and the average molecular weight.
- (2) The properties of the varnish, such as the nature of the solvent and the viscosity and resin content of the varnish.

- (3) The type of reinforcement. In the case of fabric reinforcement, factors such as cloth weight and crimp will have a large effect on mechanical properties.
- (4) Moulding conditions, i.e moulding pressure, temperature and time.

Figures 23.21 and 23.22 show how two variables, moulding pressure and resin content, affect the mechanical properties of a laminate.

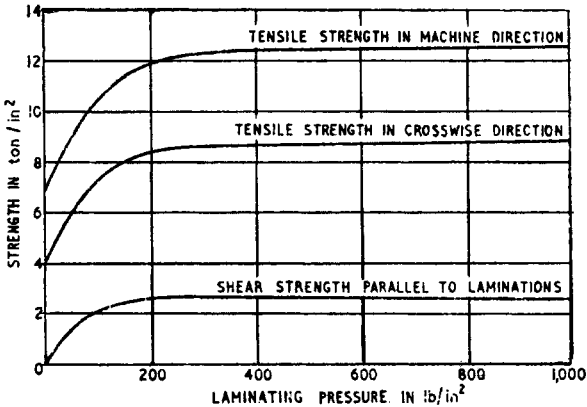


Figure 23.21. Effect of moulding pressure on the tensile and shear strength of Kraft paper laminates. (After Pepper and Barwell¹⁰)

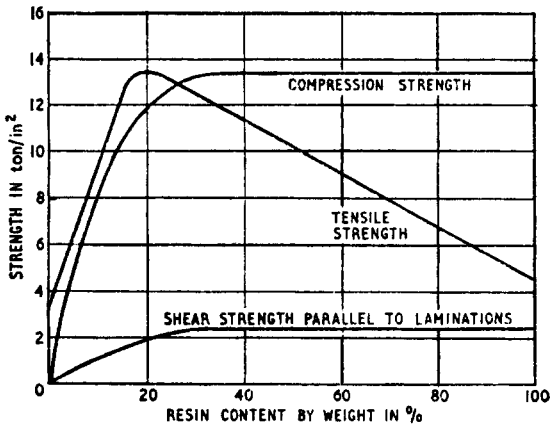


Figure 23.22. Effect of resin content on strength properties of a high-density Kraft paper laminate. (After Pepper and Barwell¹⁰)

From the above comments it will be seen that it is rather difficult to quote typical figures for laminates based on phenolic resins. Thus the figures given in Table 23.3 can be considered only as a general guide.

In the manufacture of a laminate for electrical insulation, paper, which is the best dielectric, is normally selected as the base reinforcement. An 'electrical' grade of paper is in fact a better dielectric than the resin and thus in conditions

Table 23.3 Average physical properties of phenolic resin-based laminates

<i>Property</i>	<i>Unit</i>	<i>Paper for h.t. insulation</i>	<i>Paper for l.t. insulation</i>	<i>Fine fabric</i>	<i>Asbestos felt</i>	<i>Glass fabric</i>
Tensile strength	10 ³ lbf/in ² MPa	10 69	14 97	16 110	7–15 48–104	12–35 83–240
Cross-breaking strength	10 ³ lbf/in ² MPa	20 139	27 190	19 131	16 110	25 175
Impact strength Izod (edgewise)	ft lbf J	0.2–0.35 0.27–0.47	0.35–0.45 0.47–0.61	1.5 2.0	1.0 1.35	10.0 13.5
Specific gravity	—	1.37	1.40	1.36	1.6–1.8	1.4–1.7
Power factor 800 Hz	—	0.018	0.020	0.25	—	0.01–0.04
Power factor 10 ⁶ Hz	—	0.032	0.042	0.10	0.11	0.01–0.02
Dielectric constant 10 ⁶ Hz	—	4.6	5.2	6.5	6.1	4.5–5.5
Dielectric strength normal to laminate at 90°C (0.062 in thick)	V/0.001 in KV/cm	450 177	380 150	40 15.7	100 39.4	— —

of low humidity the resin content of the laminate can be quite low, particularly if the surfaces of the laminate are protected with an insulating varnish. For humid conditions a high resin content is used since this will lead to laminates with low water absorption, an essential property for a good insulator. Tubular laminates normally show superior insulation properties to the flat sheets since they are cured layer-by-layer, which allows water of condensation to escape during manufacture. As previously mentioned, cresylic-based resins are usually used for such laminates in conjunction with ammonia as catalyst in order to achieve the best dielectric properties.

23.6.2 Applications of Phenolic Laminates

Phenolic resin–paper laminates are extensively used for high-voltage insulation applications. Laminates from other reinforcements are less suitable for this purpose but may be used for low-voltage applications. Phenolic laminates are of value not only because of their good insulation properties but also because of their good strength, high rigidity and machinability. Sheet, tubular and moulded laminates are all employed.

Cotton fabric laminates are used in the manufacture of gear wheels which are quiet running and which withstand shock loading. Since the laminates have a lower strength than steel, gear wheels made from them should be used at lower working stresses and designed with a greater face width for load transmission as compared with a similar gear made from steel. Water-lubricated bearings from phenolic–cotton or phenolic–asbestos laminates are used as bearings for steel rolling mills called to sustain bearing loads as high as 3000 lbf/in² (21 MPa).

Although phenolic resins are too dark for use in the surface layers of decorative laminates these resins are employed in impregnating the core paper. In these cases a melamine–formaldehyde resin is used for impregnating the top decorative layer. Phenolic laminates have also been used in aircraft construction and in chemical plant.

23.7 MISCELLANEOUS APPLICATIONS

Although the two most well-known applications of phenolic resins are in mouldings and laminates they are also used in a very large number of other applications. At one time *cast phenolic resins*⁸ were also an important class of plastics materials. These are made by reacting 1 mole of phenol with about 2.25 moles of formaldehyde using an alkaline catalyst. The reaction is carried out for 3 hours at 70°C to produce a resinous material which remains soluble in the water present. To prevent the reaction going to completion in the reaction vessel the alkali present is neutralised by lactic acid or phthalic acid. The large quantity of water present (from the formalin solution and a small amount of water of condensation) is then removed by vacuum distillation, during which time the polymerisation reaction continues rather more slowly under the acidic conditions (pH~4–5). Plasticisers and dyestuffs are usually incorporated before vacuum distillation. When the resin water content has reached the minimum possible consistent with pourability, the resin is cast into moulds. The resin is then hardened by heating for 3–10 days at 70–85°C. During cure, water is liberated and this is trapped in small droplets within the resin. The lower the amount of water present at the casting stage and the lower the phenol–formaldehyde ratio the smaller the droplets. Where reagents such as glycerol are incorporated into the resin, the droplets become smaller than the wavelength of visible light and the product becomes transparent.

The selection of the phenol-formaldehyde ratio of about 1:2.25 is a compromise in balancing mechanical properties (for which phenol–formaldehyde ratios of about 1:2.5 are most suitable) and curing rates (for which the optimum phenol–formaldehyde ratio is about 1:1.75). The use of a pH of 4–5 during distillation and hardening leads to a hardening rate sufficiently slow for the distillation of the water to be carried out without gelling in the reaction vessel, but not such that final hardening takes an infinitely slow time. Even so cure times are very long. It is not desirable to exceed cure temperatures of 75–80°C as this would lead to vaporisation of occluded water with subsequent void formation and blistering. Cast phenolic resins have been used for umbrella handles, knobs, propelling pencil bodies and for other purposes where attractive appearance is of importance. The advent of cheaper thermoplastics since World War II, has, however, largely ousted the cast resins from such outlets and they are thus today of negligible importance.

There has been some interest in *phenolic resin foams* during recent years but these have yet to achieve large-scale usage. They could, however, become important in the event of legislation restricting the use of polyurethanes. These foams are self-extinguishing but currently more expensive to produce than the well-established expanded polystyrene. For good control of properties mechanical mixing devices, similar to those employed with polyurethanes, are used. A resin is first blended with the foaming agent such as sodium bicarbonate. The mixture is then stirred rapidly with an acid hardener such as *p*-toluene sulphonic acid and the product metered into a trough. An exothermic resin-hardening reaction takes place, generating sufficient heat to decompose the blowing agent and foam the product. Other ingredients may be included to control pore structure and density. By varying the formulations a range of foams may be produced with densities varying from about 0.015 to 0.32 g/cm³. The foaming times vary from only a few seconds for the very low density foams to 5–10 minutes for the higher density products.

A structural grade of foam has a thermal conductivity of $0.28 \text{ Btu in ft}^{-2} \text{ h}^{-1} \text{ }^\circ\text{F}^{-1}$ (0.040 W/m K) as measured by BS874: 1956, a figure which is of the same order as that for established thermal insulating materials. The foams may be classed as self-extinguishing but in a sustained flame they char and the surface is slowly eroded by the hot gases.¹¹ The foams may be made either as large blocks which can be subsequently sliced or alternatively foaming may be carried out *in situ*, for example between cavity walls of a building.

Somewhat intermediate in nature between the moulded powders and the laminates are the *fibre-resin preform mouldings*. These are produced by making a resin-containing fibre preform, usually of the same shape as the finished moulding, and then subjecting the preform to a consolidating pressure in a compression mould. There are two principal variants of the process, the impregnation process and the beater process. In the impregnation process the selected fibre, normally of the cellulosic type and typically based on wood pulp, is fed with water to a beating or pulping machine of the type commonly used in paper making. After beating, the resulting slurry is fed to a stock tank where it is diluted with water from which it may be fed to the felting vat as required. A perforated metal felting tool is then lowered into the vat and by the application of a vacuum the pulp is deposited on to the screen. The amount deposited will depend on the degree of beating, the pulp consistency, the felting time and the degree of suction applied. The resultant felt is then presqueezed and transferred to a drying oven. The dried felt is then impregnated with a solution of resin, the solvent is evaporated and the preform may be moulded at pressures of about $500\text{--}800 \text{ lbf/in}^2$ ($3.5\text{--}5.5 \text{ MPa}$) at the usual moulding temperatures employed with phenolic resins. In the alternative beater process the resin, which can be in the form of an emulsion, dispersion, or solution, is added to the fibre at the beater stage. A preform is then made from the slurry, dried and moulded. The beater process is generally the more versatile and normally leads to products of greater impact strength.

Pulp-resin preform mouldings have the merits of light weight, low cost and good strength (see *Table 23.4*). They do, however, have a high water absorption and because of the limitations of the felting process are generally restricted to products of constant cross-section.

Table 23.4 Some physical properties of fibre-resin preform sheet¹²

Tensile strength	14 000–18 000 lbf/in ² (97–124 MPa)
Impact strength	1.5–3.0 ft lbf on $\frac{1}{2}$ in. notched Izod (2–4 J)
Shear strength	9000–15 000 lbf/in ² (62–103 MPa)
Bending strength	15 000–19 000 lbf/in ² (103–131 MPa)
Water absorption (24 h immersion)	1–10%

Preform mouldings are particularly useful in carrying containers and protective covers. Examples of their use include television receiver backs, moulded suitcases and typewriter cases. Although the finish obtained during moulding is frequently adequate in industrial applications some improvement is necessary where a good appearance is desired. Methods used include painting or

vacuum forming a thermoplastics sheet material over the outside of a moulded preform which has been coated with a suitable adhesive.

Phenolic resins are useful surface coating materials. Resols are useful for stoving lacquers for coating chemical plant, textile equipment, razor blades, brassware and food cans. Phenolic resins are used with poly(vinyl formal) as a flexible, tough and solvent-resistant wire enamel. Oil-soluble resins based on synthetic phenols form the basis of some gloss paints.

A variety of adhesives based on phenolic resins are available. These include metal cements made by combining a resol with a vinyl polymer such as poly(vinyl formal). Resols are also used for plywood glues, which may be cured using alkaline catalysts at 135°C. If resorcinol and/or paraformaldehyde are included in the formulation, slightly lower curing temperatures may be used. These glues have good resistance to aging, moisture and bacteria. Highly-filled novolak-hexa compositions form the basis of lamp capping cements.

Impregnated wood products are used in pattern making for foundry use and as stretching blocks and other similar tooling applications in the aircraft industry. These may be made by bonding wood veneers with a phenolic glue at sufficiently high pressures so that there is some impregnation of the adhesive into the wood. An alternative approach which gives a denser product is to immerse wood veneers in a resol solution under pressure. The impregnated veneers are then dried and plied together in a press. In this process the resin content of the impregnated wood may reach as high as 40%.

During the past four decades phenolic resins have become of increased significance in rubber compounding. For example, the resin based on cashew nut shell liquid, which contains phenolic bodies such as anacardic acid (*Figure 23.23*), may, when blended with hexamine, be incorporated into nitrile rubber (butadiene-acrylonitrile rubber).

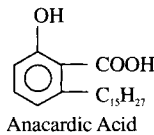


Figure 23.23

The resins act as a plasticiser during processing but they cross-link while the rubber is vulcanising to give a harder product with improved oxidation resistance, oil resistance and tensile strength. The addition of sufficient resin will lead to an ebonite-like product.

Similar products from natural rubber may be made by fluxing a cresol novolak containing hexamine with the rubber at 150°C.

In many applications the phenolic resins function primarily as binders, this being to some extent their purpose in moulding compositions, laminates and fibre-resin preform mouldings. Further examples of this function are found in brake linings, grinding wheels and flexible abrasives, resin pulp board and wallboard, sand core bonding and shell moulds for metal castings. The resins are also used in binding glass-fibre thermal insulation and in the manufacture of waste-wood board.

Other uses include impregnation of wood to improve dimensional stability and reduce water absorption, sealing of porous metal castings by impregnation, and coil impregnation, to give a rigid structure both heat and water resistant.

23.8 RESORCINOL-FORMALDEHYDE ADHESIVES

Resorcinol (1,3-dihydroxybenzene) is more reactive to formaldehyde than phenol itself, the two hydroxyl groups reinforcing each other in activating the *o*- and *p*-positions. This allows faster reactions to occur than with phenol, when compared at the same temperature, and under appropriate conditions curing can occur at normal room temperatures.

Reaction rates are at a minimum at pH 3, and, unlike with the phenol-formaldehyde condensates, which have a minimum at pH 7, setting can occur under neutral conditions.

In commercial practice resorcinol is seldom used on its own but in conjunction with phenol when condensing with formaldehyde. Such a material is Aerodux 185, introduced by Aero Research Ltd (now part of Ciba-Geigy) in 1944.

Resorcinol-formaldehyde (RF) resins do not find use in conventional plastics applications but as reactive adhesives. Their major use is in the manufacture of glued timber structures, where the ability to harden the polymer under neutral conditions (i.e. under non-acid conditions which thus does not damage the wood) and, if desired, at room temperature is a particular advantage. The bonds are very durable and 'weatherproof' and, like PF's, are resistant to insects, fungi and other micro-organisms. They also have a long storage life. Their main limitations are their cost and their naturally dark red colour, although this can on occasion be used to some effect decoratively.

The adhesive resins are of the novolak type and generally hardened by paraformaldehyde (which may be supplied mixed with coconut shell flour or diatomaceous earth) in conjunction with an accelerator such as magnesium oxide.

23.9 FRIEDEL-CRAFTS AND RELATED POLYMERS

For many years there has been a demand for rigid plastics materials which could withstand temperatures of 250°C and at the same time have good oxidation and water resistance coupled with ease of processability and reasonable cost. Such a demand led in the late 1960s to the small-scale production of a number of polymers which could be considered as being intermediate between polyphenylene, *Figure 23.24*, and the commercial phenolic resins.

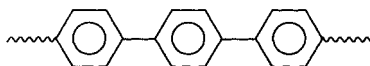


Figure 23.24

Polyphenylene is normally a brittle material (see also Chapter 21). In order to obtain useful polymers it is necessary to space the rings with ether, sulphide or methylene links to make the structure less brittle. It is also essential to be able to control the reactions so as to have available intermediates which can be processed by conventional means.

One approach by Monsanto (described in the basic patent BP 1037111) is to prepare a modified polyphenylene by reacting an aromatic sulphonyl halide such as benzene-1,3-disulphonyl dichloride with an aromatic compound having replaceable nuclear hydrogen (e.g. bisphenoxybenzene, sexiphenyl and diphenyl ether). This was discussed in Chapter 21.

Alternative approaches using Friedel–Crafts catalysts were developed independently by Phillips¹³ and Harris¹⁴ at about the same time as the Monsanto developments.

The Phillips¹³ approach involved the reaction of aryl halides with aromatic nuclei in the presence of Friedel–Crafts catalysts. Whilst many variations in the process existed three main cases were distinguishable.

- (1) Self-condensation of a monochloromethyl compound such as benzyl chloride (*Figure 23.25*).
- (2) Bifunctional reactions of two ‘monomeric’ intermediates (*Figure 23.26*).
- (3) Cross-linking of a prepolymer (*Figure 23.27*).

The Harris technique used alkaryl ethers instead of halides as illustrated in *Figure 23.28* by reaction of α,α' -dimethoxy-*p*-xylene and naphthalene.

This approach, splitting off alcohols instead of hydrogen chloride, has the advantage of being less exothermic and more easily controlled. Such materials, in spite of the use of FeCl_3 instead of SnCl_4 to effect final cross-linking, were still slow curing and were mechanically weak at elevated temperatures. This led to the introduction by Albright and Wilson of Xylok resins based on the reaction of alkaryl halides of ethers with phenols. In 1980 Albright and Wilson signed an agreement with Advanced Resins allowing the latter company to manufacture and sell Xylok resins. These materials are structurally intermediate between phenolic resins and polyphenylenes and like the former may be cross-linked by hexamethylene tetramine. A typical mechanism is given in *Figure 23.29*.

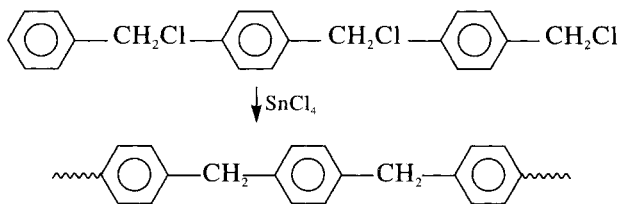


Figure 23.25

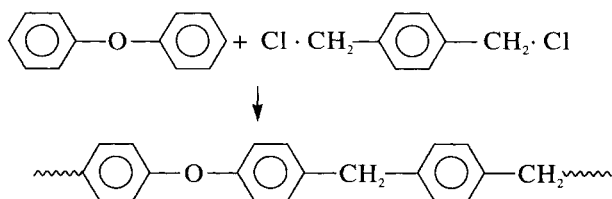


Figure 23.26

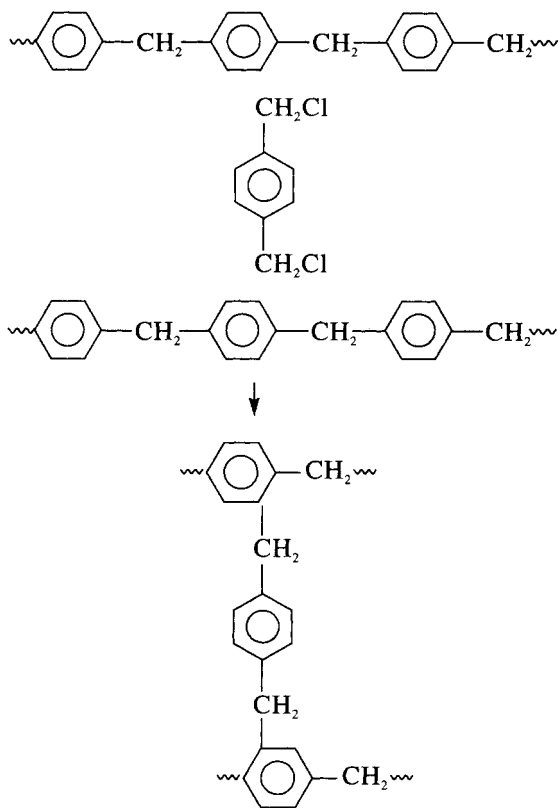


Figure 23.27

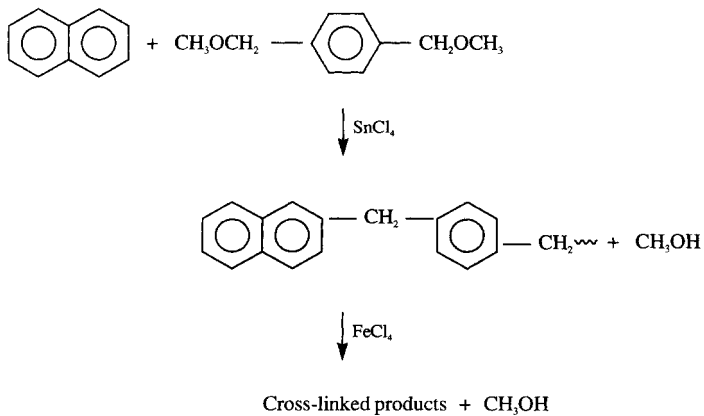


Figure 23.28

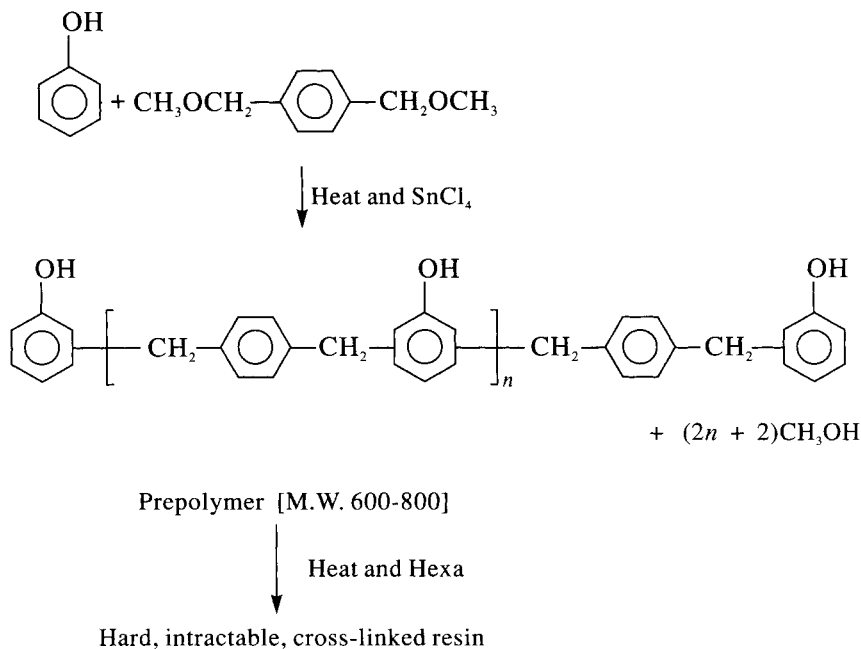


Figure 23.29

The resins are substantially more expensive than general purpose phenolic resins and are therefore special purpose resins which are of interest for the following reasons:

- (1) Resistance to deformation and degradation at temperatures of the order of 250°C unmatched by any other polymer of comparable rigidity and toughness.
- (2) Good chemical resistance.
- (3) High electric strength.
- (4) Low temperature dependence of power factor and dielectric constant and with lower absolute values than observed for phenolic resins.
- (5) Good flame resistance, low smoke generation and good ablative characteristics.

Composite laminates in conjunction with glass and asbestos fibres find some commercial application whilst those with carbon fibre are being widely evaluated. Current applications are said to include barrier, spacing and stacking functions in high-voltage transformers, blades for rotary compressors, and brake pads. Amongst areas being explored are aircraft applications using carbon and other high-modulus fibres, extended life lamp capping cements and grinding wheel resins. Moulding powders with flow and cure characteristics similar to those of general purpose phenolics and with a useful life at 250°C have also been prepared.

Polymer systems are now available which may be cured by reaction of epoxy resin compounds with the phenolic hydroxyl groups. Such reactions do not evolve volatile by-products. These materials are showing promise in the area of heat-resisting electrical insulation laminates.

23.10 PHENOLIC RESIN FIBRES

The commercial appearance of phenolic resins fibres in 1969 is, at first consideration, one of the more unlikelier developments in polymer technology. By their very nature the phenolic resins are amorphous whilst the capability of crystallisation is commonly taken as a prerequisite of an organic polymer. Crystallisability is not, however, essential with all fibres. Glass fibre, carbon fibre and even polyacrylonitrile fibres do not show conventional crystallinity. Strength is obtained via other mechanisms. In the case of phenolic resins it is obtained by cross-linking.

The PF fibres are produced by melt spinning a novolak resin of molecular weight ca 1000 and then cross-linking the molecules by exposure to gaseous formaldehyde at 100–150°C for 6–8 h or with a formaldehyde solution. The fibres were introduced under the tradename Kynol by American Kynol Inc., a subsidiary of Carborundum AG.

Whilst the original fibres are yellow, acetylation of the phenolic hydroxyl groups gives white fibres. The limiting oxygen index is 36%. The fibres therefore do not burn but only char in a flame. They have been offered for such uses as flame-resistant blankets and occupational clothing. They do, however, have rather poor abrasion resistance, which can be improved by blending with other fibres, including aromatic polyimides such as Nomex.

23.11 POLYBENZOXAZINES

The polybenzoxazines (PBZs) provide a new class of phenolic resins that were first described by Ishida in 1998 (Ref. 15). Synthesis of the resins involves three components; a phenol, a primary amine and formaldehyde. The first stage involves the formation of a multifunctional benzoxazine monomer (*Figure 23.30(a)*). The monomer can then be ring-opened at elevated temperatures (160–220°C) to yield a polymeric structure (*Figure 23.30(b)*).

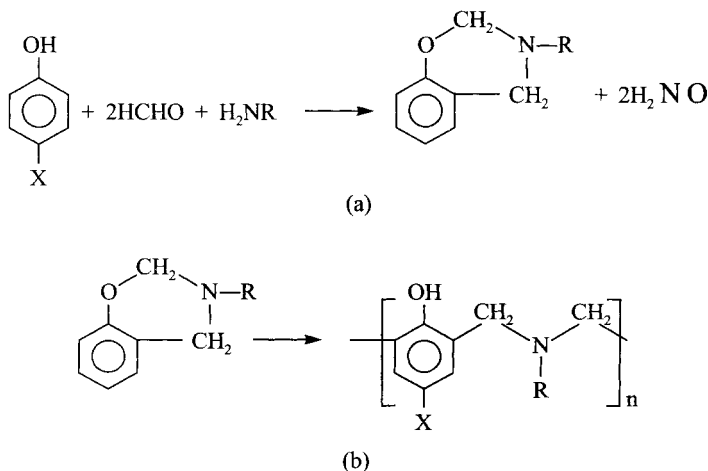


Figure 23.30 Polybenzoxazine resin

Clearly a wide range of phenols and amines are possible. Where appropriate multi-ringed phenols are used such as 4,4-dihydroxybenzophenone or bisphenol A then three-dimensional cross-linked polymers will be obtained. Amines may be aliphatic such as methylamine or aromatic such as aniline.

Since there are no condensation products in the polymerisation stage and because of the somewhat open network structure moulding shrinkage is negligible. At the same time the thermal coefficients of expansion may be less than those of epoxide resins (see Chapter 26). The rigid structure, particularly of polymers based on 4,4-dihydroxybenzophenone, is claimed to yield glass transition temperatures as high as 340°C while thermogravimetric studies suggest that the polymer is thermally stable to temperatures in excess of 400°C. Initial studies suggest that some polybenzoxazines could compete with polyimides and polyetherimides in a number of applications and it is stated that several companies are budgeting for pilot production of these materials.

References

1. KAUFMAN, M., *The First Century of Plastics*, The Plastics Institute, London (1963)
2. WHITEHOUSE, A. A. K., PRITCHETT, E. G. K., and BARNETT, G., *Phenolic Resins*, Iliffe, London (1967)
3. ROBITSCHKEK, P., and LEWIN, A., *Phenolic Resins*, Iliffe, London (1950)
4. MARTIN, R. W., *The Chemistry of Phenolic Resins*, John Wiley, New York (1956)
5. MEGSON, N. J. L., *Phenolic Resin Chemistry*, Butterworth, London (1958)
6. CARSWELL, T. S., *Phenoplasts*, Interscience, New York (1947)
7. HULTZSCH, K., *Chemie der Phenolharze*, Springer-Verlag, Berlin (1950)
8. APLEY, M., *Trans. Plast. Inst., Lond.*, **20**, 7 (1952)
9. BROWN, W. J., *Laminated Plastics*, Plastics Institute Monograph No. E4, London (1961)
10. PEPPER, K. W., and BARWELL, F. T., *J. Soc. Chem. Ind.*, **63**, 150 (1944)
11. MITCHELL, R. G. B., and SMITH, D., *Plastics (London)*, **24**, 224 (1960)
12. LEWIN, A., *Trans. Plast. Inst., Lond.*, **28**, 224 (1960)
13. PHILLIPS, L. N., *Trans. P.I.*, **32**, 298 (1964)
14. HARRIS, G. I., *Br. Polym. J.*, **2**, 270 (1970)
15. ISHIDA, A. I., *Modern Plastics International* 87 (June 1998)

Bibliography

- APLEY, M., *Cast Resins*, Plastics Institute Monograph No. 4A, London (1946)
- BROWN, W. J., *Fabric Reinforced Plastics*, Cleaver-Hume Press, London (1947)
- BROWN, W. J. *Laminated Plastics*, Plastics Institute Monograph No. E4, London (1961)
- CARSWELL, T. S., *Phenoplasts*, Interscience, New York (1947)
- DUFFIN, D. J., *Laminated Plastics*, Reinhold, New York (1958)
- GOULD, D. E., *Phenolic Resins*, Reinhold New York (1959)
- HULTZSCH, K., *Chemie der Phenolharze*, Springer-Verlag, Berlin (1950)
- KAUFMAN, M., *The First Century of Plastics*, The Plastics Institute, London (1963)
- LEARMONTH, G. S., *Laminated Plastics*, Leonard Hill, London (1951)
- MARTIN, R. W., *The Chemistry of Phenolic Resins*, John Wiley, New York (1956)
- MEGSON, N. J. L., *Phenolic Resin Chemistry*, Butterworth, London (1958)
- ROBITSCHKEK, P., and LEWIN, A., *Phenolic Resins*, Iliffe, London (1950)
- SORREL, S. E., *Paper Base Laminates*, Cleaver-Hume Press, London (1950)
- WHITEHOUSE, A. A. K., PRITCHETT, E. G. K., and BARNETT, G., *Phenolic Resins*, Iliffe, London (1967)

Reviews

- BOLLIG, F. J., and DECKER, K. H., *Kunststoffe*, **70**, 672–8 (1980)
- BOLLIG, F. J., GARDZIELLA, A., and MÜLLER, R., *Kunststoffe*, **70**, 679–83 (1980)
- GARDZIELLA, A., *Kunststoffe*, **86**, 1566–78 (1996)

Aminoplastics

24.1 INTRODUCTION

The term aminoplastics has been coined to cover a range of resinous polymers produced by interaction of amines or amides with aldehydes. Of the various polymers of this type that have been produced there are two of current commercial importance in the field of plastics, the urea-formaldehyde and the melamine-formaldehyde resins. There has in the past also been some commercial interest in aniline-formaldehyde resins and in systems containing thiourea but today these are of little or no importance. Melamine-phenol-formaldehyde resins have also been introduced for use in moulding powders, and benzoguanamine-based resins are used for surface coating applications.

Interest in aminoplastics dates from the publication of a patent by John in 1918¹ which disclosed resinous materials prepared by heating urea with commercial formalin and which suggested the use of the resultant viscous solutions as adhesives and as impregnants for fabrics. In the following years patents were taken out by Pollak and Ripper,² and Goldschmidt and Neuss,³ the former pair directing their efforts towards the manufacture of an 'organic glass', the latter group towards moulding compositions. In 1926, as a result of work by E. C. Rossiter, moulding powders based on urea-thiourea-formaldehyde were marketed under the trade name Beetle by The British Cyanides Co. Ltd (later known as British Industrial Plastics Ltd). Similar products were subsequently produced in other countries.

During the next 15 years the urea resins were also developed for use as adhesives, as textile finishing agents and in the production of surface coatings and wet-strength paper. Since World War II the development of chipboard has resulted in a large new outlet for urea-based resins which have also found other uses, such as in firelighters and foams.

In 1935 Henkel⁴ patented the production of resins based on melamine. Today these resins are important in the manufacture of decorative laminates and in tableware.

The development of the aminoplastics has been described in two interesting reviews.^{5,6}

By the mid-1990s world production of aminoplastics was estimated at about 6 000 000 t.p.a. of which more than 5 000 000 t.p.a. were urea-formaldehyde resins. The bulk of the rest were melamine-formaldehyde. Such bald statistics, however, disguise the fact that a considerable amount of aminoplastics used are actually co-condensates of urea, melamine and formaldehyde.

By far the bulk of amino resins are used in the woodworking industry for the manufacture of chipboard, plywood and as general glues and adhesives. Melamine-formaldehyde is an important component of decorative laminates. The amount of amino resins used for moulding applications is only of the order of 5% of the total.

24.2 UREA-FORMALDEHYDE RESINS

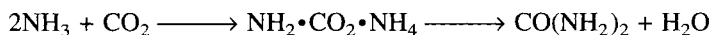
Of the various amino-resins that have been prepared, the urea-formaldehyde (U-F) resins are by far the most important commercially. Like the phenolic resins, they are, in the finished product, cross-linked (thermoset) insoluble, infusible materials. For application, a low molecular weight product or resin is first produced and this is then cross-linked only at the end of the fabrication process.

In a general comparison with phenolic resins, the U-F materials are cheaper, light in colour, are lacking in odour, have better resistance to electrical tracking but have an inferior heat resistance and a higher water absorption.

24.2.1 Raw materials

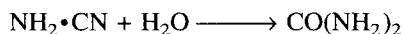
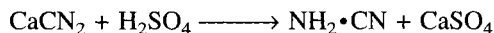
Urea is a white crystalline compound with a melting point of 132.6°C and is highly soluble in water. It is substantially cheaper than the other intermediate (formaldehyde) used in the resin preparations.

Urea is prepared commercially by the reaction of liquid carbon dioxide and ammonia in silver-lined autoclaves, at temperatures in the range 135–195°C and pressure of 70–230 atm. The reaction proceeds by way of ammonium carbamate:



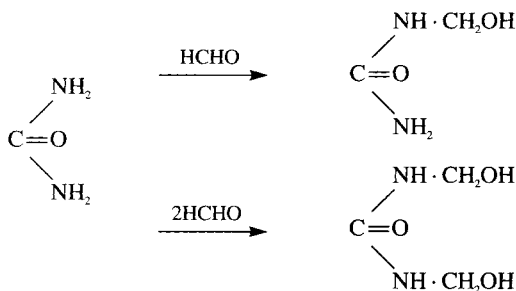
A 40–60% conversion per pass is achieved and unreacted feedstock are returned to the compressors.

Urea has been obtained from calcium cyanamide via cyanamide:



This route is now obsolescent.

The method for producing formaldehyde was described in Chapter 19. In aminoplastics manufacture it is used in the form of formalin (36–37% w/w CH_2O). As in the case of phenolic resin production, formalin with both high and low methanol content is used according to the needs of the manufacturer. The low methanol content formalin is more reactive but is also less stable and must be used soon after its preparation. For this reason some resin manufacturers prefer to use formalin with a high 7–10% methanol content.

*Figure 24.1*

24.2.2 Theories of Resinification

Urea-formaldehyde resins are usually prepared by a two-stage reaction. The first stage involves the reaction of urea and formaldehyde under neutral or mildly alkaline conditions, leading to the production of mono and dimethylol ureas (*Figure 24.1*). The ratio of mono to dimethylol compounds will depend on the urea-to-formaldehyde ratio and it is important that there should be enough formaldehyde to allow some dimethylol urea formation.

If the product of the first stage, which in practice usually also contains unreacted urea and formaldehyde, is then subjected to acid conditions at elevated temperatures the following sequence of events is observed during the second stage:

- (1) A solution is produced from which, if cooled, a white precipitate would be obtained.
- (2) As heating proceeds, the temperature at which precipitation occurs drops progressively until a stage is reached when the condensation products remain in solution at room temperature.
- (3) With further heating there is an increase in viscosity and the syrup sets to an insoluble and irreversible gel which eventually converts, with the evolution of water and formaldehyde to a hard, colourless, transparent and infusible mass.

For technical purposes it is often convenient to both arrest the reaction prior to gelation by changing to a slightly alkaline pH and to remove some if not all of the water. The first hardening reaction may then be carried out when desired by changing once again to an acid pH.

The precise mechanisms involved during the second stage are not fully understood although a number of theories have been proposed, for example by Brookes,⁷ Kadowaki,⁸ Marvel,⁹ Redfarn,¹⁰ Thurston,¹¹ de Jong and de Jonge,¹² and Zigeuner.¹³

The subject has been extensively reviewed by Vale and Taylor¹⁴, who place particular emphasis on the work described in references 12 and 13.

With the present state of knowledge it appears that in the first part of the second-stage methylol ureas condense with each other by reaction of an $\sim\text{CH}_2\text{OH}$ group of one molecule with an $\sim\text{NH}_2$ group of another (*Figure 24.2*).

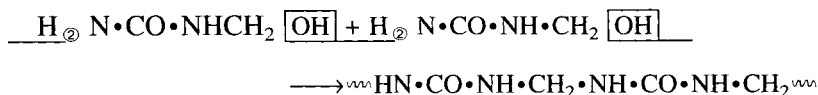


Figure 24.2

Since NH groups (as found in dimethylol urea) are apparently less reactive the initial reaction products appear to be based on linear polymers of the form



These probably form the basis of the amorphous precipitates formed on cooling. The more soluble resins produced on continuation of the reaction probably contain pendant methylol groups formed by reactions of the NH groups with free formaldehyde (Figure 24.3 I).

These methylol groups and the methylol groups on the chain ends of the initial reaction product can then react with other methylol groups to give either linkages or with amine groups to give methylene linkages. Furthermore the ether linkages on heating may break down to methylene linkages with the evolution of formaldehyde (Figure 24.3 II and III).

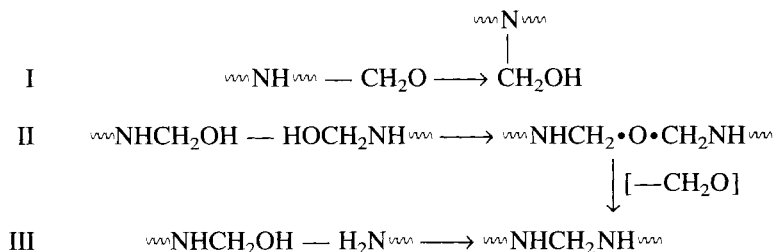


Figure 24.3

When reactions II and III occur on average more than twice per molecule the resin gels, and cross-linking may be considered to have occurred.

24.2.3 U-F Moulding Materials

Thermosetting compositions based on urea-formaldehyde are widely employed because of their low cost, wide colour range, rigidity and good electrical properties.

Manufacture

A moulding powder based on urea-formaldehyde will contain a number of ingredients. Those most commonly employed include the following:

- (1) Resin.
- (2) Filler.
- (3) Pigment.
- (4) Hardener (more commonly referred to as an accelerator).
- (5) Stabiliser.

- (6) Plasticiser.
- (7) Lubricant.

The first stage of resin preparation is to dissolve urea into the 36% w/w formalin which has been adjusted to a pH of 8 with caustic soda. Since formaldehyde interferes with normal functioning of universal indicator a pH meter is used when making pH adjustments. The blending may be carried out without heating in a glass-lined or stainless-steel reactor for about 90 minutes. In an alternative process the blending is carried out at about 40°C for 30 minutes. In some cases the pH, which may drop during reaction, is adjusted by addition of small quantities of hexamine. The urea-formaldehyde ratios normally employed are in the range 1:1.3 to 1:1.5. Only a small amount of reaction occurs in the first stage so that the solution at the end of this process contains urea, formaldehyde, and mono- and demethylol urea, the latter in insufficient concentration at this stage to separate out.

Only a limited range of fillers is used commercially with U-F resins. Bleached wood pulp is employed for the widest range of bright colours and in slightly translucent mouldings. Woodflour, which is significantly cheaper, may also be used. Unpigmented, this gives mouldings brown in colour and somewhat translucent in thin sections. To mask the brown colour heavy pigmentation is commonly employed and this results in opaque mouldings. For mouldings of enhanced translucency, chopped regenerated cellulose (Cellophane) film, which is free from voids and has a refractive index (1.565) close to that of the resin (1.55–1.56) can be incorporated. Fabric fillers and minerals fillers and not commonly employed with U-F resins.

A wide variety of pigments is now used in U-F moulding compositions. Their principal requirements are that they should not affect the stability of moulding characteristics of the power, that they should be stable to processing conditions, be unaffected by conditions of service, including insolubility in any solvents with which the mouldings might come into contact, be light fast, and not interfere with the electrical properties.

In order to obtain a sufficient rate of cure at moulding temperatures it is usual to add about 0.2–2.0% of a 'hardener' (accelerator). This functions by decomposing at moulding temperatures to give an acidic body that will accelerate the cure rate. A very large number of such latent acid catalysts have been described in the literature, of which some of the more prominent are ammonium sulphamate, ammonium phenoxyacetate, ethylene sulphite and trimethyl phosphate.

Urea-formaldehyde powders have a limited shelf-life but some improvement is made by incorporating a stabiliser such as hexamine into the moulding power. In some formulations the cure rate and the related time for flow are controlled by keeping the latent acid catalyst fixed and adjusting the stabiliser.

Plasticisers are used in special grades of moulding powders. Their main virtue is that they enable more highly condensed resins to be used and thus reduce curing shrinkage whilst maintaining good flow properties. Glyceryl α -tolyl ether (monocresyl glycidyl ether) is often used for this purpose. Plasticisers may also be used in small quantities to improve the flow of other grades.

Metal stearates such as zinc, magnesium or aluminium stearates are commonly used as lubricants at about 1% concentration. Other materials that have been used successfully include oxidised paraffin wax and sulphonated castor oil.

In typical manufacturing processes the freshly prepared urea-formaldehyde initial reaction product is mixed with the filler (usually with a dry weight

resin-filler ratio of about 2:1) and other ingredients except pigment in a trough mixer. This process, which takes about two hours at 60°C, enables thorough impregnation of the wet base with the resin solution and also advances the resinification reaction. After a check has been made that it is slightly alkaline the resulting wet base is then fed to a drier which may be either of the turbine or rotary type. The turbine drier consists of a number of slowly rotating circular trays stacked one above the other in a large oven. Each of the trays has a number of radial slits. The powder is fed to the top tray where it rests for one revolution when, by means of scraper blades, it is pushed through the slits on the second tray, where the process is repeated. In a typical process the residence time of the mixture in the drier is about two hours at 100°C. In an alternative process the wet base is fed into a rotary drier in which it remains for about $\frac{3}{4}$ -1 hour whilst being subjected to counterblast air at 120-130°C. This process reduces the water content from about 40% to about 6% and also advances the condensation.

On emerging from the drier the base is hammer-milled and then ball-milled for 6-9 hours. The pigments are added at the ball-mill stage. During this process samples are taken and checked for colour and processing characteristics. It is frequently necessary to make slight adjustments to the formulation by adding further pigment or other ingredients at this stage. The ball-milling process ensures a good dispersion of pigment and gives a fine powder that will produce mouldings of excellent finish. On the other hand the powder has a high bulk factor and problems of air and gas trappings will occur during moulding. These problems are overcome by densifying the product.

One method of densification is to heat the powder as it passes along a belt and to drop the heated powder into the nip of a two-roll mill. In this process the material passes directly through the rolls to form a strip which is then hammer-milled to give powder which is in the form of tiny flat flakes. In another process the fine powder is slowly stirred in a large pot and water, or a water-methanol blend, or steam, run into the mixture. The particles partly cohere in a damp conditions and on subsequent drying give densified granules. A third process is to charge the powder into an internal mixer which is at a temperature about 100°C. The particles cohere and after about two minutes the batch is fed to a hammermill to give a coarse granule. More recent processes involve the use of continuous compounders, such as the Buss Ko-Kneader.

As an alternative to the wet process described above, moulding compositions may be made by mixing a powdered resin or a methylol derivative with other ingredients on a two-roll mill or in an internal mixer. The condensation reaction proceeds during this process and when deemed sufficiently advanced, the composition is sheeted off and disintegrated to the desired particle size. This dry process is not known to be used in any current commercial operation.

Control tests on the moulding powder include measurement of water content, flow, powder density and rate of cure.

From the above discussion it will be recognised that in addition to differences in colour, commercial urea-formaldehyde moulding powders may differ in the following respects:

- (1) The nature of the filler used.
- (2) The ease of flow (dependent on the degree of heating during the drying stages, and in some cases on the heating operations associated with densifying).

- (3) The speed of cure, partly related to the ease of flow but associated with the amounts of hardener and stabiliser.
- (4) The type of grind.
- (5) The presence of absence of plasticiser.

It is these differences which determine the range of grades at present commercially available.

Processing

Urea-formaldehyde moulding powders may be moulded without difficulty on conventional compression and transfer moulding equipment. The powders, however, have limited storage life. They should thus be stored in a cool place and, where possible, used within a few months of manufacture.

Moulding temperatures in the range 125–160°C are employed. The low temperatures are used with thick sections and the high temperatures for thin sections. Mouldings may easily be over-cured by moulding for too long and/or at too high a temperature and this is made manifest by blistering, bleaching and a distinct fishy smell. Compression moulding pressures recommended range from 1 to 4 'ton/in² (15–60 MPa), the higher pressures being usually employed for deep draw articles. The cure time will depend on the thickness of the moulding and on the mould temperature. Using a typical powder, an $\frac{1}{8}$ in thick moulding will require about 55 seconds cure time at 145°C. Much shorter times (~10–20 seconds) are now employed industrially for such articles as bottle caps (which have a section thickness somewhat less than $\frac{1}{8}$ in), which are moulded at the higher end of the moulding temperature range. The amount of cure carried out should depend on the properties required of the moulding and on the economics of the process. It has been shown¹⁵ that for the best balance of mechanical and electrical properties the degree of cure required coincides with that giving the best water resistance. Thus in practice a moulding is deemed properly cured if, sawn through its thickest section, it is unaffected in appearance, or cannot be scratched with a fingernail, after 10 minutes immersion in boiling water.

Preheating techniques are commonly employed since these lead to shorter cures, easier flow and generally better products. The high power factor of the material enables high-frequency preheaters to be used successfully. It is also frequently advantageous to pellet the powders as in the case of phenolics.

Urea-formaldehyde moulding powders may be transfer moulded. Pressures of 4–10 ton/in² (60–150 MPa), calculated on the area of the transfer pot, are generally recommended.

As in the case of the phenolics, the advent of the in-line screw injection moulding machine for thermoplastics led to its adaptation in the late 1960s for urea-formaldehyde moulding powders. Compared with compression and transfer moulding faster cycle times are possible, there is no need for pelleting and preheating and the process is more readily adaptable to automation. However, because the basic machine costs are high the economies of changing from compression to injection moulding are complex and at the present time compression moulding is still by far the most important process in terms of tonnage handled.

Conventional U-F moulding powders originally formulated for compression moulding are often satisfactory but special injection grades have been developed. Ideally the moulding material should have good flow characteristics between 70

and 150°C, be unaffected by long residence times in the barrel but should be capable of almost instant cure in the moulded cavity, at least once the cavity has been filled.

In practice barrel temperatures of 75–100°C are commonly employed using a grade which is capable of flow in this range. Fast cures in the mould cavity are achieved by using mould temperatures in the range 130–150°C and by a controlled amount of frictional heat being generated in the nozzle and to some extent sprues, runners and gates. This frictional heat will be determined by injection pressure (ca 15 000–25 000 lbf/in²; 104–172 MPa), melt viscosity and nozzle dimensions.

Whilst the injection moulding process has now been widely accepted for phenolics the transition from compression moulding has been less extensive with U-F materials. The basic reason for this is that the U-F materials are more difficult to mould. This has been associated with filler orientation during moulding, which can lead to stress peaks in the finished product which the somewhat brittle resin is less able to withstand than can a phenolic resin.

In order to overcome such disadvantages the injection-compression process has been developed. A conventional compression press is coupled to a screw preplasticising unit which can deliver preheated and softened material direct to a compression mould cavity.

Properties and applications

When they were first introduced, the value of U-F moulding powders lay in their availability in a wide range of colours, at that time a novelty amongst thermosetting moulding composition. The wide colour range possible continues to be a reason for the widespread use of the material but other useful features have also become manifest.

The major desirable features of U-F mouldings are:

- (1) Low cost. The cheaper grades are sometimes lower in weight cost than the general purposes phenolics. (It is to be noted that U-Fs have a somewhat higher density).
- (2) Wide colour range.
- (3) They do not impart taste and odour to foodstuffs and beverages with which they come in contact.
- (4) Good electrical insulation properties with particularly good resistance to tracking.
- (5) Resistance to continuous heat up to a temperature of 70°C.

Some typical values of physical properties of mouldings from urea formaldehyde compositions are given in *Table 24.1*.

Recent estimates suggest that in the early 1990s about 43% of U-F moulding powders were used in electrical and electronic applications. The bulk of these applications were for plugs, sockets and switches, where the good electrical insulation properties at low frequencies, particularly the good tracking resistance, and low cost have led to dominance over P-Fs and maintained a competitive position with newer thermoplastics. Both alpha-cellulose and woodflour-filled grades have been used but the latter type now appears to be obsolescent. Statistics also indicate that about 27% of the market is for domestic applications such as pot and pan handles and tableware, but these figures may include usage

Table 24.1 Properties of mouldings prepared from urea–formaldehyde and melamine–formaldehyde mouldings compositions (Testing according to BS 2782)

Property	Units	Urea-formaldehyde				Melamine-formaldehyde			Melamine-phenolic	GP phenolic
		α -cellulose filled	Woodflour filled	Plasticised	Translucent	Cellulose filled	Glass filled	Mineral filled		
Specific gravity	—	1.5–1.6	1.5–1.6	1.5–1.6	~1.5	1.5–1.55	~2.0	~1.8	1.5–1.6	1.35
Tensile Strength	10^3 lbf/in ²	7.5–11.5	7.5–11.5	7–9.5	7–10	8–12	6–10	4–6	6–8	8
	MPa	52–80	52–80	48–66	48–69	55–83	41–69	28–41	41–55	55
Impact strength	ft/lbf	0.20–0.35	0.16–0.35	0.16–0.24	0.14–0.2	0.15–0.24	0.16–0.23	0.12–0.22	0.12–0.15	0.16
Cross-breaking strength	10^3 lbf/in ²	11–17	11–16.5	13.5–15.5	13–17	13–21	9–14	6–11	10–12	11.5
	MPa	76–117	76–114	93–107	89–117	89–144	62–96	41–76	69–83	80
Dielectric strength (90°C)	V/0.001 in	120–200	60–180	100–200	70–130	160–240	150–250	200–250	30–150	75–175
Volume resistivity	Ω m	10^{13} – 10^{15}	10^{13} – 10^{15}	10^{14} – 10^{15}	—	10^9 – 10^{10}	10^{15} – 10^{16}	10^{15} – 10^{16}	10^{11} – 10^{12}	10^{12} – 10^{13}
Water absorption										
24 h at 24°C	mg	50–130	40–170	50–90	50–100	10–50	10–20	7–14	—	—
30 min at 100°C	mg	180–460	250–600	300–450	300–600	40–110	20–35	15–40	—	—

of M-F materials (see Section 24.3). In the view of the author, the limited heat resistance, water resistance and stain resistance of U-F materials severely reduces their suitability for such domestic appliances, and they would not be a preferred choice. Another, more satisfactory, application area is in the sanitary sector, with nearly 20% of the market, for such uses as toilet seats and miscellaneous bathroom equipment.

At one time a major market was for bottle caps and closures, where the low cost, wide colour range and freedom from taste and odour were attractive features. This market has, however, been extensively eroded by the big tonnage thermoplastics, and it now accounts for less than 5% of U-F moulding powder consumption. Design changes have also led to a reduction in the use of U-Fs for applications such as hair-dryer housings and vacuum flask jugs and cups, which were well-known applications at one time. Because of their non-thermoplastic nature and resistance to detergents and dry-cleaning solvents, many buttons are made from U-F moulding powders. Imitation horn effects may be achieved by blending normal grades with grades of high translucency.

Miscellaneous uses include meat trays, toys, knobs, switches and lampshades, U-F lampshades are generally strictly utilitarian in design and of limited aesthetic appeal. It is important in this application to ensure adequate ventilation of the air space above the lamp in order to prevent overheating and subsequent cracking of the shade. For similar reasons fittings for ceiling light bowls, as often used in bathrooms and kitchens, may fail through lack of adequate ventilation.

U-F moulding materials are relatively much less important than they were 30 years ago. Western European production in 1991 was approximately 70 000 tonnes, slightly greater than P-F moulding material production. U-F resin used for this application is, however, probably less than 5% of total U-F resin production.

24.2.4 Adhesives and Related Uses

By far the bulk of U-F resins are used as adhesives for the particle board, plywood and furniture industries.

To prepare a suitable resin, formalin is first neutralised to a pH of 7.5 and urea is then dissolved into it (U-F molar ratio ~1:2). Sodium formate may be added as a buffer to regulate the pH. The mixture is boiled under reflux, typically for about 15 minutes, to give dimethylol urea and other low molecular weight products. The resins are then acidified to pH 4, conveniently with formic acid, and reacted for a further 5–20 minutes. The resulting resin is then stabilised by neutralising to a pH 7.5 with alkali to give a water-soluble resin with an approximately 50% solids content. When the resin is to be used in aqueous solution, as is normally the case, it is then partially dehydrated to give a 70% solids content by vacuum distillation. For some uses, for example for application in tropical countries, the resin is spray dried to ensure greater stability.

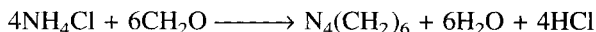
The finished product is checked for viscosity, solids content, pH value (which must be in the range of 7.3–7.5) and of its reactivity with a standard hardener.

Resins are commonly available with U-F molar ratios ranging from 1:1.05 to 1:2.2. Since formaldehyde is more expensive than urea the high F-U ratio resins are more expensive. They do, however, have greater clarity, the best water resistance, marginally superior mechanical properties, longer shelf life (up to two years) and greatest reactivity. The degree of condensation is quite important

since, if it was insufficient, the resin would be absorbed into the wood and would thus be unavailable to act as adhesive. Wood penetration by the adhesive may be reduced by incorporation into the latter of some rye or wood flour which at the same time improves adhesion spreading properties and reduces cost.

Concern over the unpleasant nature of excessive emissions of formaldehyde during processing has led to legislation and codes of practice in a number of countries which has led to reductions in the F–U ratio employed (e.g. Guidelines and Classifications for Control of Wood-based Materials introduced in Germany in 1994). For example, in chipboard glues the F–U ratio has been reduced to below 1.1:1 which has the effect of reducing the mechanical strength, reactivity and water resistance. This has led to partial substitution of urea with melamine which leads to adhesives superior in these respects. (For a further discussion on melamine–formaldehyde resins see Section 24.3.)

The resins are hardened by acidic conditions. Phosphoric acid, or more commonly ammonium chloride, an acid donor, is employed. The ammonium chloride functions by reaction with formaldehyde to give hydrochloric acid. Hexamine is also formed during this reaction.



About 1.5 parts ammonium chloride per 100 parts of the resin solution are generally used. The hardener is added as an aqueous solution.

At one time urea–formaldehyde was used extensively in the manufacture of plywood but the product is today less important than heretofore. For this purpose a resin (typically U–F molar ratio 1:1.8)–hardener mixture is coated on to wood veneers which are plied together and pressed at 95–110°C under pressure at 200–800 lbf/in² (1.38–5.52 MPa). U–F resin-bonded plywood is suitable for indoor application but is generally unsuitable for outdoor work where phenol–formaldehyde, resorcinol–formaldehyde or melamine modified resins are more suitable.

The resins continue to be used in large quantities in general wood assembly work. In most cases the resin–hardener mixture is applied to the surfaces to be joined and then clamped under pressure while hardening occurs. It is also possible to coat the resin on to one surface and the hardener on the other surface, allowing them to come into contact *in situ* and thus eliminating pot-life problems. Gap-filling resins may be produced by incorporating plasticisers such as furfuryl alcohol and fillers to reduce shrinkage and consequent cracking and crazing.

One of the largest applications of U–F resins at the present time is in the manufacture of chipboard. Wood chips are mixed with about 10% of resin–hardener solution and the mixture pressed in a multi-daylight press for about eight minutes at 150°C. Since the odour of formaldehyde is disagreeable it is important that little of the pungent chemical be released into the press shop during the opening of the presses. For this reason the resin should have a low free formaldehyde content. Since a low degree of condensation is desirable to ensure good dispersion, a rather low F–U ratio is necessary in order to achieve a low free formaldehyde content.

Wood chipboard is free from grain and is thus essentially isotropic in its behaviour. The mechanical properties are approximately the same as the average of the properties of the original wood measured along and across the grain. The water resistance of chipboard is poor but, being isotropic, it does not warp as long as it is able to swell freely in all directions.

24.2.5 Foams and Firelighters

Foams may be made from urea-formaldehyde resins using simple techniques. In one process the resin is mixed with a foaming detergent, whipped up with air in a mixing device and blended with an acid, such as phosphoric acid, as it leaves the mixer. The foams may be formed *in situ* in building cavity walls but, because of the large amounts of water present, it is necessary that the foam be formed between porous surfaces. Typical products have a closed cell content of about 80% and have little mechanical strength, as they are very friable. They have a very low thermal conductivity with a K value of 0.15–0.20. Btu in ft⁻² h⁻¹ F⁻¹ (0.022–0.029 W/mK), thus comparing very favourable with other insulating materials. Foams ranging from 0.5 to 3.0 lb/ft³ (0.008–0.048 g/cm³) may be produced; those with a density of about 0.75 lb/ft³ (0.012 g/cm³) having the lowest conductivity. Such foams are very cheap and are now being made *in situ* in building applications in Britain. Foams have also been used as an aid to floral decoration and in ground form as an artificial snow in cinema and television productions.

A rather strange but nevertheless large-scale application of U-F resins is in the manufacture of firelighters, made by a modification of the foam process. The resin solution is blended with a small amount of detergent and then whisked with paraffin. A hardener is added and the resin allowed to set. In effect the product is a U-F foam saturated with paraffin.

Another unorthodox application is to form a U-F foam on airport runways to act as an arrester bed to stop aircraft that overshoot during emergency landings or abortive take-offs.

24.2.6 Other Applications

Modification of urea-formaldehyde resins with other reagents gives rise to a number of useful materials. For example, co-condensation of urea-formaldehyde and a monohydric alcohol in the presence of small quantities of an acidic catalyst will involve simultaneous etherification and resinification. *n*-Propanol, *n*-butanol and isobutanol are commonly used for this purpose. As an example *n*-butanol will react with the methylol urea as shown in *Figure 24.4*.

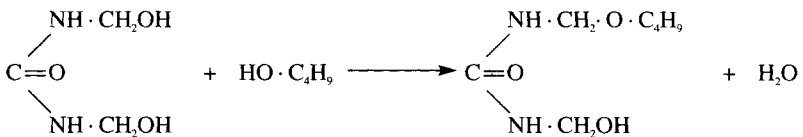


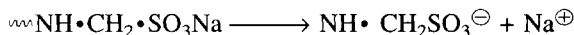
Figure 24.4

By varying reaction conditions and reactant proportions differing products may be obtained. Many of the alkoxy groups are retained during cure and the resins have a degree of thermoplasticity. Soluble in organic solvents and used in conjunction with plasticising alkyd resins, these materials form useful stoving lacquers. Air-drying lacquers, suitable as wood finishes, may be obtained by addition of acid hardeners.

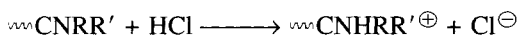
Whereas the butylated resins have enhanced solubility in organic solvents, enhanced solubility in water (which is rather limited in resins of high molecular weight) is required for some purposes and this may be achieved in a number of ways. For example, in acid condensation of urea and formaldehyde in the presence of sodium bisulphite the following reaction takes place:



Ionisation occurs in aqueous solution to give a resin of negative charge, as in, for example, a number of 'anionic resins':



Modification of urea resins with certain organic bases, e.g. triethylenetetramine, will give resins with basic groups which form ionisable salts in the presence of acids:



These resins are referred to as 'cationic resins'. Paper with improved wet strength may be obtained by adding an ionic resin at the beater stage of a paper-making operation. For the best results a high molecular weight resin is required.

Urea resins find extensive use in textile finishing. For example, cellulose fabrics may be padded into aqueous solutions of hydroxymethyl ureas or their methyl ethers. Excess material is removed and the resins are hardened *in situ*, using metal salt catalysts, by passing the fabric through ovens at 130–160°C. Although there is negligible difference in the appearance of the fabric, a considerable measure of crease resistance is acquired. Such resin treatment does, however, lead to two immediate problems. Firstly the cellulose fabric has lower tear and tensile strengths. This problem is partially overcome by mercerisation (steeping in sodium hydroxide solution) before resin treatment. The second problem occurs where the fabric is subjected to repeated bleaching action since the resin reacts with hypochlorite bleach to give chloramines, which break down on ironing, forming hydrochloric acid, which tenderises the fabric. This problem has been progressively reduced in recent years by the use of cyclic urea derivatives which do not form chloramines.

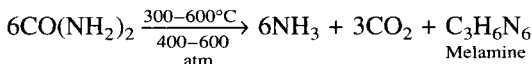
24.3 MELAMINE-FORMALDEHYDE RESINS^{14, 16}

Melamine (1,3,5-triamino-2,4,6-triazine) was first prepared by Liebig in 1835. For a hundred years the material remained no more than a laboratory curiosity until Henkel⁴ patented the production of resins by condensation with formaldehyde. Today large quantities of melamine-formaldehyde resins are used in the manufacture of moulding compositions, laminates, adhesives, surface coatings and other applications. Although in many respects superior in properties to the urea-based resins they are also significantly more expensive.

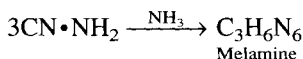
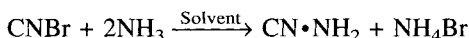
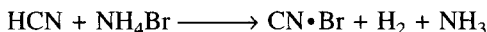
24.3.1. Melamine

A number of methods of producing melamine have been described in the literature.¹⁴ These include:

- (1) Heating dicyanodiamide, either with ammonia or on its own under pressure.
- (2) Fusion of dicyanodiamide with a guanidine salt.
- (3) From urea.



- (4) Electrolysis of dilute solutions of hydrogen cyanide in ammonium bromide to give cyanogen bromide. This is then dissolved in a solvent such as tetrahydrofuran and reacted with gaseous ammonia to produce cyanamide. The cyanamide is then heated in an autoclave at about 190–200°C in the presence of ammonia and the melamine, recovered by filtration.



Of these methods the first named was for many years the most important commercially. Dicyanodiamide ('dicy') is prepared by heating cyanamide solution at 70–80°C. The cyanamide itself is prepared from calcium cyanamide (Figure 24.5).

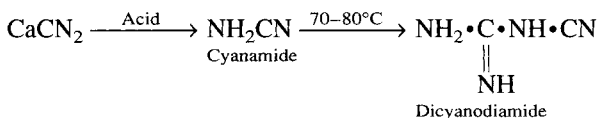


Figure 24.5

If 'dicy' is heated just above its melting point of 209°C there is a vigorous exothermic reaction results in the evolution of ammonia and the formation of some melamine together with a number of complex water-insoluble de-ammoniation products. In order to achieve a high yield of melamine in commercial manufacture the reaction is carried out in the presence of ammonia at about 300°C under pressure (Figure 24.6).

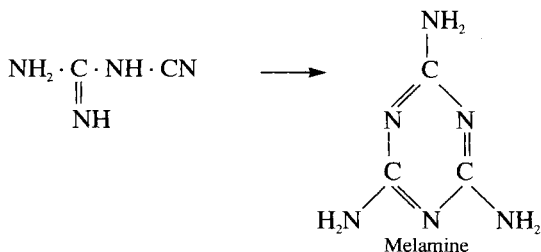


Figure 24.6

It will be noted that dicyanodiamide is the dimer of cyanamide and melamine is the trimer.

Today melamine is usually prepared from urea. The detailed mechanism of this reaction is believed to be as follows (*Figure 24.7*).

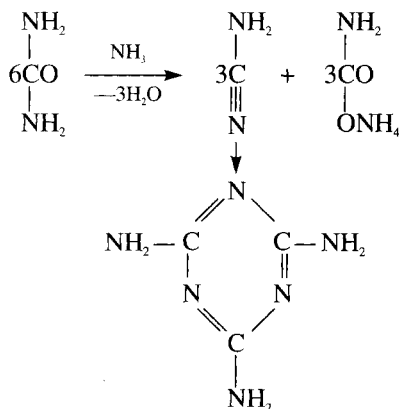


Figure 24.7

Only one melamine molecule is formed from six urea molecules, whilst three molecules of ammonia carbamate are formed. Whilst this can be recycled to urea the conversion from urea to melamine per cycle is at most 35%. Both the main route and the recycling operation involve high pressures and the low process efficiency offsets some of the apparent economic attractions of the route compared to those from 'dicy'.

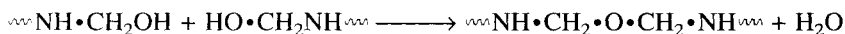
Melamine, a non-hygroscopic, white crystalline solid, melts with decomposition above 347°C and sublimates at temperatures below the melting point. It is only slightly soluble in water; 100 ml of water dissolve 0.38 g at 20°C and 3.7 g at 90°C. It is weakly basic and forms well-defined salts with acids.

24.3.2 Resinification

Reaction of melamine with neutralised formaldehyde at about 80–100°C leads to the production of mixture of water-soluble methylolmelamines. These hydroxy-methyl derivatives can possess up to six methylol groups per molecule and include trimethylolmelamine and hexamethylolmelamine (*Figure 24.8*) The methylol content of the mixture will depend on the melamine formaldehyde ratio and on the reaction conditions.

On further heating the methylolmelamines condense and a point is reached where hydrophobic resin separates out on cooling. The resinification is strongly dependent on the pH and is at a minimum at about pH 10.0–10.5. An increase or decrease of pH from this value will result in a considerable increase in resinification rates.

There is some evidence that the principal resinification reaction involves methylol–methylol condensations.¹⁷



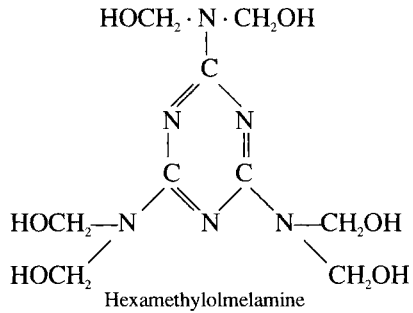
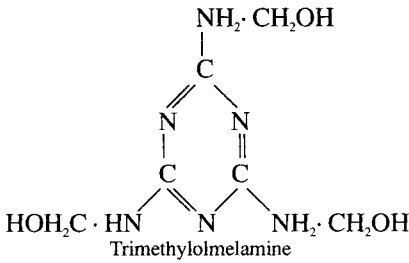
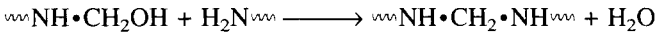


Figure 24.8

Methylene links may also be formed by the following reactions



In commercial practice the resin is condensed to a point close to the hydrophobe point and then either applied to the substrate, or converted into a moulding powder, before proceeding with the final cure.

In a typical process a jacketed still fitted with a stirrer and reflux condenser in charged with 240 parts 37% w/w (40% w/v) formalin and the pH adjusted to 8.0–8.5 using sodium carbonate solution with the aid of a pH meter. One hundred and twenty six parts of melamine (to give a melamine formaldehyde ratio of 1:3) are charged into the still and the temperature raised to 85°C. The melamine goes into solution and forms methylol derivatives. For treatment of fabrics, paper and leather this product may be diluted and cooled for immediate use. It may also be spray dried to give a more stable product. Cooling the solution would yield crystalline trimethylolmelamine, which may be air dried but which is less soluble in water than the spray-dried product.

For laminating and other purposes the initial product is further heated to about 85°C with continuous stirring. After about 30 minutes, and at regular intervals thereafter, samples of the resin are taken and added to ice-cold water. Diminished water tolerance is indicated when the resin solution becomes cloudy on entering the water. Reaction is then continued until the stage is reached when addition of 3 cm³ of water will cause 1 cm³ of resin to become turbid.

Reactions may be carried out at lower pH values and higher temperatures in order to achieve faster reactions. For some applications where a high degree of

fibre impregnation is required, hydrophilic resin may also be produced. Such hydrophilic resins have limited stability in aqueous solution and must either be used within a few hours of manufacture or spray dried.

The more hydrophobic resins have only a slightly greater stability in solution with a shelf-life of just a few days. Some improvement may be achieved by diluting the resin content down to about 50% solids content with industrial methylated spirit. The diluted resin should then be adjusted to a pH of 9.0–9.5 to improve the stability. The addition of about 0.1% borax (anhydrous) calculated on the weight of the solids content is useful in obtaining this pH and maintaining it for several months.¹⁸ It is conveniently added as an aqueous solution. The stabilised resins should be stored at 20–35°C. Too low a storage temperature will cause precipitation, too high a temperature, gelation. Precipitation may also occur if the resin is insufficiently condensed, and gelation with over-condensation.

24.3.3 Moulding Powders

Melamine–formaldehyde moulding powders are generally prepared by methods similar to those used with urea–formaldehyde material. In a typical process an aqueous syrup, containing resin with a melamine–formaldehyde molar ratio of 1:2, is compounded with fillers, pigments, lubricants, stabilisers and in some cases accelerators in a dough-type mixer. The product is then dried and ball-milled by processes similar to those described in Section 24.2.3. In one process described in the literature, magnesium carbonate is employed to act as a pH stabiliser during storage. For the more common decorative moulding powders α -cellulose is used as a filler. Some bleached woodflour is sometimes added to reduce shrinkage cracks near inserts. Because of the high refractive index of the cured resin (~1.65) it is not possible to obtain highly translucent mouldings using regenerated cellulose fillers as is possible with U–F moulding powders.

Industrial grade materials employ fillers such as asbestos, silica and glass fibre. These are incorporated by dry-blending methods similar to those used with woodflour-filled phenolic compositions.

Mouldings from melamine–formaldehyde powders are superior to the urea–formaldehyde plastics in a number of respects.

These include:

- (1) Lower water absorption, especially with mineral-filled resins.
- (2) Better resistance to staining by aqueous solutions such as fruit juices and beverages. Further improvement in this respect is still desirable and somewhat better results are claimed using benzoguanamine with the melamine.
- (3) Electrical properties, which are initially similar to those of urea–formaldehyde resins, are maintained better in damp conditions and at elevated temperatures.
- (4) Better heat resistance.
- (5) Greater hardness.

Compared with the phenolic resins they have a better colour range, track resistance and scratch resistance. They have a similar order of heat resistance, although their dimensional stability when exposed to hot dry conditions is not so

good. Melamine-formaldehyde moulding materials are more expensive than general purpose urea-formaldehyde and phenol-formaldehyde resins.

For high-duty electrical applications the mineral-filled melamine-based compositions have superior electrical insulation and heat resistance to the cellulose-filled grades. The use of glass fibre leads to mouldings of higher mechanical strength, improved dimensional stability and higher heat resistance than with the fillers. Mineral-filled melamine-based powders may be used when phenolics and urea-formaldehyde compositions are unsuitable. They are thus to some extent competitive with the melamine-phenolics, the alkyd moulding powders and, to some small extent, epoxy moulding materials. It is therefore not surprising to find that usage of mineral-filled M-F moulding powder is currently very small.

An interesting use of melamine resins in compression moulding involves decorative foils. A suitably printed or decorated grade of paper is impregnated with resin and dried. A compression moulding is then prepared using a melamine-formaldehyde, or some other moulding powder. Shortly before the cure is complete the mould is opened, the foil placed in position and the resin in the foil cured in the position so that the foil actually bonds on to the moulding.

Melamine-based compositions are easily moulded in conventional compression and transfer-moulding equipment. Moulding temperatures are usually in the range 145–165°C and moulding pressures 2–4 ton/in² (30–60 MPa). In transfer moulding pressures of 5–10 ton/in² (75–150 MPa) are used. An $\frac{1}{8}$ in thick moulding required about 2½ minutes cure at 150°C but shorter times are possible with preheated powder.

The injection moulding of melamine-formaldehyde moulding powders is now carried out on a small scale. Temperatures are somewhat higher than for U-F (e.g. barrel temperatures 100–115°C; mould temperatures 163–177°C). Otherwise the considerations are the same as for the urea-formaldehyde compositions.

The curing time employed depends on the properties required of the finished product. For example, cold-water absorption increases and electrical breakdown decreases as the curing time increases. The effect of cure time on the properties of moulding has been investigated by Morgan and Vale¹⁹ (see *Figure 24.9*). They have suggested that for an optimum combination of electrical and mechanical properties with minimum boiling-water absorption and low after-shrinkage the dye test provides a useful guide to cure. In this test^{20,21} the mouldings are immersed for 10 minutes in a boiling 0.01% aqueous solution of Rhodamine B. The moulding is deemed adequately cured if the mouldings remain unchanged in colour except at flash lines or at other points where the resin skin has been removed.

The principal application of melamine-formaldehyde moulding compositions is for the manufacture of tableware, largely because of their wide colour range, surface hardness and stain resistance. The stain resistance does, however, leave something to be desired and one aim of current research is to discover alternative materials superior in this respect. Cellulose-filled compositions also find a small outlet for trays, clock cases and radio cabinets and other purposes. The mineral-filled powders are used in electrical applications and knobs and handles for kitchen utensils.

As with the U-F moulding powders the relative importance of M-F moulding powders for other plastics materials and also in other uses for melamine-formaldehyde resins has declined.

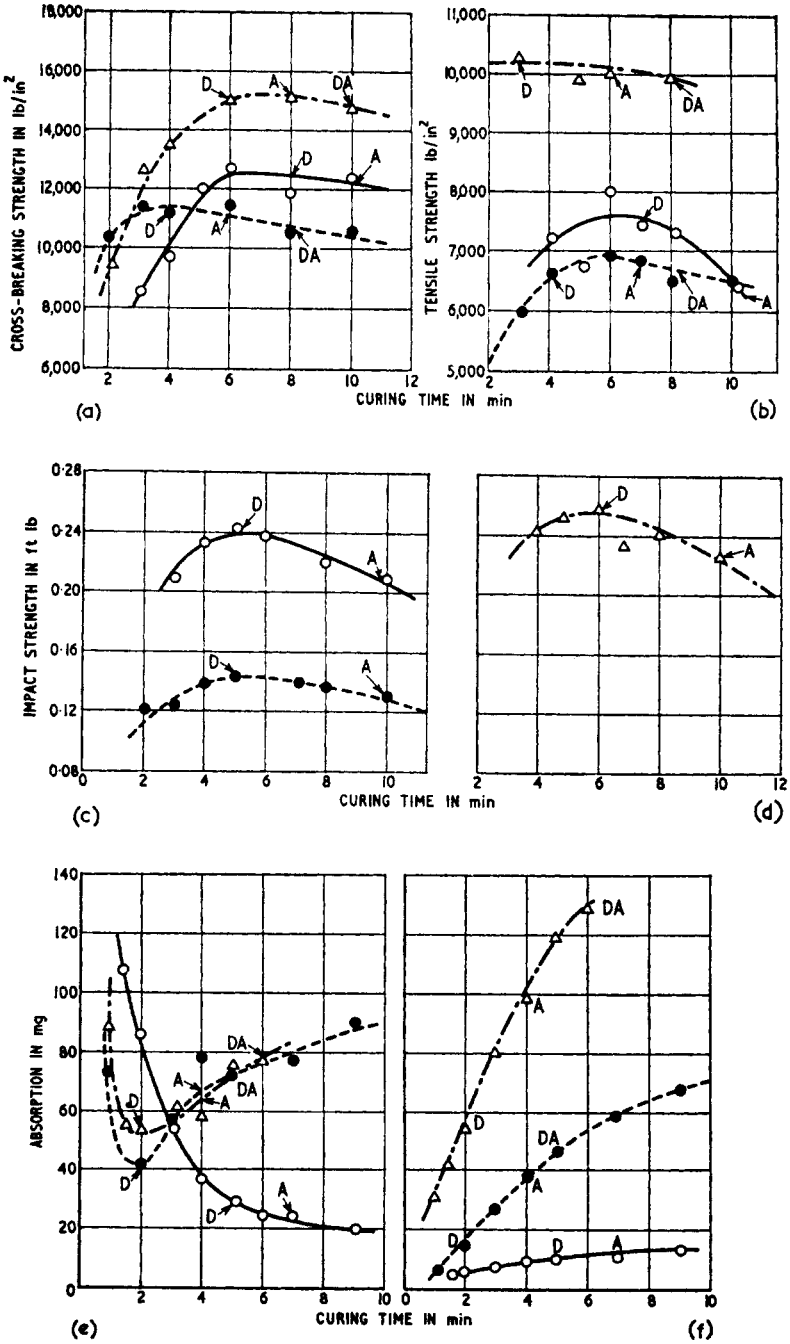
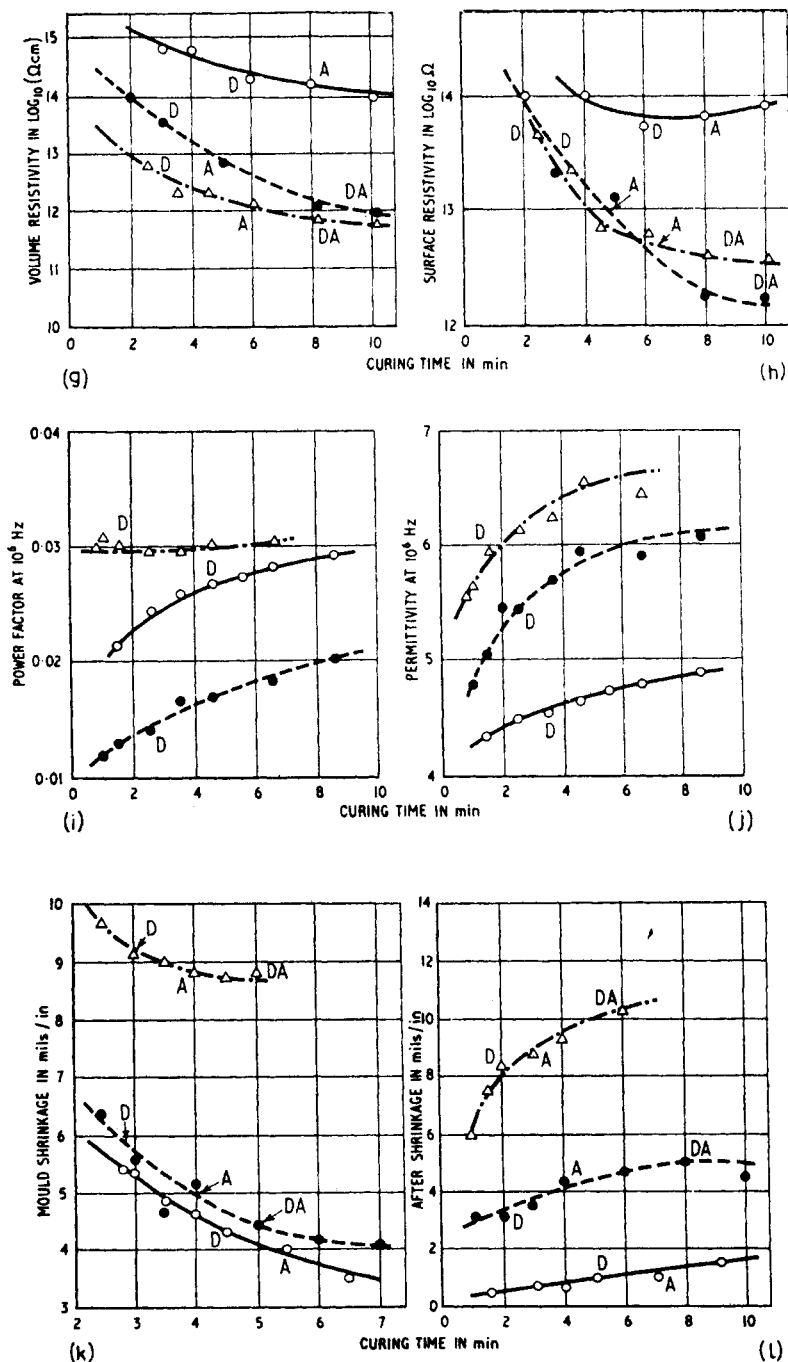


Figure 24.9. Effect of cure time on some properties of M-F mouldings. Cure temperature: cellulose filled 295–308°F; mineral filled 300–320°F; ○ glass-filled material, ● asbestos-filled material, △ cellulose-filled material; (a) Cross-breaking strength; (b) tensile strength; (c) impact strength; (d) impact strength; (e) water absorption (mg), boiling water 30 min; (f) cold water 24 h, 23°C;



(g) volume resistivity; (h) surface resistivity; (i) power factor; (j) permittivity; (k) mould shrinkage; (l) after-shrinkage. The letters D, A and DA indicate the time of optimum cure indicated by the dye test D (see text by boiling in 10% H_2SO_4 (A) and boiling in a mixture of 0.9% H_2SO_4 and 0.025% Kition Red (DA). (After Morgan and Vale¹⁹)

In the early 1990s M–F moulding materials were estimated at about 7% of the total thermosetting moulding powder market in Western Europe. Although this percentage has remained virtually constant for many years (indicating a usage of about 11 000 tonnes), it has to be borne in mind that the importance of thermosetting moulding materials relative to thermoplastics has declined substantially over the past 40 years. It is an interesting point that because of its use in tableware, melamine–formaldehyde moulding materials are better known to the general public than any other moulding material of such limited consumption.

24.3.4 Laminates Containing Melamine–Formaldehyde Resin

The high hardness, good scratch resistance, freedom from colour and heat resistance of melamine–formaldehyde resins suggest possible use in laminating applications. The use of laminates prepared using only melamine resins as the bonding agent is, however, limited to some electrical applications because of the comparatively high cost of the resin compared with that of P–F resins. On the other hand a very large quantity of decorative laminates are produced in which the surface layers are impregnated with melamine resins and the base layers with phenolic resins. These products are well known under such names as Formica and Waverite.

Resins for this purpose generally use melamine–formaldehyde ratios of 1:2.2 to 1:3. Where electrical grade laminates are required the condensing catalyst employed is triethanolamine instead of sodium carbonate.

Decorative laminates have a core or base of Kraft paper impregnated with a phenolic resin. A printed pattern layer impregnated with a melamine–formaldehyde or urea–thiourea–formaldehyde resin is then laid on the core and on top of this a melamine resin-impregnated protective translucent outer sheet. The assembly is then cured at 125–150°C in multi-daylight presses in the usual way.

Decorative laminates have achieved remarkable success because of their heat resistance, scratch resistance and solvent resistance. Their availability in a wide range of colours has led to their well-known applications in table tops and as a wall-cladding in public buildings and public transport vehicles.

The electrical grade laminates are made by impregnating a desized glass cloth with a triethanolamine-catalysed resin (as mentioned above). The dried cloth is frequently precured for about 1 hour at 100°C before the final pressing operation. A typical cure for 15-ply laminate would be 10–15 minutes at 140°C under a pressure of 250–1000 lbf/in² (1.7–7 MPa). Cloth based on alkali glass yields laminates with poor electrical insulation properties. Much better results are obtained using electrical grade glass which has been flame-cleaned. The use of certain amino silane treatments is claimed to give even better physical and electrical insulation properties.

Glass-reinforced melamine–formaldehyde laminates are valuable because of their good heat resistance (they can be used at temperatures up to 200°C) coupled with good electrical insulation properties; including resistance to tracking.

24.3.5 Miscellaneous Applications

In addition to their use in moulding powders and laminates, melamine–formaldehyde resins are widely used in many forms.

Hot setting adhesives, prepared in the same way as laminating resins, give colourless glue lines and are resistant to boiling water. Their use alone has been limited because of high cost but useful products may be made by using them in conjunction with a urea-based resin or with cheapening extenders such as starch or flour.

As already mentioned in Section 24.2.4 melamine is now widely used in conjunction with urea (and formaldehyde) to produce adhesives of good strength, reactivity and water resistance but with low ratios of formaldehyde to amine (i.e. urea and melamine).

Melamine-formaldehyde condensates are also useful in textile finishing. For example, they are useful agents for permanent glazing, rot proofing, wool shrinkage control and, in conjunction with phosphorus compounds, flame-proofing.

Compositions containing water-repellent constituents such as stearamide may also improve water repellency.

Modified melamine resins are also employed commercially. Alkylated resins analogous to the alkylated urea-formaldehyde resins provide superior coatings but are more expensive than the urea-based products.

Treatment of hexahydroxymethylmelamine with an excess of methanol under acid conditions yields the hexamethyl ether of hexahydroxymethylmelamine (HHMM). Not only will this material condense with itself in the presence of a strong acid catalyst to form thermoset structures but in addition it may be used as a cross-linking agent in many polymer systems. Such polymers require an active hydrogen atom such as in a hydroxyl group and cross-linking occurs by a *trans*-etherification mechanism. Typical polymers are the acrylics, alkyds and epoxides, HHMM having been particularly recommended in water-based coating resins.

Paper with enhanced wet-strength may be obtained by incorporating melamine resin acid colloid into the pulp. Melamine resin acid colloid is obtained by dissolving a lightly condensed melamine resin or trihydroxymethylmelamine, which are both normally basic in nature, in dilute hydrochloric acid. Further condensation occurs in solution and eventually a colloidal solution is formed in which the particles have a positive charge. Careful control over the constitution of the colloidal solution must be exercised in order to obtain products of maximum stability.

24.4 MELAMINE-PHENOLIC RESINS

Moulding powders based on melamine-phenol-formaldehyde resins were introduced by Bakelite Ltd, in the early 1960s. Some of the principal physical properties of mouldings from these materials are given in *Table 24.1*.

The principal characteristic of these materials is the wide range of colours possible, including many intense bright colours. The melamine-phenolics may be considered to be intermediate between the phenolic moulding materials and those from melamine-formaldehyde. As a result they have better moulding latitude and mouldings have better dry heat dimensional stability than the melamine-formaldehyde materials. Their tracking resistance is not as good as melamine-formaldehyde materials but often adequate to pass tracking tests. The main applications of these materials are as handles for saucepans, frying pans, steam irons and coffee pots where there is a requirement for a coloured heat-

resistant material. It was never likely that the melamine–phenolics would absorb much of the market held by melamine resins, irrespective of price, since this market is largely dependent on either the non-odorous nature of the good tracking resistance of the material used. Neither of these two requirements were fulfilled by the melamine–phenolics. Future developments thus seem to lie in the creation of new markets for a coloured, heat-resistant material intermediate in price between the phenolic and melamine materials.

24.5 ANILINE–FORMALDEHYDE RESINS²²

Although occasionally in demand because of their good electrical insulation properties, aniline–formaldehyde resins are today only rarely encountered. They may be employed in two ways, either as an unfilled moulding material or in the manufacture of laminates.

To produce a moulding composition, aniline is first treated with hydrochloric acid to produce water-soluble aniline hydrochloride. The aniline hydrochloride solution is then run into a large wooden vat and formaldehyde solution is run in at a slow but uniform rate, the whole mix being subject to continuous agitation. Reaction occurs immediately to give a deep orange-red product. The resin is still a water-soluble material and so it is fed into a 10% caustic soda solution to react with the hydrochloride, thus releasing the resin as a creamy yellow slurry. The slurry is washed with a counter-current of fresh water, dried and ball-milled.

Because of the lack of solubility in the usual solvents, aniline–formaldehyde laminates are made by a ‘pre-mix’ method. In this process the aniline hydrochloride–formaldehyde product is run into a bath of paper pulp rather than of caustic soda. Soda is then added to precipitate the resin on to the paper fibres. The pulp is then passed through a paper-making machine to give a paper with a 50% resin content.

Aniline–formaldehyde resin has very poor flow properties and may be moulded only with difficulty, and mouldings are confined to simple shapes. The resin is essentially thermoplastic and does not cross-link with the evolution of volatiles during pressing. Long pressing times, about 90 minutes for a $\frac{1}{2}$ in thick sheet, are required to achieve a suitable product.

Laminated sheets may be made by plying up the impregnated paper and pressing at 3000 lbf/in² (20 MPa) moulding pressure and 160–170°C for 150 minutes, followed by 75 minutes cooling in a typical process. A few shaped mouldings may also be made from impregnated paper, by moulding at higher moulding pressures. In one commercial example a hexagonal circuit breaker lifting rod was moulded at 7000 lbf/in² (48 MPa).

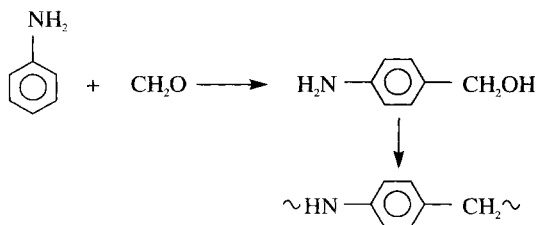


Figure 24.10

As with the other aminoplastics, the chemistry of resin formation is incompletely understood. It is, however, believed that under acid conditions at aniline–formaldehyde ratios of about 1:1.2, which are similar to those used in practice, the reaction proceeds via *p*-aminobenzyl alcohol with subsequent condensation between amino and hydroxyl groups (Figure 24.10).

It is further believed that the excess formaldehyde then reacts at the *ortho*-position to give a lightly cross-linked polymer with very limited thermoplasticity (Figure 24.11).

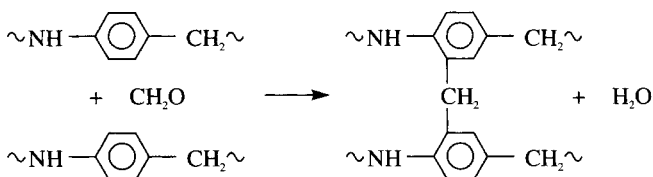


Figure 24.11

Such condensation reactions occur on mixing the two components. The resultant comparative intractability of the material is one of the main reasons for its industrial eclipse.

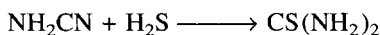
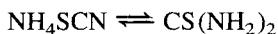
Some typical properties of aniline–formaldehyde mouldings are given in Table 24.2.

Table 24.2 Typical properties of aniline–formaldehyde mouldings

Specific gravity	1.2
Rockwell hardness	M 100, 125
Water absorption (24 h)	0.08% (ASTM D.570)
Tensile strength	10 500 lbf/in ² (73 MPa)
Impact strength	0.33 ft lbf/in ² notch (Izod)
Dielectric constant	3.56–3.72 (100 Hz–100 MHz)
Power factor 100 Hz	0.00226
1 MHz	0.00624
100 MHz	0.00318
Upper Service Temperature	~90°C
Track resistance	between phenolics and U-Fs
Resistant to alkalis, most organic solvents	
Attacked by acids	

24.6 RESINS CONTAINING THIOUREA

Thiourea may be produced either by fusion of ammonium thiocyanate or by the interaction of hydrogen sulphide and cyanamide.



The first process is an equilibrium reaction which yields only a 25% conversion of thiourea after about 4 hours at 140–145°C. Prolonged or excessive

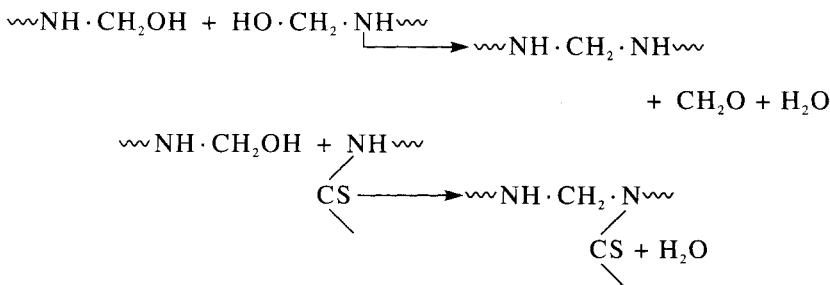


Figure 24.12

heating will cause decomposition of the thiourea whilst pressure changes and catalysts have no effect on the equilibrium. Pure thiourea is a crystalline compound melting at 181–182°C and is soluble in water.

Thiourea will react with neutralised formalin at 20–30°C to form methylol derivatives which are slowly deposited from solution. Heating of methylol thiourea aqueous solutions at about 60°C will cause the formation of resins, the reaction being accelerated by acidic conditions. As the resin average molecular weight increases with further reaction the resin becomes hydrophobic and separates from the aqueous phase on cooling. Further reaction leads to separation at reaction temperatures, in contrast to urea–formaldehyde resins, which can form homogeneous transparent gels in aqueous dispersion.

Polymer formation is apparently due to hydroxymethyl–methyl and hydroxy-methyl–amino reaction (Figure 24.12.).

In comparison with urea-based resins, thiourea resins are slower curing and the products are somewhat more brittle. They are more water-repellent than the U–F resins.

At one time thiourea–urea–formaldehyde resins were of importance for moulding powders and laminating resins because of their improved water resistance. They have now been almost completely superseded by melamine–formaldehyde resins with their superior water resistance. It is, however, understood that a small amount of thiourea-containing resin is still used in the manufacture of decorative laminates.

References

1. *British Patent* 151,016
2. *British Patent* 171,094; *British Patent* 181,014; *British Patent* 193,420; *British Patent* 201,906; *British Patent* 206,512; *British Patent* 213,567; *British Patent* 238,904; *British Patent* 240,840; *British Patent* 248,729
3. *British Patent* 187,605; *British Patent* 202,651; *British Patent* 208,761
4. *British Patent* 455,008
5. BLAKEY, W., *Chem. and Ind.*, 1349 (1964)
6. DINGLEY, C. S., *The Story of B.I.P.*, British Industrial Plastics Ltd., Birmingham (1963)
7. BROOKES, A., *Plastics Monograph* No. 2, Institute of the Plastics Industry, London (1946)
8. KADOWAKI, H., *Bull. Chem. Soc. Japan*, **11**, 248, (1936)
9. MARVEL, C. S., *et al.*, *J. Am. Chem. Soc.*, **68**, 1681 (1946)
10. REDFARN, C. A., *Brit. Plastics*, **14**, 6 (1942)
11. THURSTON, J. T., Unpublished paper given at the Gibson Island conference on Polymeric Materials (1941)
12. DE JONG, J. I., and DE JONGE, J., *Rec. Trav. Chim.*, **72**, 207 and 213 (1953)
13. ZIGEUNER, G., *Monatsh.*, **82**, 175 (1951); **83**, 1091 (1952); **86**, 165 (1955)

14. VALE, C. P., and TAYLOR, W. G. K., *Aminoplastics*, Iliffe, London (1964)
15. HOFFTON, J., *Brit. Plastics*, **14**, 350 (1942)
16. MILLS, F. J., Paper in *Plastics Progress* 1953 (Ed. MORGAN, P.), Iliffe, London (1953)
17. GAMS, A., WIDNER, G., and FISCH, W., *Brit Plastics*, **14**, 508 (1943)
18. *British Patent* 738.033
19. MORGAN, D. E., and VALE, C. P., Paper in S.C.I. Monograph No. 5 *The Physical Properties of Polymers*, Society of the Chemical Industry, London (1959)
20. VALE, C. P., *Trans. Plastics Inst.*, **20**, 29 (1952)
21. BS 1322
22. *Plastics* (London), **15**, 34 (1950)

Bibliography

- BLAIS, J. F., *Amino Resins*, Reinhold, New York (1959)
- MEYER, B., *Urea Formaldehyde Resins*, Addison-Wesley, Reading (Mass.) (1979)
- UPDEGRAFF, I. H., *Encyclopedia of Polymer Science and Technology* (2nd edition), Vol. 1, pp 725–89 (1985)
- VALE, C. P., *Aminoplastics*, Cleaver-Hume Press, London (1950)
- VALE, C. P., and TAYLOR, W. G. K., *Aminoplastics*, Iliffe, London (1964)

Reviews

- GÖTZE, T., and KELLER, K., *Kunststoffe*, **70**, 684–6 (1980)
- EISELE, W., and WITTMANN, O., *Kunststoffe*, **70**, 687–9 (1980)
- GARDZIELLA, A., *Kunststoffe*, **86**, 1566–1578 (1996)

25

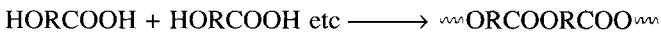
Polyesters

25.1 INTRODUCTION

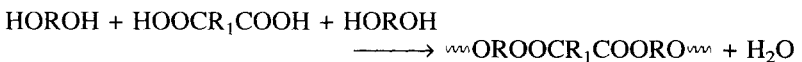
Polyesters are encountered in many forms. They are important as laminating resins, moulding compositions, fibres, films, surface coating resins, rubbers and plasticisers. The common factor in these widely different materials is that they all contain a number of ester linkages in the main chain. (There are also a number of polymers such as poly(vinyl acetate) which contain a number of ester groups in side chains but these are not generally considered within the term polyester resins.)

These polymers may be produced by a variety of techniques, of which the following are technically important:

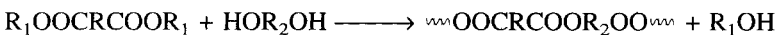
- (1) Self-condensation of ω -hydroxy acids, commercially the least important route:



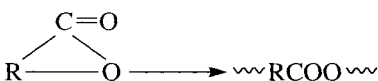
- (2) Condensation of polyhydroxy compounds with polybasic acids, e.g. a glycol with a dicarboxylic acid:



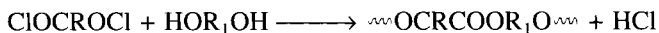
- (3) Ester exchange:



- (4) Ring opening of a lactone, e.g. of ϵ -caprolactone with dihydroxy or trihydroxy initiators:



- (5) Alcoholysis of the acid chloride of a dicarboxylic acid with a polyhydroxy alcohol:



Credit for the preparation of the first polyester resin is given variously to Berzelius in 1847 and to Gay-Lussac and Pelouze in 1883² Their first use came about in the early years of this century for surface coatings where they are well known as *alkyd* resins, the word alkyd being derived somewhat freely from alcohol and acid. Of particular importance in coatings are the *glyptals*, glycerol-phthalic anhydride condensates. Although these materials were also used at one time for moulding materials they were very slow curing even at 200°C and are now obsolete and quite different from present day alkyd moulding powders.

Linear polyesters were studied by Carothers during his classical researches into the development of the nylons but it was left to Whinfield and Dickson to discover poly(ethylene terephthalate) (BP 578 079), now of great importance in the manufacture of fibres (e.g. Terylene, Dacron) and films (e.g. Melinex, Mylar). The fibres were first announced in 1941.

At about the same time, an allyl resin known as CR39 was introduced in the United States as a low-pressure laminating resin. This was followed in about 1946 with the introduction of unsaturated polyester laminating resins which are today of great importance in the manufacture of glass-reinforced plastics. Alkyd moulding powders were introduced in 1948 and have since found specialised applications as electrical insulators.

With the expiry of the basic ICI patents on poly(ethylene terephthalate) there was considerable development in terephthalate polymers in the early 1970s. More than a dozen companies introduced poly(butylene terephthalate) as an engineering plastics material whilst a polyether-ester thermoplastic rubber was introduced by Du Pont as Hytre. Poly(ethylene terephthalate) was also the basis of the glass-filled engineering polymer (Rynite) introduced by Du Pont in the late 1970s. Towards the end of the 1970s poly(ethylene terephthalate) was used for the manufacture of biaxially oriented bottles for beer, colas and other carbonated drinks, and this application has since become of major importance. Similar processes are now used for making wide-neck jars.

Highly aromatic thermoplastic polyesters first became available in the 1960s but the original materials were somewhat difficult to process. These were followed in the 1970s by somewhat more processable materials, commonly referred to as polyarylates. More recently there has been considerable activity in *liquid crystal polyesters*, which are in interest as self-reinforcing heat-resisting engineering thermoplastics.

Such is the diversity of polyester materials that it has to be stressed that their common feature is only the ester (—COO—) link and that this often only comprises a small part of the molecule. Nevertheless it may influence the properties of the polymer in the following ways:

- (1) It is, chemically, a point of weakness, being susceptible to hydrolysis, ammonolysis and ester interchange, the first two reactions leading to chain scission. In some cases the reactivity is influenced by the nature of the adjacent groupings.
- (2) As a polar group it can adversely affect high-frequency electrical insulation properties. Its influence is generally lower below T_g unless the

portion of the polymer containing the ester group has some mobility below the main T_g .

- (3) The polar ester group may act as a proton acceptor, allowing interactions with other groupings either of an inter- or an intramolecular nature.
- (4) The ester link appears to enhance chain flexibility of an otherwise polymethylenic chain. At the same time it generally increases interchain attraction and in terms of the effects on melting points and rigidity the effects appear largely self-cancelling.

25.2 UNSATURATED POLYESTER LAMINATING RESINS

The polyester laminating resins are viscous, generally pale yellow coloured materials of a low degree of polymerisation (~8–10), i.e. molecular weight of about 2000. They are produced by condensing a glycol with both an unsaturated and a saturated dicarboxylic acid. The unsaturated acid provides a site for subsequent cross-linking whilst provision of a saturated acid reduces the number of sites for cross-linking and hence reduces the cross-link density and brittleness of the end-product. In practice the polyester resin, which may vary from a very highly viscous liquid to a brittle solid depending on composition, is mixed with a reactive diluent such as styrene. This eases working, often reduces the cost and enhances reactivity of the polyester. Before applying the resin to the reinforcement a curing system is blended into the resin. This may be so varied that curing times may range from a few minutes to several hours whilst the cure may be arranged to proceed either at ambient or elevated temperatures. In the case of cold-curing systems it is obviously necessary to apply the resin to the reinforcement as soon as possible after the catalyst system has been added and before gelation and cure occur. The usual reinforcement is glass fibre, as a preform, cloth, mat or rovings but sisal or more conventional fabrics may be used.

Since cross-linking occurs via an addition mechanism across the double bonds in the polyesters and the reactive diluent there are no volatiles given off during cure (c.f. phenolic and amino-resins) and it is thus possible to cure without pressure (see *Figure 25.1*). Since room temperature cures are also possible the resins are most useful in the manufacture of large structures such as boats and car bodies.

Small quantities of higher molecular weight resin in powder form are also manufactured. They are used in solution or emulsion form as binders for glass-fibre preforms and also for the manufacture of preimpregnated cloths.

25.2.1 Selection of Raw Materials

1,2-Propylene glycol is probably the most important glycol used in the manufacture of the laminating resins. It gives resins which are less crystalline and more compatible with styrene than those obtained using ethylene glycol. Propylene glycol is produced from propylene via propylene oxide. The use of glycols higher in the homologous series gives products which are more flexible and have greater water resistance. They do not appear to be used on a large scale commercially.

Products such as diethylene glycol and triethylene glycol, obtained by side reactions in the preparation of ethylene glycol, are sometimes used but they

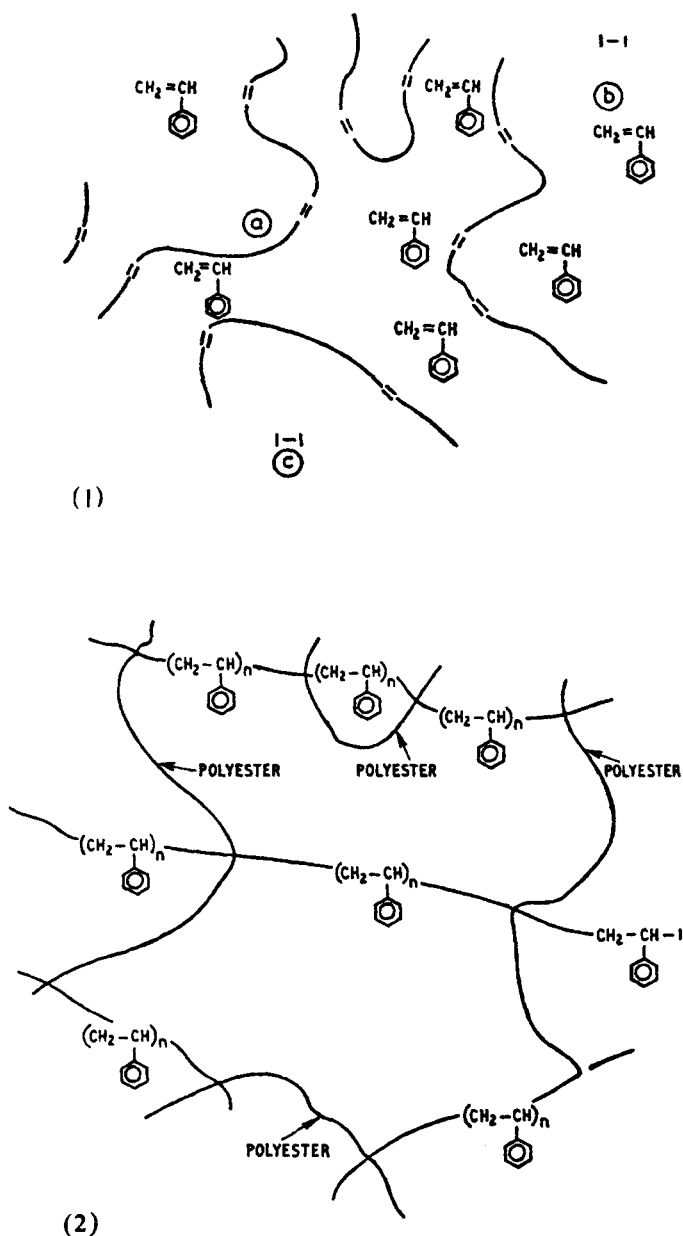


Figure 25.1. The nature of cured polyester laminating resins.

- (1) Structures present in polyester resin ready for laminating:
 - (a) low molecular weight unsaturated resin molecules
 - (b) reactive diluent (styrene) molecules
 - (c) initiator (catalyst) molecules
- (2) Structures present in cured polyester resin. Cross-linking via an addition copolymerisation reaction. The value of $n \sim 2-3$ on average in general purpose resins

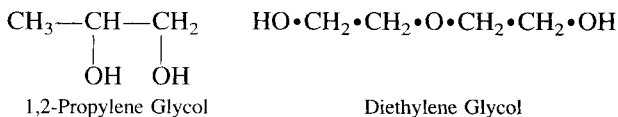


Figure 25.2

give products with greater water absorption and inferior electrical properties (Figure 25.2).

Most conventional general purpose resins employ either maleic acid (usually as the anhydride) or its *trans*-isomer fumaric acid (which does not form an anhydride) as the unsaturated acid (Figure 25.3).

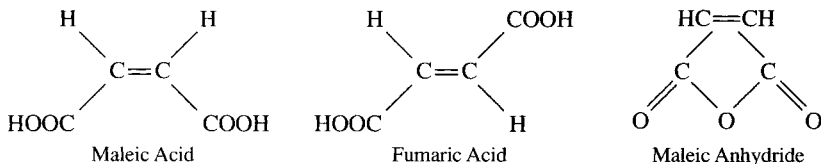


Figure 25.3

Maleic anhydride is commonly prepared by passing a mixture of benzene vapour and air over a catalyst (e.g. a vanadium derivative) at elevated temperatures (e.g. 450°C). It is a crystalline solid melting at 52.6°C (the acid melts at 130°C).

Fumaric acid may be prepared by heating maleic acid, with or without catalysts. It is also obtained as by-product in the manufacture of phthalic anhydride from naphthalene. The acid is a solid melting at 284°C. Fumaric acid is sometimes preferred to maleic anhydride as it is less corrosive, it tends to give lighter coloured products and the resins have slightly greater heat resistance.

Saturated acids

The prime function of the saturated acid is to space out the double bonds and thus reduce the density of cross-linking. Phthalic anhydride is most commonly used for this purpose because it provides an inflexible link and maintains the rigidity in the cured resin. It has been used in increasing proportions during the past decade since its low price enables cheaper resins to be made. The most detrimental effect of this is to reduce the heat resistance of the laminates but this is frequently unimportant. It is usually produced by catalytic oxidation of *o*-xylene but sometimes naphthalene and is a crystalline solid melting at 131°C.

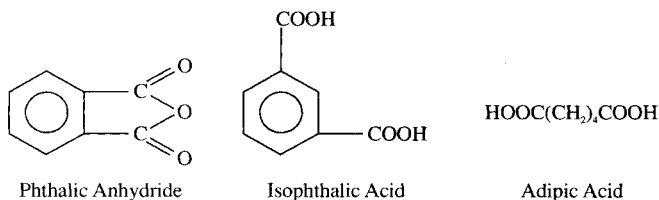


Figure 25.4

Isophthalic acid (m.p. 347°C), made by oxidation of *m*-xylene, has also been introduced for resins. The resins have higher heat distortion temperatures and flexural moduli and better craze resistance. They are also useful in the preparation of resilient gel coats.

Systems based on isophthalic acid often show better water and alkali resistance than those based on phthalic anhydride. This is not thought to be due to inherent differences between the phthalic and isophthalic structures but is ascribed to the fact that isophthalate resins have generally considerably higher viscosities which enable them to be diluted with greater amounts of styrene. It is the additional proportion of styrene which gives the improved water and alkali resistance.

Where a flexible resin is required adipic and, rarely, sebacic acids are used. Whereas the phthalic acids give a rigid link these materials give highly flexible linkages and hence flexibility in the cured resin. Flexible resins are of value in gel coats.

Diluents

Because of its low price, compatibility, low viscosity and ease of use styrene is the preferred reactive diluent in general purpose resins. Methyl methacrylate is sometimes used, but as it does not copolymerise alone with most unsaturated polyesters, usually in conjunction with styrene in resins for translucent sheeting. Vinyl toluene and diallyl phthalate are also occasionally employed. The use of many other monomers is described in the literature.

Special materials

A number of special purpose resins are available which employ somewhat unusual acids and diluents. A resin of improved heat resistance is obtained by using 'Nadic' anhydride, the Diels-Alder reaction product of cyclopentadiene and maleic anhydride (*Figure 25.5*).

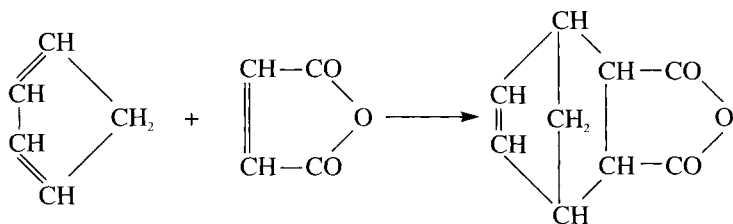


Figure 25.5

A substantial improvement in heat resistance may also be obtained by replacing the styrene with triallyl cyanurate (*Figure 25.6*).

This monomer is prepared by reacting cyanuric chloride with excess allyl alcohol in the presence of sodium hydroxide at 15–20°C. Laminates based on polyester resins containing triallyl cyanurate are claimed to be able to withstand a temperature of 250°C for short periods.

Commercial use of triallyl cyanurate is severely limited by the high price and the high curing exotherm of polyester-triallyl cyanurate systems. The exotherm

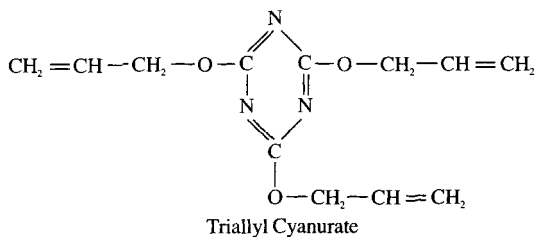


Figure 25.6

has been shown to be in part due to an isomeric transformation to triallyl isocyanurate. This latter material is now manufactured in Japan and imparts very good heat resistance with a relatively low exotherm. It is, however, too expensive for general purpose applications.

For many applications it is necessary that the resin has reasonable self-extinguishing properties. Such properties can be achieved and transparency retained by the use of HET-acid (chlorendic acid). This is obtained by reacting hexachlorocyclopentadiene with maleic anhydride and converting the resulting anhydride adduct into the acid by exposure to moist air (Figure 25.7).

The self-extinguishing properties of the resin are due to the high chlorine content of the acid (54.8%). The double bond of the acid is unreactive and it is

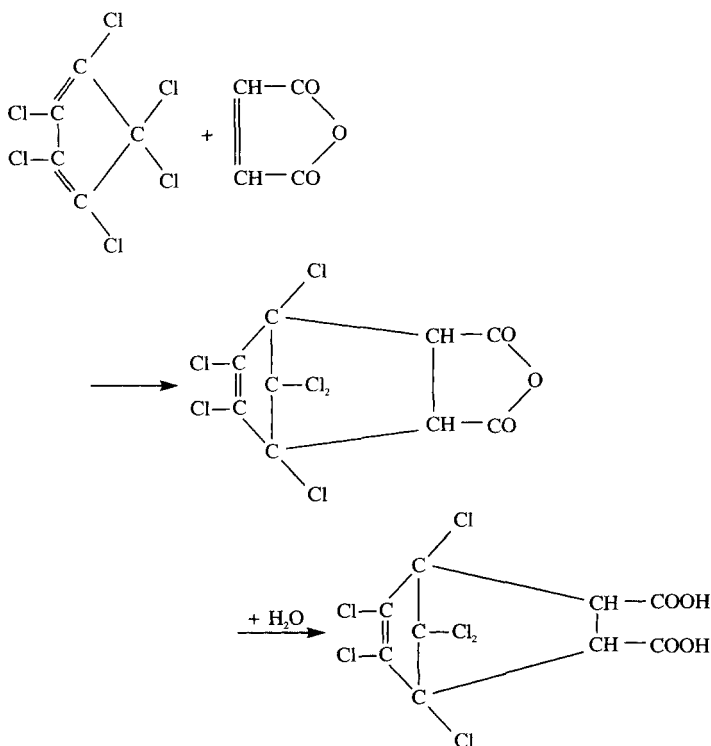


Figure 25.7

necessary to use it in conjunction with an unsaturated acid such as fumaric acid to provide for cross-linking.

An alternative approach is first to produce a polyester resin containing an excess of maleic acid residues (maleate groups) and then to react this with the hexachlorocyclopentadiene to form the adduct *in situ* (Figure 25.8).

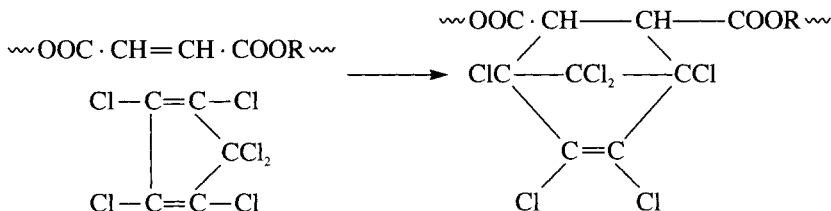


Figure 25.8

Laminates prepared from highly chlorinated resins of this type tend to discolour on prolonged exposure to light and this retarded the early development of these resins. Stabilisers have, however, been developed and current resins are substantially superior to the early resins of this type.

The self-extinguishing characteristics of the chlorine-containing resins are improved by incorporation of antimony oxide but this approach is not possible where translucent sheet is required. As an alternative to chlorine-based systems a number of bromine-containing resins have been prepared and, whilst claimed to be more effective, are not currently widely used. It is probably true to say that fire-retarding additives are used more commonly than polymers containing halogen groupings.

Many other acids, glycols and reactive monomers have been described in the literature but these remain of either minor or academic importance. In a number of cases this is simply because of the high cost of the chemical and a reduction in cost due to its widespread use in some other application could well lead to extensive use in polyester resins.

Besides resin and reactive diluent, additives are commonly incorporated into polyester resins. These include not only curing agents and fillers (see Section 25.2.3) but also ultraviolet stabilisers. The latter are particularly important for outdoor applications such as roof lighting, benzotriazoles being particularly effective.

25.2.2 Production of Resins

Polyester laminating resins are produced by heating the component acids and glycols at 150–200°C for several hours, e.g. 12 hours. In order to obtain a good colour and to prevent premature gelation the reaction is carried out under an inert blanket of carbon dioxide or nitrogen. The reaction mixture is agitated to facilitate reaction and to prevent local overheating. A typical charge for a general purpose resin would be:

Propylene glycol	146 parts
Maleic anhydride	114 parts
Phthalic anhydride	86 parts

The molar ratios of these three ingredients in the order above is 1.1:0.67:0.33. The slight excess of glycol is primarily to allow for evaporation losses. Xylene is often used to facilitate the removal of water of condensation by means of azeotropic distillation. The reaction is followed by measuring the acid number of small samples periodically removed from the reactor. (The acid number is the number of milligrams of potassium hydroxide equivalent to the acidity present in one gram of resin.) Where there are equimolecular proportions of glycol and acid the number average molecular weight is given by $56\,000/\text{acid number}$. Since there is some deviation from equimolecular equivalence in practice, care should be taken in using this relationship. Reaction is usually stopped when the acid number is between 25 and 50, the heaters are switched off and any xylene presents is allowed to boil off into a receiver.

When the resin temperature drops below the boiling point of the reactive diluent (usually styrene) the resin is pumped into a blending tank containing suitability inhibited diluent. It is common practice to employ a mixture of inhibitors in order to obtain a balance of properties in respect of colour, storage stability and gelation rate of catalysed resin. A typical system based on the above polyester formulation would be:

Styrene	148 parts
Benzyltrimethylammonium chloride	0.38 parts
Hydroquinone	0.05 parts
Quinone	0.005 parts

The blend is allowed to cool further and the resin is transferred into drums for shipping and storage.

Quality control tests on the resins most commonly employed are for specific gravity, viscosity, colour, clarity and gel time under standard conditions, including fixed amount of curing system.

25.2.3 Curing Systems

The cross-linking reaction is carried out after the resin has been applied to the glass fibre. In practice the curing is carried out either at elevated temperatures of about 100°C where press mouldings are being produced, or at room temperature in the case of large hand lay-up structures.

Benzoyl peroxide is most commonly used for elevated temperature curing. The peroxide is generally supplied as a paste (~50%) in a liquid such as dimethyl phthalate to reduce explosion hazards and to facilitate mixing. The curing cycle in pressure moulding processes is normally less than five minutes.

In the presence of certain aromatic tertiary amines such as dimethylaniline, benzoyl peroxide will bring about the room temperature cure of general purpose polyester resins.

More frequently either methyl ethyl ketone peroxide or cyclohexanone peroxide is used for room temperature curing in conjunction with a cobalt compound such as a naphthenate, octoate or other organic solvent-soluble soap. The peroxides (strictly speaking polymerisation initiators) are referred to as 'catalysts' and the cobalt compound as an 'accelerator'. Other curing systems have been devised but are seldom used.

Commercial *methyl ethyl ketone peroxide* (MEKP) is a mixture of compounds and is a liquid usually supplied blended into dimethyl phthalate, the mixture

containing about 60% peroxide. Its activity varies according to the composition of the mixture. It is useful in that it can easily be metered into the resin from a burette but great care must be taken in order to obtain adequate dispersion into the resin. It is also difficult to detect small quantities of this corrosive material which may have been spilt on the skin and elsewhere.

Cyclohexanone peroxide, a white powder, another mixture of peroxidic materials, has a similar reactivity to MEKP. Usually supplied as a 50% paste in dimethyl or dibutyl phthalate, it has to be weighed out, but it is easier to follow dispersion and to observe spillage. The quantity of peroxide used is generally 0.5–3% of the polyester.

Cobalt naphthenate is generally supplied in solution in styrene, the solution commonly having a cobalt concentration of 0.5–1.0%. The cobalt solution is normally used in quantities of 0.5–4.0% based on the polyester. The accelerator solution is rather unstable as the styrene will tend to polymerise and thus although the accelerator may be metered from burettes, the latter will block up unless frequently cleaned. Cobalt naphthenate solutions in white spirit and dimethyl phthalate have proved unsatisfactory. In the first case dispersion is difficult and laminates remain highly coloured whilst with the latter inferior end-products are obtained and the solution is unstable. Stable solutions of cobalt octoate in dimethyl phthalate are possible and these are often preferred because they impart less colour to the laminate.

An interest has been developed in the use of vanadium naphthenates as accelerators. In 1956 the author³ found that if MEKP was added to a polyester resin containing vanadium naphthenate the resin set almost immediately, that is, while the peroxide was still being stirred in. Whereas this effect was quite reproducible with the sample of naphthenate used, subsequent workers have not always obtained the same result. It would thus appear that the curing characteristics are very dependent on the particular grade of resin and of vanadium naphthenate used. It was also observed by the author that the gelation rate did not always increase with increased temperature or accelerator concentration and in some instances there was a retardation. Subsequent workers⁴ have found that whilst the behaviour of the naphthenate varies according to such factors as the resin and catalyst used, certain vanadium systems are of value where a high productivity in hand lay-up techniques is desired.

The peroxides and accelerator should not be brought into contact with each other as they form an explosive mixture. When the resin is to be used, first the accelerator and then the peroxide are carefully dispersed into the resin, which may also contain inert fillers and thixotropic agents.

According to the concentration of catalyst and accelerator used, the resin will gel in any time from five minutes to several hours. Gelation will be followed by a rise in temperature, which may reach 200°C (see *Figure 25.9*). Where the resin is applied to the glass mat before gelation, the high surface/volume ratio facilitates removal of heat and little temperature rise is noted. Gelation and the exothermic reaction are followed by hardening and the resin becomes rigid. Maximum mechanical strength is not, however, attained for about a week or more. Hardening is accompanied by substantial volumetric shrinkage (~8%) and for this reason polyester resins are used only infrequently for casting purposes.

Unsaturated polyesters are invariably susceptible to air inhibition and surfaces may remain undercured, soft and in some cases tacky if freely exposed to air during the curing period. The degree of surface undercure varies to some extent with the

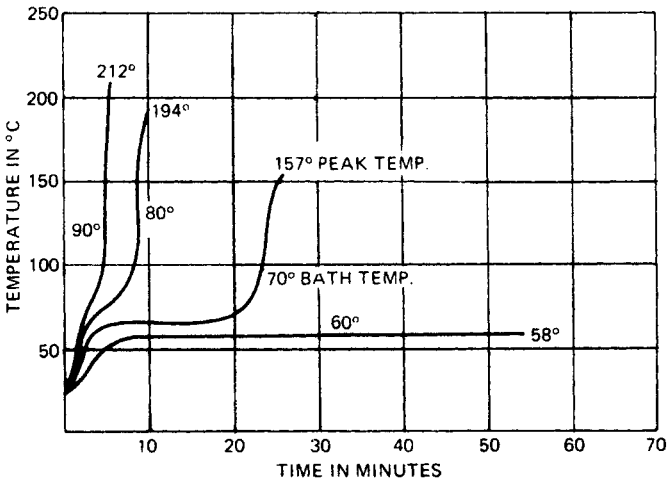


Figure 25.9. Typical exotherm curves for polyester resin cured with 1% benzoyl peroxide over a range of bath temperatures. (Test tubes of 19 mm dia are filled to height of 8 cm with a mixture of resin plus peroxide. The tubes are immersed in a glycerin bath to the level of the resin surface. Temperature is measured with a thermocouple needle whose point is half-way down the resin column)

resin formulation and the hardening system employed. Where the resin is to be used in hand lay-up techniques or for surface coatings air inhibition may cause problems. A common way of avoiding difficulties is to blend a small amount of paraffin wax (or other incompatible material) in with the resin. This blooms out on to the surface, forming a protective layer over the resin during cure.

25.2.4 Structure and Properties

The cured resins, being cross-linked, are rigid and do not flow on heating. The styrene, phthalic anhydride, maleic anhydride and propylene glycol residues are predominantly hydrocarbon but are interspersed with a number of ester groups. These latter groups provide a site for hydrolytic degradation, particularly in alkaline environments. The polar nature of the ester group leads to the resin having a higher power factor and dielectric constant than the hydrocarbon polymers and this limits their use as high-frequency electrical insulators.

Many mechanical properties are dependent on the density of cross-links and on the rigidity of the molecules between cross-links. It has already been shown that cross-link intensity may be controlled by varying the ratio of unsaturated to saturated acids whereas rigidity is to a large extent determined by the structure of the saturated acid employed.

25.2.5 Polyester-Glass Fibre Laminates

Glass fibres are the preferred form of reinforcement for polyester resins since they provide the strongest laminates. Fabrics from other fibres may, however, be used and can in some instances provide adequate reinforcement at lower cost. Glass fibres are available in a number of forms, of which the following are the most important:

- (1) Glass cloth. A range of cloths is available and the finest of these are used in order to obtain the best mechanical properties. They are, however, expensive in use and they are used only in certain specialised applications such as in the aircraft industry and for decorative purposes.
- (2) Chopped strand mat. This consists of chopped strands (bundles of glass filaments) about 2 in long bound together by a resinous binder. This type of mat is used extensively in glass-reinforced polyester structures.
- (3) Needle mat. This is similar to chopped strand mat except that the mat is held together by a loose stitching rather than a binder.
- (4) Preforms. Preformed shapes may be made by depositing glass fibres on to a preform mould. The fibres are then held together by spraying them with a binder.

Other types of glass structures used include rovings, yarns, tapes, rovings fabrics and surfacing mats.

Various types of glass are available. Low-alkali aluminium borosilicate (E glass) fibres confer good weathering and electrical insulation properties and are the staple product of the glass fibre/resin moulding industry, the resulting composites being used, for example, for car bodies, surfboards and skis. Magnesium aluminium silicate (S glass) fibres are stronger and are used, for example, in pressure bottles, in rocket motor cases and for missile shells, all made by filament winding. At one time an alkali glass (A glass) with an alkali content of 10–15% was used for non-critical applications but this has declined in importance. In order that good adhesion should be achieved between resin and glass it is necessary to remove any size (in the case of woven cloths) and then to apply a finish to the fibres. The function of a finish is to provide a bond between the inorganic glass and the organic resin. Today the most important of these finishes are based on silane compounds, e.g. Garan treatment. In a typical system vinyl trichlorosilane is hydrolysed in the presence of glass fibre and this condenses with hydroxyl groups on the surface of the glass (*Figure 25.10*).

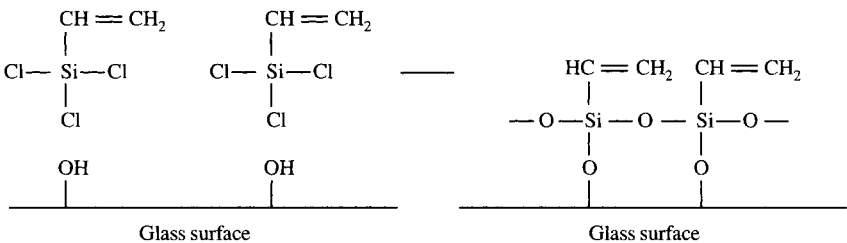


Figure 25.10

A number of different binder materials are in use for chopped strand mat and include starch, polyvinyl acetate and polyesters. The binder used depends on the end use of the laminate and the method of fabrication.

Methods of producing laminates have been dealt with in detail in other publications⁵⁻⁹ and so details will not be given here.

The major process today is the hand lay-up technique in which resin is stippled and rolled into the glass mat (or cloth) by hand. Moulds are easy to fabricate and large structures may be made at little cost.

For mass production purposes matched metal moulding techniques are employed. Here the preform or mat is placed in a heated mould and the resin poured on. The press is closed and light pressure ($\sim 50 \text{ lbf/in}^2$) applied. Curing schedules are usually about three minutes at 120°C . It is possible to produce laminates using less resin with pressure moulding than with hand lay-up techniques and this results in better mechanical properties.

A number of techniques intermediate between these two extreme processes also exist involving vacuum bags, vacuum impregnation, rubber plungers and other devices. In addition there are such diverse processes as filament winding, cold moulding, e.g. the Resinfect process, and extrusion techniques using glass filaments.

Inert fillers are sometimes mixed with the resin in an effort to reduce cost. However, many fillers increase the viscosity to such an extent that with hand lay-up methods much more of the resin–filler mix is required to impregnate the mat. Since greater difficulty in working may also prolong processing time and there is invariably a marked drop in mechanical properties care must be taken before making a decision whether or not to employ fillers.

There is one particular type of filler whose value can be in no doubt. This is the so-called thixotropic filler exemplified by certain fine silicas and silicates which appear to increase the viscosity of the resin on standing. These are useful in minimising drainage of resins from vertical and near-vertical surfaces during hand lay-up operations.

Some typical properties of polyester–glass laminates are given in *Table 25.1*. From these figures it will be seen that laminates can have very high tensile strengths. On the other hand some laminates made by hand lay-up processes may have mechanical properties not very different from those of thermoplastics such as the polyacetals and unplasticised PVC.

Table 25.1

<i>Property</i>	<i>Hand lay-up mat laminate</i>	<i>Press formed mat laminate</i>	<i>Fine square woven cloth laminate</i>	<i>Rod from rovings</i>
Specific gravity	1.4–1.5	1.5–1.8	~ 2.0	2.19
Tensile strength (10^3 lbf/in^2)	8–17	18–25	30–45	150
(MPa)	55–117	124–173	210–310	1030
Flexural strength (10^3 lbf/in^2)	10–20	20–27	40–55	155
(MPa)	69–138	138–190	267–380	1100
Flexural modulus (10^6 lbf/in^2)	~ 0.5	~ 0.6	1–2	6.6
(MPa)	3440	4150	6890–1380	45 500
Power factor (10^6 Hz)	0.02–0.08	0.02–0.08	0.02–0.05	—
Dielectric constant (10^6 Hz)	3.2–4.5	3.2–4.5	3.6–4.2	—
Water absorption (%)	0.2–0.8	0.2–0.8	0.2–0.8	—

The most desirable features of polyester-glass laminates are:

- (1) They can be used to construct large mouldings without complicated equipment.
- (2) Good strength and rigidity although much less dense than most metals.
- (3) They can be used to make large, tough, low-density, translucent panels.
- (4) They can be used to make the materials fire retardant where desired.

- (5) Superior heat resistance to most rigid thermoplastics, particularly those that are available in sheet form.

Because of their favourable price, polyesters are preferred to epoxide and furane resins for general purpose laminates and account for at least 95% of the low-pressure laminates produced. The epoxide resins find specialised uses for chemical, electrical and heat-resistant applications and for optimum mechanical properties. The furane resins have a limited use in chemical plant. The use of high-pressure laminates from phenolic, aminoplastic and silicone resins is discussed elsewhere in this book.

World production of unsaturated polyester resins in 1997 was of the order of 1.7×10^6 tonnes, with the USA accounting for about 45% and Western Europe 27%. Over 75% is used in reinforced plastics, with the rest being used for such diverse applications as car repair putties, 'cultured marble', wood substitution and surface coatings. The pattern of consumption in 1993 of reinforced polyesters in the USA was reported as:

	<i>Tonnes</i>	<i>%</i>
Construction	190	26
Marine applications	116	16
Land transport	93	13
Corrosion-resistant products	89	12
Other	244	33

(These figures include reinforcement, filler etc.)

and has probably changed little since then.

The largest single outlet for polyester-glass laminates is in sheeting for roofing and building insulation and accounts for about one-third of the resin produced. For the greatest transparency it is important that the refractive indices of glass, cured resins and binder be identical. For this reason the glass fibre and resin suppliers provide raw materials which are specially made to approximate to these requirements. This outlet is now being challenged by rigid PVC sheeting, which is much cheaper than fire-retardant polyester laminates.

Polyester resins have been widely accepted in the manufacture of boat hulls, including minesweepers. Such hulls are competitive in price with those built from traditional materials and are easier to maintain and repair.

The third major outlet is in land transport, where the ability to form large structures has been used in the building of sports car bodies, in lorry cabs, in panelling for lorries, particularly translucent roofing panels, and in public transport vehicles. In such applications the number of mouldings required is quite small. The polyester-glass structures are less suitable for large-quantity production since in these circumstances the equipment requirements rise steeply and it eventually becomes more economical to use the more traditional stamped metal shapings.

Aircraft radomes, ducting, spinners and other parts are often prepared from polyester resins in conjunction with glass cloth or mat. The principal virtue here is the high strength/weight ratio possible, particularly when glass cloth is used. Land, sea and air transport applications account for almost half the polyester resin produced.

Other applications include such diverse items as chemical plant, stacking chairs, swimming pools, trays and sports equipment.

For some years there has been concern at the amount of styrene vapour in workshops preparing reinforced polyester laminates. More recently this has increased interest in polyester-polyurethane hybrids and in the further development of closed moulding and resin transfer moulding techniques as well as greater use of lower styrene levels.

25.2.6 Water-Extended Polyesters

The applications of the unsaturated polyester resins were increased in the late 1960s by the introduction of water-extended polyesters. In these materials water is dispersed into the resin in very tiny droplets (ca 2–5 μm diameter). Up to 90% of the system can consist of water but more commonly about equal parts of resin and water are used. The water component has two basic virtues in this system; it is very cheap and because of its high specific heat it is a good heat sink for moderating cure exotherms and also giving good heat shielding properties of interest in ablation studies.

The basic patent (US Patent 3256219) indicates that the system is viable with conventional resins although special grades have been developed that are said to be particularly suitable. One example in the patent recommends the use of a polyester prepared using a maleic acid, phthalic acid and propylene glycol ratio of 2:1:33 and with an acid value of 40. To 500 g of such a resin are added 10 g of benzoyl peroxide and 167 g of styrene. Water 600 g is then stirred in at 5–10°C until a white creamy water-in-oil emulsion is obtained. A solution of 0.8 g of dimethyl-*p*-toluidine in 100 g of styrene is stirred into the emulsion and the resin is cast between plates and cured at 50°C.

The products are cellular white materials resembling Plaster of Paris. Originally suggested for a wide variety of applications, interest now seems to centre on Plaster of Paris replacements (because of their low breakage rate) and as a wood substitute. The greatest problem restricting current development is the tendency to lose water slowly from the casting, with subsequent cracking and warping.

25.2.7 Allyl resins¹⁰

A number of useful resins have been prepared from allyl compounds, i.e. derivatives of allyl alcohol $\text{CH}_2 = \text{CH} \cdot \text{CH}_2\text{OH}$. One of these, diethylene glycol

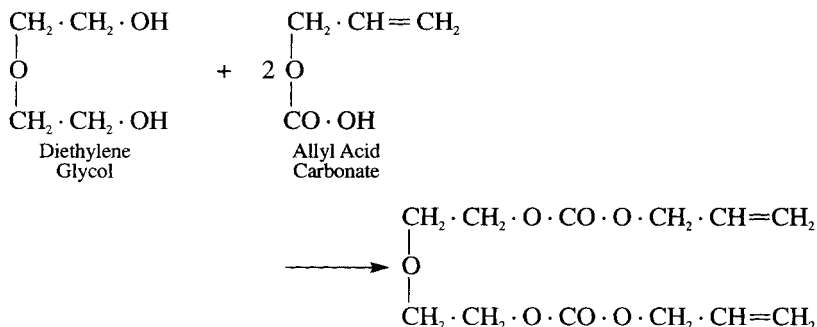


Figure 25.11

bisallyl carbonate, was one of the first polyester-type materials to be developed for laminating and casting. It was introduced in about 1941 by the Pittsburgh Plate Glass Company as Allymer CR39 and was produced by the reaction shown in *Figure 25.11*. It could be cured with benzoyl peroxide at 80°C. It is used today for spectacle lenses.

Diallyl phthalate (see also Section 25.3) has also been used as a laminating resin but because of its higher price it has been largely replaced by the glycol-saturated acid-unsaturated acid polyesters.

Other allyl compounds described in the literature include diallyl carbonate, diallyl isophthalate and diallyl benzene phosphonate.

25.3 POLYESTER MOULDING COMPOSITIONS

Although phenolic and amino moulding powders remain by far the most important of the thermosetting moulding compositions a number of new materials have been introduced¹¹ over the last 30 years based on polyester, epoxide and silicone resins.

Five classes of polyester compound may be recognised:

- (1) Dough moulding compounds (DMC).
- (2) Sheet moulding compounds (SMC).
- (3) Alkyd moulding compositions, sometimes referred to as 'polyester alkyds'.
- (4) Diallyl phthalate compounds.
- (5) Diallyl isophthalate compounds.

The dough moulding compounds were originally developed in an attempt to combine the mechanical properties of polyester-glass laminates with the speed of cure of conventional moulding powder. In spite of their somewhat high cost they have now established themselves in a number of applications where a mechanically strong electrical insulant is required.

Dough moulding compositions, also known as bulk moulding compounds, are prepared by blending resin, powdered mineral filler, reinforcing fibre, pigment and lubricant in a dough mixer, usually of the Z-blade type. The resins are similar to conventional laminating resins, a fairly rigid type being preferred so that cured mouldings may be extracted from the mould at 160°C without undue distortion. Organic peroxides such as benzoyl peroxide and tertiary butyl perbenzoate are commonly used as 'catalysts'. The choice of 'catalyst' will influence cure conditions and will also be a factor in whether or not surface cracks appear on the mouldings. Mineral fillers such as calcium carbonate are employed not only to reduce costs but to reduce shrinkage and to aid the flow since an incorrect viscosity may lead to such faults as fibre bunching and resin-starved areas. Although glass fibre (E type) is most commonly employed as the reinforcing fibre, sisal is used in cheaper compositions. Stearic acid or a metal stearate are the usual lubricants.

Formulations for the three typical DMC grades are given in *Table 25.2*.

The non-fibrous components are first mixed together and the fibrous materials are then added. The properties of components are critically dependent on the mixing procedures since these will affect dispersion and fibre degradation.

Table 25.2

	<i>Low-cost general purpose</i>	<i>High-grade mechanical</i>	<i>High-grade electrical</i>
Polyester resin	100	100	100
E glass $\frac{1}{2}$ in length	20	—	90
E glass $\frac{3}{4}$ in length	—	85	—
Calcium carbonate	240	150	—
Fine silica	—	—	—
Sisal	40	—	—
Benzoyl peroxide	1	1	1
Calcium stearate	2	2	f2
Pigment	2	2	2

In common with all polyester moulding compositions the dough moulding compounds cure without evolution of volatiles and thus pressures as low as 200 lbf/in² (1.4 MPa), but normally about 1000 lbf/in² (6.9 MPa), may be used. The material, of putty-like consistency, is first preformed into a ball shape and loaded into the mould of a fast-acting press in such a way that there should be a minimum of weld lines and undesirable fibre alignment. Temperatures in the range 110–170°C may be employed and at the higher temperatures cure times of less than one minute are possible.

Dough or bulk moulding compounds can suffer from a number of disadvantages of which the most important are:

- (1) Problems of easy metering and handling of the materials before loading into the mould.
- (2) Tendency of thick sections to crack.
- (3) Warping, difficulty of moulding to close tolerances and wavy or fibre-patterned surfaces or faults arising from the high shrinkage during cure.
- (4) Difficulties in moulding large structural parts with no control on fibre orientation.

The first problem has been largely overcome by the availability of dough moulding compounds in extruded lengths which can easily be chopped to a desired controlled length. The second problem has been overcome by incorporating a proportion of a thermoplastic polymer such as polystyrene or PVC into the compound (e.g. BP 936 351 to British Industrial Plastics Ltd), an approach similar to that used with the so-called *low-profile polyester resins* or low shrink resins). These last named polymers are prepared by making a blend of a thermoplastic (e.g. acrylic polymers)–styrene system with a polyester–styrene system. When this blend is cured at elevated temperatures an opaque (viz. multi-phase) product is obtained with very low, and indeed sometimes negative, moulding shrinkage. Such mouldings have very smooth surfaces to which paint may be applied with very little pretreatment and warping is also minimised. It is interesting to note that this effect is not obtained with room temperature cures or in the presence of styrene homopolymerisation inhibitors such as t-butyl catechol. Whilst the mechanism for this phenomenon is not fully understood it would appear that some of the styrene contained in the dispersed thermoplastic–styrene phase will tend to volatilise during the high-temperature curing process, giving a microcellular structure whose expansion can exceed the

curing shrinkage. Generally speaking the greater the rate of cure the greater the expansion (or at least the less the shrinkage). This may be controlled by varying the initiator, the density of double bonds in the polyester and the moulding temperature. A wide spectrum of other properties may be obtained by varying the ratios of thermoplastic/polyester/styrene. A number of different thermoplastics may be used and amongst those quoted in the literature are poly(methyl methacrylate), polystyrene, PVC polyethylene and polycaprolactone, a particular form of polyester considered in Section 21.7.

By the early 1980s *high-gloss DMCs* using low-profile resins were finding use in kitchen appliances such as steam iron bases, toaster end-plates and casings for electric fires.

Manufacture of traditional dough moulding compounds involves intensive shear and hence extensive damage to fibres so that strengths obtained with GRP laminates are seldom realised. This problem is largely avoided with the *sheet moulding compounds*, which were introduced in about 1967 and by 1972 were being produced at the rate of about 20 000 tonnes per year. Resin, lubricant, filler thickening agents and curing systems are blended together and then coated on to two polyethylene films. Chopped glass rovings are then fed between the resin layers, which are subsequently sandwiched together and compacted as indicated in *Figure 25.12*. For moulding, blanks may easily be cut to the appropriate weight and shape. There appears to be no reason why this system should not be extended to allow predetermined fibre orientation or to superimpose oriented continuous filament on the chopped randomly oriented fibres where this is desirable. Low-profile resins are often used with these compounds whose main applications are in car parts, baths and doors.

The 'polyester' alkyd moulding compositions are also based on a resin similar to those used for laminating. They are prepared by blending the resin with cellulose pulp, mineral filler, lubricants, pigments and peroxide curing agents on

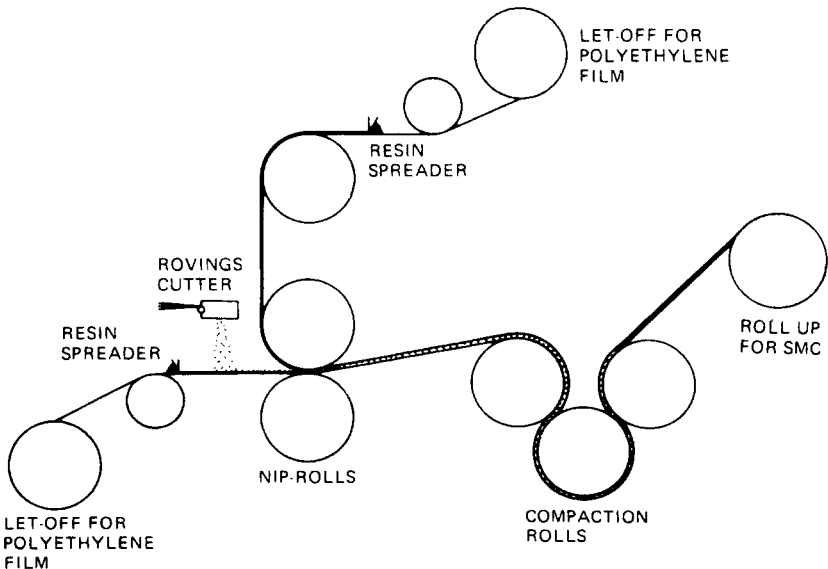


Figure 25.12. Outline of machine for preparing sheet moulding compounds (SMC)

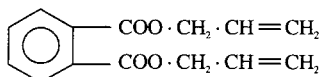


Figure 25.13

hot rolls until thoroughly mixed and of the desired flow properties. The resultant hide is removed, cooled, crushed and ground.

On heating with a peroxide, diallyl phthalate will polymerise and eventually cross-link because of the presence of two double bonds (Figure 25.13).

This monomer has been used as the basis of a laminating resin and as a reactive diluent in polyester laminating resins, but at the present time its principal value is in moulding compositions. It is possible to heat the monomer under carefully controlled conditions to give a soluble and stable partial polymer in the form of a white powder. The powder may then be blended with fillers, peroxide catalysts and other ingredients in the same manner as the polyester alkyds to form a moulding powder. Similar materials may be obtained from diallyl isophthalate.

The diallyl phthalate (DAP) resins compare favourably with the phenolic resins in their electrical insulation characteristics under conditions of dry and wet heat. The diallyl isophthalate (DAIP) compositions are more expensive but have better heat resistance and are claimed to be capable of withstanding temperatures as high as 220°C for long periods. Both the DAP and the DAIP materials are superior to the phenolics in their tracking resistance and in their availability in a wide range of colours. They do, however, tend to show a higher shrinkage on cure and in cases where this may be important, e.g. thin walls round inserts, it may be necessary to employ epoxide moulding compositions (see Chapter 26).

The 'polyester alkyd' resins are lower in cost than the DAP resins but are weaker mechanically, have a lower resistance to cracking round inserts and do not maintain their electrical properties so well under severe humid conditions. Fast-curing grades are available which will cure in as little as 20 seconds.

Some pertinent properties of the various polyester compounds are compared with those of a GP phenolic composition in Table 25.3.

The alkyd moulding compositions are used almost entirely in electrical applications where the cheaper phenolic and amino-resins are unsuitable.

Table 25.3 Properties of thermosetting polyester mouldings

	<i>P-FGP</i>	<i>DMC (GP)</i>	<i>Polyester alkyd</i>	<i>DAP alkyd</i>	<i>DAIP alkyd</i>	<i>Units</i>
Moulding temperature*	150–170	140–160	140–165	150–165	150–165	°C
Cure time (cup flow test)*	60–70	25–40	20–30	60–90	60–90	s
Shrinkage	0.007	0.004	0.009	0.009	0.006	cm/cm
Impact strength	0.12–0.2	2.0–4.0	0.13–0.18	0.12–0.18	0.09–0.13	ft lb
Specific gravity	1.35	2.0–2.1	1.7–1.8	1.64	1.8	
Power factor (800 Hz)	0.1–0.4	0.01–0.05	0.01–0.05	0.03–0.05	—	
Power factor (10 ⁶ Hz)	0.03–0.05	0.01–0.03	0.02–0.04	0.02–0.04	0.04–0.06	
Dielectric constant (800 Hz)	6–10	5.5–6.5	4.5–5.5	4.0–5.5	—	
Dielectric constant (10 ⁶ Hz)	4.5–5.5	5.0–6.0	4.5–5.0	3.5–5.0	4.0–6.0	
Volume resistivity	10 ¹² –10 ¹⁴	>10 ¹⁶	>10 ¹⁶	>10 ¹⁶	>10 ¹⁶	Ωm
Dielectric strength (90°C)	39–97	78–117	94–135	117–156	117–156	kV/cm
Water absorption	45–65	15–30	40–70	5–15	10–20	mg

Except where marked by an asterisk these results were obtained by tests methods as laid down in BS771.

25.4 FIBRE-FORMING AND FILM-FORMING POLYESTERS

Fibre-forming polyesters have been the subject of extensive investigations ever since Carothers began his classical researches that led to the development of the nylons. However, whilst Carothers largely confined his researches to aliphatic polyesters, J. R. Whinfield and J. T. Dickson, working at the Calico Printers Association in England, investigated aromatic materials and this led to the discovery and successful exploitation of poly(ethylene terephthalate) well known as a fibre (Terylene, Dacron) and to a lesser extent in film form (Melinex, Mylar) and as a moulding material (now becoming important for blown bottles).

SERIES	REPEAT - UNIT STRUCTURES
(1) POLY(ALKYLENE BIPHENYL-4, 4'-DICARBOXYLATES)	$-O \cdot (CH_2)_n \cdot O \cdot OC \text{ } \bigcirc \text{ } \bigcirc \text{ } CO-$
(2) POLY-(p-PHENYLENE ALKANEDIATES)	$-O \text{ } \bigcirc \text{ } O \cdot OC \cdot (CH_2)_n \cdot CO-$
(3) POLY(ALKYLENE TEREPHTHALATES)	$-O \cdot (CH_2)_n \cdot O \cdot OC \text{ } \bigcirc \text{ } CO-$
(4) POLY(ALKYLENE SUCCINATES)	$-O \cdot (CH_2)_n \cdot O \cdot OC \cdot (CH_2)_2 CO-$
(5) POLY(DECAMETHYLENE ALKANEDIATES)	$-O \cdot (CH_2)_{10} \cdot O \cdot OC \cdot (CH_2)_n CO-$
(6) POLY(ALKYLENE ADIPATES)	$-O \cdot (CH_2)_n \cdot O \cdot OC \cdot (CH_2)_4 CO-$

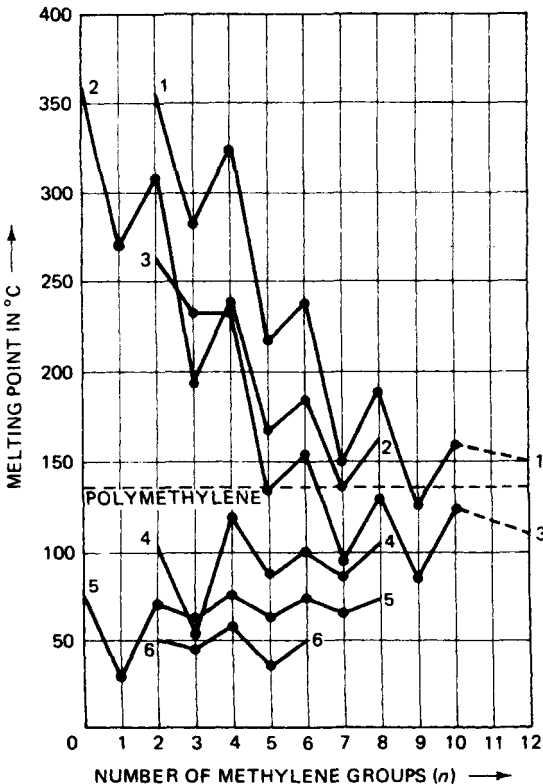


Figure 25.14. Melting points (T_m) of some homologous polyesters (ref. 15)

Figure 25.14 shows the influence of the ester group concentration on the melting point of six different classes of linear polyester. For the three aromatic classes of linear polyester, decreasing the concentration of ester groups apparently leads to a reduction in melting point. However, in each of the three classes a decrease in ester concentration is accompanied by a decrease in *p*-phenylene group concentration. Thus on the evidence of these three groups alone it is not clear whether the change in melting point is due to a decrease in ester group or *p*-phenylene group concentration. This uncertainty is resolved by considering the three aliphatic classes, in which it is seen that the ester group concentration has little effect on the melting point. In fact a decrease in ester group concentration leads to a slight increase in the melting point.

In Chapter 4 it was argued that the melting point (T_m) could be related to the heat of fusion (ΔH) and entropy of fusion (ΔS) by the expression

$$T_m = \frac{\Delta H}{\Delta S}$$

It is reasonable to consider that in an ester group the in-chain ether link $-\text{C}-\text{O}-\text{C}-$ increases the chain flexibility compared with a polymethylene chain to decrease the heat of fusion. At the same time there will be some increase in interchain attraction via the carbonyl group which will decrease the entropy of fusion. Since these two effects almost cancel each other out there is almost no change in melting point with change in ester group concentration.

With all six series of polyester illustrated in Figure 25.14, as the number of methylene groups in the repeating unit increases so the polymer becomes more like a linear polyethylene (polymethylene). Thus the melting points for five of the six classes are seen to converge towards that of the melting point of polymethylene. In the case of the sixth class, the poly(alkylene adipates), there would appear no reason to believe that additional data on other specific members of the class would not lead to a similar conclusion.

It will also be noted that, in common with other polymers produced by condensation and rearrangement polymerisation methods, the T_m of a polymer with an odd number of methylene groups in the aliphatic portion of the repeat unit is lower than for the polymer with one more but an even number of methylene groups.

Generally speaking the highest melting points are obtained where the in-chain aromatic ring is of the *p*-phenylene type. This is typified by the data of Figure

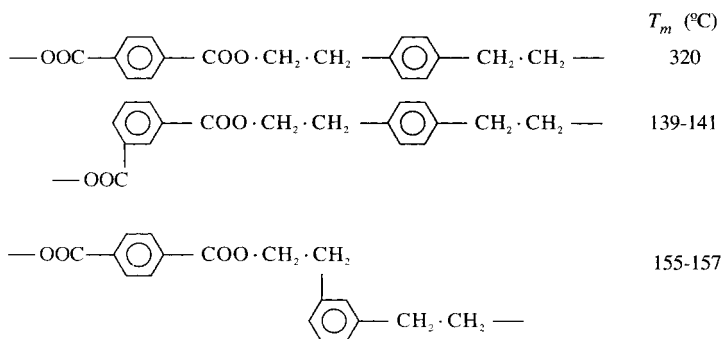


Figure 25.15



Figure 25.16

25.15. It is believed that this difference, which is typical of many polymers, is due to the higher entropy of fusion of the *m*-linked polymers.

Substitution of hydrogen atoms in the polymer backbone can have a number of effects. Consider the two diols in Figure 25.16. In the case of the 1,2-propylene glycol both head–head and head–tail modes of addition will be possible and the chain will be irregular; this will tend to inhibit crystallisation. In the three structures given in Figure 25.17 the symmetry is undisturbed and the polymers are crystallisable. The lower melting point of the substituted polymers may be expected to be due to the chain-separating effects of the methyl group. Being on an aromatic ring the methyl groups would not have the chain-stiffening effect that occurs with aromatic polymers (e.g. polypropylene c.f. polyethylene and poly(methyl methacrylate) c.f. poly(methyl acrylate)).

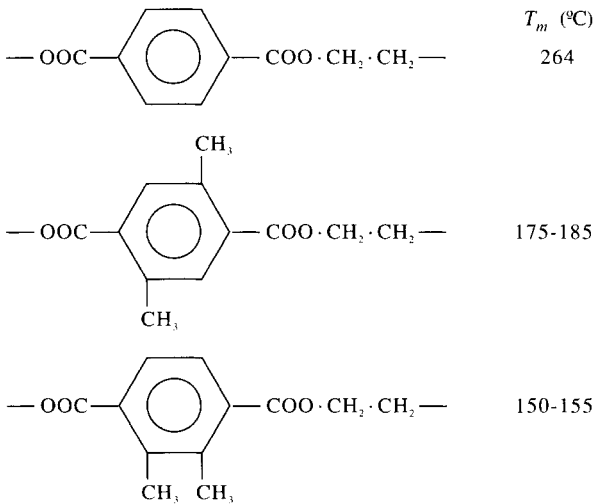


Figure 25.17

Where there is symmetrical disubstitution of an aliphatic hydrogen then, as might be expected, the T_m is usually raised, as seen from the data in Figure 25.18.

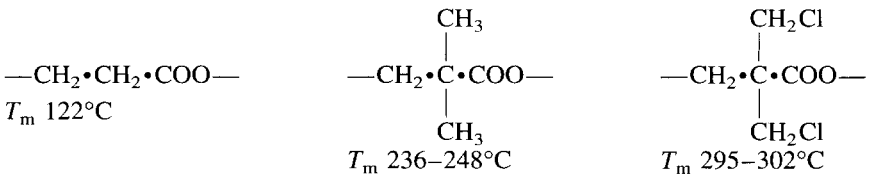
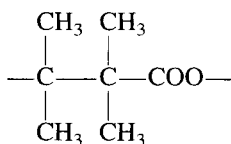


Figure 25.18

One anomaly is the product:



which has a T_m of only 165°C.

Table 25.4 summarises some effects of structure on T_m .

From the above comments it will be expected that terephthalic acid would be an important intermediate in the production of linear crystallisable polyesters, and so it has proved.

The acid is commonly prepared from *p*-xylene by an oxidation process. Although the *p*-xylene may be prepared from coal tar it is usually produced from

Table 25.4 The melting points of certain polyesters (ref. 15)

Series	T_m (°C) for $n =$										
	0	1	2	3	4	5	6	7	8	9	10
1	—	—	254	190	220	150	170	—	—	—	—
2	—	—	254	160	188	100	170	—	—	—	135
3	—	—	265	—	320	—	155	—	220	—	125
4	225	172	125	115	—	—	—	—	—	—	—
5	>300	—	270	213	230	175	181	—	143	—	—
6	—	—	273	—	—	—	240	—	—	—	182
7	—	—	82	—	86	84	90	—	—	—	98
8	—	—	17	29	67	30	47	—	—	—	61
9	—	225	122	—	53	55	52	—	66	76	74
10	230	—	66	—	125	—	57	—	73	—	53
11	—	—	188	—	185	164	167	—	—	—	156
12	—	—	220	150	170	—	160	—	—	—	—

Series

Unit Structure

- Poly(ethylene alkylenedioxy-4,4'-dibenzoates)
—O•(CH₂)₂•O•OC•φ•O•(CH₂)_n•O•φ•CO—
- Poly(alkylene diphenoxyethane-4,4'-dicarboxylates)
—O•(CH₂)_n•O•OC•φ•O•(CH₂)₂•O•φ•CO—
- Poly(*p*-phenylenedialkyl terephthalates)
—O•(CH₂)_{n/2}•φ•(CH₂)_{n/2}•O•OC•φ•CO—
- Poly(*p*-2-ethylenoxyphenyl alkanooates)
—O•(CH₂)₂•O•φ•(CH₂)_n•CO—
- Poly-(1,4-*trans*-cyclohexylene alkanedioates)
—O•C₅H₁₀•O•OC•(CH₂)_n•CO—
- Poly(alkylene dianilinoethane-4,4'-dicarboxylates)
—~O•(CH₂)_n•O•OC•φ•NH•(CH₂)₂•NH•φ•CO—
- Poly(alkylene sulphonyl-4,4'-divalrates)
—O•(CH₂)_n•O•OC•(CH₂)₄•SO₂•(CH₂)₄•CO—
- Poly(alkylene diglycollates)
—O•(CH₂)_n•O•OC•CH₂•O•CH₂•CO—
- Poly(alkylene carboxylates)
—(CH₂)_n•CO•O—
- Poly(*p*-phenylenedialkyl adipates)
—O•(CH₂)_{n/2}•φ•(CH₂)_{n/2}•O•OC•(CH₂)₄•CO—
- Poly(alkylene ethylenedisulphonyl-4,4'-divalrates)
—O•(CH₂)_n•O•OC•(CH₂)₄•SO₂•(CH₂)₂•SO₂•(CH₂)₄•CO—
- Poly(ethylene alkylene-4,4'-dibenzoates)
—O•(CH₂)₂•O•OC•φ•(CH₂)_n•φ•CO—

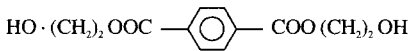
Note that in series 3 and 10 the value of n in the table is the total number of methylene groups in the glycol portion of the repeat unit.

petroleum fractions by the process of reforming, and this is today the principal route to the acid.

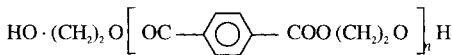
As shown in the introductory section to this chapter, polyesters may be produced in many ways, one of which is the method of ester exchange. This has been of importance in the manufacture of linear polyesters for a number of reasons which include the following:

- (1) In many cases simple esters are more easily purified than their intractable parent acids. For example, *p*-xylene is difficult to obtain in pure form because of the closeness of its boiling point to the other isomeric xylenes (*o*-144°C; *m*-138.8°C; *p*-138.5°C). It is thus difficult to produce terephthalic acid, which sublimes at 300°C, in a pure form.
- (2) Esters are usually lower melting (e.g. dimethyl terephthalate melts at 142°C) and are more miscible with other components.
- (3) Condensation reactions may be faster.
- (4) Reaction mechanisms may be different and involve more desirable catalysts.

In the case of ester exchange for the manufacture of poly(ethylene terephthalate), a low molecular weight diester, known as 'the monomer', is first prepared by reacting 1 mol of dimethyl terephthalate with about 2.1–2.2 mol ethylene glycol at about 150°C in the presence of catalysts such as antimony trioxide and cobaltous acetate:

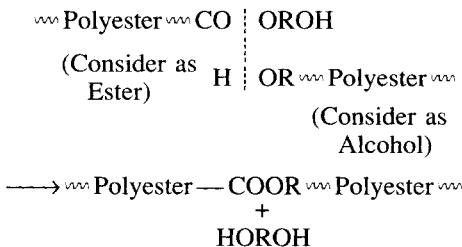


In addition to this diester, di-2-hydroxyethyl terephthalate, some oligomers of general structure:



Where $n = 1, 2, 3$

are also produced. Methanol formed during the condensation is removed using a distillation column. The 'monomer' is then heated to 270–285°C with removal of volatiles under reduced pressures down to 1 mmHg. This invokes an 'alcoholysis reaction' which is useful in that it enables high molecular mass material to be achieved with a non-equivalence of monomer:



This reaction may involve complex catalyst systems.

In recent years, however, the ester exchange reaction has been decreasingly used, with manufacturers now usually preferring to use direct acid glycol condensation with purified terephthalic acid.

PET suitable for bottle manufacture is produced by a modified process. Here the high-viscosity polymer melt is subjected to a rapid quenching in water to produce clear amorphous pellets. These are further polymerised in the solid phase at temperatures just below the T_m . This is useful to reduce aldehyde content, since aldehyde-forming degradation reactions occur less in the lower temperature solid phase polymerisations. Aldehydes can impart a taste to beverages and it is important to keep the aldehyde content to below 2.5 p.p.m.

The process is also being increasingly modified by copolymerising with isophthalic acid (IPA) or cyclohexanedimethanol (CHDM) to improve clarity, toughness and barrier properties, properties of particular importance in bottle and film applications (see Section 25.5).

Some data on the crystallinity of poly(ethylene terephthalate), together with its T_g , are given in *Table 25.5*. Whilst the melting point is similar to that of another important fibre-forming polymer, nylon 66, the glass transition temperature (variously reported between 67 and 80°C) is somewhat higher. This stresses the point that the relationship between T_g and T_m suggested in Chapter 4 is not a perfect one. It is also clear that in order to produce fibres and films, orientation must take place above the T_g and below the T_m , i.e. a process of hot drawing is necessary.

The solubility parameter of poly(ethylene terephthalate) is about 21.8 MPa^{1/2} but because it is a highly crystalline material only proton donors that are capable of interaction with the ester groups are effective. A mixture of phenol and tetrachloroethane is often used when measuring molecular weights, which are about 20 000 in the case of commercial polymers.

Although it is a polar polymer, its electrical insulating properties at room temperature are good even at high frequencies owing to the fact that since room temperature is well below the transition temperature dipole orientation is severely restricted. Some data on the crystallinity of poly(ethylene terephthalate) are presented in *Table 25.5*.

Table 25.5 Crystallinity data for poly(ethylene terephthalate)

Molecular configuration	almost completely extended
Cell dimensions	$a = 4.56 \text{ \AA}$ $b = 5.94 \text{ \AA}$ $c = 10.75 \text{ \AA}$ (chain axis)
Density of cell	1.47 g/cm ³
Amorphous density	1.33 g/cm ³
Density of oriented polymer	1.38–1.39 g/cm ³
Density of crystalline polymer (unoriented)	~1.45 g/cm ³
Crystalline melting point (T_m)	265°C
Maximum rate of crystallisation—at	170°C
Glass transition temperature (T_g)	67°C

Poly(ethylene terephthalate) film is produced by quenching extruded film to the amorphous state and then reheating and stretching the sheet approximately three-fold in each direction at 80–100°C. In a two-stage process machine direction stretching induces 10–14% crystallinity and this is raised to 20–25% by

transverse orientation. In order to stabilise the biaxially oriented film it is annealed under restraint at 180–210°C, this increasing the crystallinity to 40–42% and reducing the tendency to shrink on heating.

Some typical properties of commercial poly(ethylene terephthalate) film, e.g. Melinex (ICI), Mylar (Du Pont), are given in Table 25.6.

Table 25.6 Typical properties of polyester films (ASTM Test Methods)

Property	Units	Poly(ethylene terephthalate)	Kodel
Specific gravity	—	1.39	1.226
Tensile strength	10 ³ lbf/in ² MPa	17–25 117–173	10–17 69–117
Elongation at break	%	50–130	45
Dielectric strength	V/0.001 in kV/cm	4000 1580	>4000 >1580
Dielectric constant (60 Hz)		3.16	3.1
(20°C) (10 ⁶ Hz)		2.98	2.9
Power factor (60 Hz)		0.002	0.005
(20°C) (10 ⁶ Hz)		0.014	0.014
Volume resistivity	Ω	10 ²¹	—
Water absorption (24 h immersion)	%	0.55	0.30

The principal uses of poly(ethylene terephthalate) film are electrical, particularly in capacitors, as slot liners for motors and for recording tape. Its high strength and dimensional stability have led to a number of drawing office applications. The film is also a useful packaging material whilst metallised products have a number of uses as a decorative material.

With one exception no other high molecular weight linear polyesters have achieved any sort of commercial significance for films and fibres. The one exception is the condensation polymer of dimethyl terephthalate and 1,4-cyclohexylene glycol (also known as 1,4-cyclohexanedimethanol) (Figure 25.19).

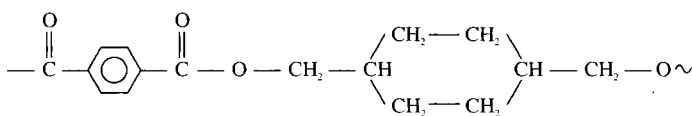


Figure 25.19

This polymer has a slightly stiffer chain and hence slightly higher melting point and heat distortion temperatures than poly(ethylene terephthalate). Films are available (Kodel–Kodak) which have been biaxially stretched about 200% from polymer with molecular weights of about 25 000. They are similar electrically to poly(ethylene terephthalate), are weaker mechanically but have superior resistance to water and in weathering stability.¹² Some properties are given in Table 25.6.

Fibres are also available from poly-(1,4-cyclohexylenedimethylene terephthalate) and are marketed as Kodar (Kodak) and Vestan (Hüls).

25.5 POLY(ETHYLENE TEREPHTHALATE) MOULDING MATERIALS

In 1997 it was estimated that global production of PET was about 16.7×10^6 t.p.a., of which 12 million tonnes was used in textiles, 2 million tonnes for audio and video film (with a small quantity for technical mouldings) and 3 million tonnes for packaging, particularly bottles. The tremendous growth in the bottles market from zero in the late 1970s to 1.5 million tonnes in the USA alone in 1998 is, in consumption terms, one of the most spectacular examples of growth in plastics materials in recent times and will be considered later in this section.

Because of its rather high transition temperature (of about 80°C) only a limited amount of crystallisation can occur during cooling after injection moulding poly(ethylene terephthalate). Such mouldings are transparent and amorphous and are of little value. When they are heated above 80°C crystallisation can occur and they show considerable distortion, shrinkage and clouding. Injection moulding is also difficult because of the sensitivity of melts to traces of moisture.

For this reason the idea of moulding poly(ethylene terephthalate) was for many years not a technical proposition. However, developments with nucleating agents in the early 1960s led to the production in 1966 of semi-finished products such as rod and pipe by a continuous casting process developed by Glanzstoff-AG of Obernburg/Main. These materials had a high hardness, creep resistance and rigidity, with a water absorption similar to that of acetal resins, but have a disadvantage of sensitivity to hot water and alkaline solutions.

In the same year AKZO introduced a poly(ethylene terephthalate) moulding and extrusion material known as Arnite PETP. This material was one of several introduced in the mid-1960s as engineering thermoplastics; others include the polysulphones, phenoxies and poly(phenylene oxide) (all considered in Chapter 21). The principal properties claimed for Arnite PETP are its high gloss, hard scratch resistance surface and a high rigidity. Some of its properties are given in Table 25.7.

The moulding of Arnite PETP must be carried out with dried material and because of the free-flowing nature of the melt, restricted nozzles should be used

Table 25.7 Some properties of poly(ethylene terephthalate) moulding material ('Arnite') (ASTM Test Methods unless otherwise stated.)

Property	Value	Units
Specific gravity	1.37–1.38	
Crystalline melting point (VPV)	250–255	$^\circ\text{C}$
Moisture absorption (in water)		
24 h at 23°C	0.02	%
2 h at 100°C	0.10	%
Vicat softening point	261	$^\circ\text{C}$
Tensile strength (at yield)	71.5	MPa
(at break)	52.9	MPa
Izod impact strength	0.8	ft lbf in $^{-1}$ notch
Rockwell hardness (<i>M</i> scale)	106	
Dielectric constant 10^6 Hz	3.37	
Dissipation factor 10^3 Hz	0.0055	
10^6 Hz	0.0208	

and a back flow valve fitted to screw injection moulding machines. Cylinder temperatures are about 260°C and mould temperatures as high as 140°C to promote a controlled crystallisation. Because of this high temperature it is generally recommended that the mould be thermally insulated from the locking mechanism and other machine parts.

An interesting feature of poly(ethylene terephthalate) is that according to the moulding conditions two quite dissimilar products, one amorphous, the other transparent, may be obtained, this being a consequence of having a T_g of about 80°C. For both types, however, there are certain common points to be observed. As with other polymers that are slightly hygroscopic *and* which require high melt temperatures the granules must be thoroughly dry, particular care being necessary with reworked material. In addition, because of the low melt viscosity injection, moulding screws should be fitted with back flow valves and the barrel nozzles should have shut-off valves. Melt temperatures are of the order of 260°C.

To produce amorphous transparent mouldings, mould temperatures should be kept well below the T_g , a temperature of less than 50°C generally being recommended. Providing that wall thicknesses do not exceed 5–6 mm the melt cools very rapidly and there is not enough time for significant crystallisation to occur in the short time interval that the material is between T_m and T_g . With thicker sections it may not be possible to extract the heat out of the melt at a sufficient rate and some crystallisation may occur. It is also important to use grades which do not contain additives that accelerate crystallisation. Amorphous mouldings should not be used above T_g .

Crystalline, opaque, mouldings are produced by using a mould temperature of about 130°C and grades containing crystallisation 'accelerators'. The crystalline grades retain their shape up to temperatures near to T_m and therefore for many applications may be used above T_m .

In spite of the introduction of Arnite PETP the use of poly(ethylene terephthalate) as a moulding material remained at a low level for many years. In the 1970s it became recognised that reinforcement of the polymer with glass fibre had an even greater influence on modulus and rigidity than with other engineering plastics. For example, at 23°C and 50% RH the flexural modulus of unfilled crystalline poly(ethylene terephthalate) is slightly less than that of a polyacetal. On the other hand, at a glass-fibre loading of 30% the modulus of the polyester is some 10% higher (11 000 MPa c.f. 10 000 MPa). At 50% fibre loading the modulus is as high as 15 000 MPa.

By the late 1980s it was estimated that 90% of crystalline PET moulding materials were glass filled. Their major use was in electrical and electronic applications. Thin, complex sections such as transformer bobbins may be formed easily because of the ease of flow of the polymer even when fibre filled. These materials have also been used for the housings and components for toasters, coffee machines, industrial plugs and sockets, car heater housings and water meter housings. Tougher grades are used for car grilles and fuel filler flaps. Amorphous grades are used mainly for bottles.

Towards the end of the 1970s Du Pont introduced Rynite. This is a poly(ethylene terephthalate) nucleated with an ionomer, containing a plasticiser (thought to be n-pentyl glycol dibenzoate) and only available in glass-fibre-filled form (at 30, 45, and 55% filler levels). Although T_g is slightly reduced, due to the presence of the plasticiser, to about 55–60°C the polymer is very rigid, exceeding that of a polysulphone. It is less water sensitive than an unfilled polymer. Apart

from its poor tracking resistance, a common feature of many highly aromatic polymers, its electrical properties are generally good whilst, as with the Arnite-type materials, fire-retarding grades are now available.

In the late 1970s the benefits of biaxial stretching of poly(ethylene terephthalate) were extended from sheet film to bottle manufacture. As a result important new markets were opened. For some years the plastics industry had made great efforts to secure part of the market for the packaging of carbonated beverages. In the early 1970s it seemed that this hope would be fulfilled by the use of the nitrile resins (Chapter 16) but toxicity problems largely associated with residual acrylonitrile made this impossible. Fortunately the recognition that nitrile resins could no longer be considered for this market coincided with the development of techniques for bottle blowing poly(ethylene terephthalate). In 1978 estimates for USA consumption of poly(ethylene terephthalate) for bottles were in the range 68 000–86 000 tonnes. By 1998 the corresponding figure was 1 430 000 tonnes. As discussed in the previous section, this involves special polymer grades and, as was also mentioned, copolymers with isophthalic acid or cyclohexanedimethanol are being increasingly used to improve clarity, toughness and barrier properties. Whilst the USA market has been dominated by the carbonated beverage market the process has been extended, particularly in Europe, to produce bottles for other purposes such as fruit juice concentrates and sauces. Wide-necked jars, for coffee and for other materials, also made their appearance.

Success in bottle blowing involves first the production of a substantially amorphous parison by *injecting* into a cold mould. The parison is then withdrawn from the mould, heated (for example by infrared heaters) and subjected to a stretch-blow process that biaxially stretches the parison, giving a thin-wall containers of high strength and toughness combined with a low permeability to oxygen and carbon dioxide. Further reductions in gas permeability may be achieved using multi-layer parison extrudates. For example, in Britain PET bottles coated with vinylidene chloride-based copolymers are used for packaging beer. There has also been some interest in poly-*m*-xylylene adipamide (see Chapter 18) and, more particularly, ethylene–vinyl alcohol copolymers as barrier materials.

A further substantial development, although not on the scale of the bottle and film markets, had been the use of thermoformed PET sheet for menu trays. The high heat distortion temperature of 220°C allows these products to be used in both traditional and microwave ovens.

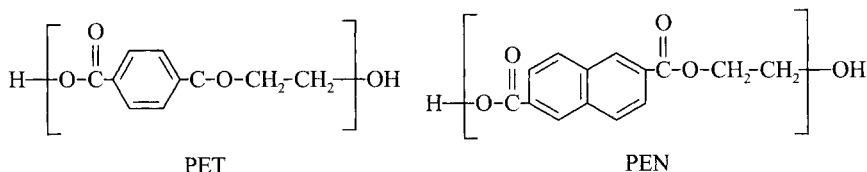
In attempts to reduce the T_g of PET and hence facilitate injection moulding a number of copolymers based on PET have been prepared. Thus a copolyester containing 3-methylpentane-2,4-diol was found to give much slower crystallisation rates during moulding operations. The use of isophthalic acid as a partial replacement for terephthalic acid also retards crystallinity and this has been used commercially with 1,4-cyclohexylene glycol instead of ethylene glycol (see Section 25.7). The considerable success of PET for making bottles and similar products, together with continuing demand for PET film, had led to an upsurge in companies supplying PET materials. By 1987 nine companies were supplying PET materials in Western Europe for injection moulding, seven for bottle manufacture and eight for film.

As with many other plastics materials being manufactured in a large number of countries statistics for capacity and usage are subject to considerable uncertainty. One estimate was that in 1997 capacity for making 'container' grades was about 6 000 000 t.p.a. with consumption at about 4 000 000 t.p.a.

Other estimates placed the film and bottle market to be of a similar size in Japan while globally the bottle market was about 20% of the total. Together with other data this suggests that the fibre and filament market absorbs about 72% of PET capacity, containers about 19%, film about 7% and mouldings 2%. Considerable quantities of PET bottles are, however, recycled into fibres for use, for example, in outdoor clothing.

25.5.1 Poly(ethylene naphthalate) (PEN)

As long ago as the 1940s it was known that poly(ethylene naphthalate) had higher temperature resistance, higher tensile strength, higher UV resistance and better oxygen and water barrier properties than poly(ethylene terephthalate). Commercial interest only became significant when, in the late 1980s, Amoco commenced manufacture of the precursor dimethyl-2,6-naphthalene dicarboxylate increasing their nameplate capacity to 27 000 t.p.a. in 1998. By 1989 Shell were producing PEN in commercial quantities (Hipertuf) and by the late 1990s they were joined by 3M, Du Pont, Eastman and ICI.



Structurally the difference between PEN and PET is in the double (naphthenic) ring of the former compared to the single (benzene) ring of the latter. This leads to a stiffer chain so that both T_g and T_m are higher for PEN than for PET (T_g is 124°C for PEN, 75°C for PET; T_m is 270–273°C for PEN and 256–265°C for PET). Although PEN crystallises at a slower rate than PET, crystallization is (as with PET) enhanced by biaxial orientation and the barrier properties are much superior to PET with up to a fivefold enhancement in some cases. (As with many crystalline polymers the maximum rate of crystallisation occurs at temperatures about midway between T_g and T_m in the case of both PEN and PET). At the present time PEN is significantly more expensive than PET partly due to the economies of scale and partly due to the fact that the transesterification route used with PEN is inherently more expensive than the direct acid routes now used with PET. This has led to the availability of copolymers and of blends which have intermediate properties.

The copolymers are prepared using a mixture of dimethyl terephthalate and dimethyl naphthalate. Published data indicates a reasonably linear relationship between T_g and copolymer composition on the lines discussed in Section 4.2, e.g. T_g for a 50:50 copolymer is about 100°C which is about mid-way between T_g figures for the two homopolymers. In line with most other copolymers there is no such linearity in the crystalline melting point (T_m). As comonomer levels are introduced T_m drops from the values for both homopolymers and indeed crystallisation only readily occurs where one of the components is dominant, i.e. 80%. Thus commercial copolymers are usually classified into two types:

- (a) low terephthalate ('low tere') copolymers which may be considered as being effectively >80% PEN in nature;

(b) high terephthalate ('high tere') copolymers which may be considered as being >80% PET in nature.

Blends are created by physically mixing two or more different resins in varying amounts. While in theory it may be considered that the PEN and PET molecules will be separate entities in the mix it has been reported that substantial transesterification can occur during prolonged melting in an extruder leading to block polymers whose block length would, presumably, decrease with melt mixing time. Considerable development effort has been required to produce blends of acceptable quality.

As with PET, the market for PEN is in three main areas:

- (a) fibres;
- (b) films;
- (c) bottles and other blown containers.

While detailed discussion of the merits of PEN fibres is largely outside the scope of this book mention may be made of the success in preliminary trials of (yacht) sailcloths made from PEN fibre. PEN fibres have a modulus roughly $2.5\times$ that of PET, exhibit excellent flex life and also show very good UV resistance. It is understood that the one yacht fitted with PEN sailcloth in the 1996 Olympics won the gold medal in its event.

Film is said to have been the first commercial application for PEN but has only recently become more widely available (e.g. Kaladex – ICI). The materials are particularly interesting for electrical insulation as a consequence of their very good heat resistance (UL continuous use ratings of 180°C (electrical) and 160°C (mechanical); see Section 9.2.1 for explanation). Film is also being used for purposes where heating may be involved in manufacture and/or service such as flexible warming circuits and battery heaters, business machines with high operating temperatures, tapes and labels and embossing films. PEN is also used in a tape storage cartridge.

However, the greatest interest and potential for PEN is in the blown container market. Replacing PET with PEN increases the range of materials that may be packaged because of the higher process temperatures and lower permeability to gases of the latter. Because of the high material cost the market for homopolymers is largely limited to medical applications due to the sterilizability of the material but there is also potential for use in baby foods (with hot filling possible above 100°C) and for bottled wines and beers. The low terephthalate copolymers, because of their high cost as well as slightly inferior properties to the homopolymers, would also seem to have a limited market. The high terephthalate resins would appear to have the greatest potential in that they are less expensive and widen the end-use envelope sufficiently by allowing hot filling to nearly 100°C. Products of interest include jams, carbonated soft drinks, juices, cosmetics and chemical containers.

The quality of blends is strongly dependent on mixing techniques but encouraging results have been obtained, particularly in respect of improving barrier properties.

25.6 POLY(BUTYLENE TEREPHTHALATE)

The expiry of the original poly(ethylene terephthalate) patents provided the catalysts for developments not only with poly(ethylene terephthalate) but also

with related polymers. As a consequence in the early 1970s many companies became involved in the manufacture of poly(butylene terephthalate), often abbreviated to PBT or PBTP and also known as poly(tetramethylene terephthalate), itself often abbreviated to PTMT.

In the USA producers included Eastman Kodak (Tenite PTMT), General Electric Corporation of America (Valox), and American Celanese (Celanex). In Europe major producers by the end of the decade were AKZO (Arnite PBTP), BASF (Ultradur), Bayer (Pocan) and Ciba-Geigy (Crastin). Other producers included ATO, Hüls, Montedison and Dynamit Nobel. With the total Western European market at the end of the decade only about 7000 tonnes other companies at one time involved in the market such as ICI (Deroton) withdrew.

By 1998, however, the Western European market had grown to over 90 000 t.p.a., that for the United States to about 140 000 t.p.a. and that for Japan to just over 60 000 t.p.a. There are also about a dozen USA and Western European manufacturers. Statistics on capacity are somewhat meaningless, as the polymer can be made using the same plant as employed for the manufacture of the much larger tonnage material PET. It is, however, quite clear that the market for injection moulded PBT is very much greater than that for injection moulded PET.

A large number of grades is available, one supplier alone offering about 40, including unreinforced, glass- and carbon-fibre reinforced, mineral filler reinforced, impact modified, elastomer modified, flame retardant and various combinations of the foregoing.

The polymer is produced by reacting terephthalic acid with butane-1,4-diol. Because of the longer sequence of methyl groups in the repeating unit the chains are both more flexible and less polar than poly(ethylene terephthalate). This leads to lower values for T_m (ca 224°C) and T_g (22–43°C). The advantage of lower processing temperatures is offset by lower heat distortion temperatures. At the 1.86 MPa stress level in the ASTM test for deflection temperature under load values as low as 50–65°C are obtained. Vicat softening points are also lower than for poly(ethylene terephthalate) (170–180°C c.f. 261°C). Typical properties are given in *Table 25.7*. As may be expected from a more hydrocarbon structure, poly(butylene terephthalate) is a somewhat better electrical insulator than poly(ethylene terephthalate). It also has good stability to aliphatic hydrocarbons, alcohols and ethers but is swollen by low molecular weight esters, by ketones and by partially halogenated hydrocarbons.

As with poly(ethylene terephthalate) there is particular interest in glass-fibre-filled grades. As seen from *Table 25.8*, the glass has a profound effect on such properties as flexural modulus and impact strength whilst creep resistance is also markedly improved.

About 90% of the polymer is injection moulded. Like poly(ethylene terephthalate) the polymer is susceptible to hydrolysis so that the granules must be thoroughly dried before moulding. At temperatures above 270°C the material decomposes quite rapidly so that melt temperatures during processing are usually in the range 240–270°C. The low T_g facilitates rapid crystallisation when cooling in the mould, which is typically held about 50°C, and this allows short moulding cycles. High injection speeds are generally recommended, particularly with glass-filled grades, in order to obtain a good finish.

The use of PBT as an engineering material is more a consequence of a balance of good properties rather than of a few outstanding ones. It does not possess the toughness of polycarbonate, the abrasion resistance of an aliphatic polyamide, the heat resistance of a polysulphone, polyketone or poly(phenylene sulphide) or

Table 25.8 Comparative properties of PET, PTT and PBT polymers

<i>Property</i>	<i>Units</i>	<i>PET</i>	<i>PTT</i>	<i>PBT unfilled</i>	<i>PBT 30% glass filled</i>
Specific gravity		1.37–1.4	1.35	1.31–1.34	1.52
Melting point	°C	265	225	228	228
Glass Transition	°C	80	45–75	25	25
Deflection temperature @ 1.8 MPa	°C	65	59	65	223
Notched Izod impact	J/m	37	48	53	85
Tensile strength	MPa	61.7	59.3	56	117
Flexural modulus	GPa	3.11	2.76	2.34	7.6–8.3
Moulding shrinkage	m/m	0.030	0.020	0.020	0.002–0.004
Dielectric constant @ 1 MHz		3.0	3.0	3.1	
Dissipation factor @ 1 MHz		0.02	0.015	0.02	
Rockwell hardness	M scale	106	–	68–85	90

the low water absorption of a modified PPO. As it is a polyester, there will be a substantial number of common chemicals that will either attack it or cause swelling, particularly at temperatures above the T_g .

However, PBT shows a good balance of properties and when it is suitably modified by, for example, glass fibre or fire retardants, some very useful compounds can be produced. The particular characteristics emphasised by the suppliers include:

- (1) High softening temperatures (glass-fibre-filled grades are better than polycarbonates and modified PPOs).
- (2) High rigidity, with some filled grades having a flexural modulus as high as 11 000 MPa, a figure only exceeded by PPS amongst the engineering thermoplastics.
- (3) Good electrical insulation properties with exceptional tracking resistance for an engineering thermoplastic and, in particular, for an aromatic polymer. In tracking resistance most grades are generally superior to most grades of polycarbonates, modified PPOs, PPS and the polyetherimides.
- (4) Low friction and good abrasion resistance.
- (5) Good impact strength at low temperatures and excellent creep rupture strength.
- (6) Low water absorption and good chemical resistance, including resistance to stress cracking.
- (7) Good dimensional stability, partially as a consequence of the low water absorption but also because of a low coefficient of thermal expansion.
- (8) Capability of compounding to give UL94 V-0 flammability ratings.
- (9) Good mouldability, with easy flow and rapid setting.

It should, however, be noted that good flame retardancy is only achieved with the use of flame retardant additives and that some of the best of these, such as the brominated diphenyls and brominated diphenyl ethers, are restricted in their use in some countries.

PBT has tended to replace polyamides in a number of precision parts due to its better dimensional stability.

Poly(butylene terephthalate) finds use as an engineering material on account of its dimensional stability, particularly in water, and its resistance to hydrocarbon oils without showing stress-cracking. The stiffness of glass-filled grades is also of some importance. Typical applications include pump housings, impellers, bearing bushings, gear wheels and in measuring equipment.

As with poly(ethylene terephthalate) PBT-based copolymers have been introduced to overcome some of the deficiencies of the homopolymer. For example, the rather low notched impact strength of unreinforced grades has been overcome by partial replacement of the terephthalic acid with a longer chain aliphatic dicarboxylic acid. Improved toughness has also been obtained by grafting about 5% of ethylene and vinyl acetate onto the polyester backbone.

There has also been active interest in blends of PBT with other polymers. These include blends with PMMA and polyether-ester rubbers and blends with a silicone/polycarbonate block copolymer.

Blends of PBT with polycarbonates have been widely used for car bumpers. Interest in PBT/PET blends and PBT/ASA has arisen because of the good surface finish possible even with glass-reinforced grades. Copolyesters based on PBT but with some longer chain diol or acid are also now produced.

In the late 1990s it has been estimated that in Western Europe the market share was:

Electronics/electrical applications	34%
Automotive applications	40%
Household goods	9%
Other	17%

Amongst the diverse uses in the electrical/electronics field are coil formers, miniature circuit breakers, picture-tube mountings, edge connectors and telephone distribution boxes.

In the automotive sector PBT compounds are widely used for small interior mouldings such as ashtrays, foot pedals, door handles and safety belt components, whilst external uses include windscreen wipe holders and exterior mirror housings. There has also been extensive use of PBT/PC blends for bumpers but these have more recently tended to be replaced by polypropylene. To counter this development at least one manufacturer has used ABS as an impact modifier to produce a more competitive material.

Business machinery applications include keys for keyboards, typewriter ribbon guides, plug and socket connectors and optical cable sheathing.

In household applications PBT has found use not just because of its high heat distortion temperature, rigidity, very good electrical insulation properties and dimensional stability but also because of the resistance of the material to many liquids and chemicals encountered in the home. These include detergents and cleaners, oils and fats, fruit and vegetable juices, beverages, many foodstuffs and spices. Established applications include oven door handles, component parts of coffee makers and deep friers, electric iron housings, styling hair brush components and heated hair curlers.

Miscellaneous uses include textile bobbins, guns for hot melt adhesives and bilge pump housings. These materials are normally found in reinforced form. In addition to glass fibres, other fillers such as glass beads, talc and mica are used in conjunction with coupling agents.

Carbon-fibre-filled grades exhibit interesting tribological properties and useful antistatic behaviour.

Blends with polybutadiene rubber as the disperse phase have improved toughness but show only moderate thermal aging. Newer grades have been achieved by impact modification using cross-linked acrylic materials. Although these show better heat aging, they do not have such good impact properties as the polybutadiene-modified grades.

25.7 POLY(TRIMETHYLENE TEREPHTHALATE)

Although poly(trimethylene terephthalate) has been known for many years it was only introduced by Shell in the late 1990s as a consequence of a breakthrough in the synthesis of the monomer 1,3-propane diol which enabled the polymer to be produced at costs suitable for commercialisation. The polymer itself is prepared by melt condensation of the diol with terephthalic acid.

In line with the common observation of condensation or rearrangement polymers containing an odd number of methylene groups in the repeat unit, T_m is less than that for PET and PBT but as shown in *Figure 25.14* is only very slightly less than for PBT.

In most respects PTT can be considered as intermediate in properties between PBT and PET but does appear to possess two special properties:

- (1) The repeat length in the triclinic polymer crystals (75.3 nm) is significantly less than for PBT (86.3 nm) and PET (99.5 nm). This has been claimed to make the crystal more spring-like in the long axis resulting in enhanced resilience and wear resistance in carpet fibres to a level approaching that of polyamide fibres.
- (2) Glass-filled grades have a higher flexural modulus than corresponding PBT and PET materials (For 30%w/w glass-filled PTT the modulus is quoted as 10.35 GPa, for PBT 7.60 GPa and for PET (at the slightly lower glass content of 28%) 8.97 GPa.

As is common for crystalline thermoplastics the deflection temperature of unfilled grades is similar to T_g (quoted as being in the range 45–70°C) while for glass-filled grades it is much closer to the T_m of 225°C.

25.8 POLY-(1,4-CYCLOHEXYLENEDIMETHYLENETEREPHTHALATE) (PCT)

Replacement of ethylene glycol with 1,4-cyclohexylene glycol (also known as cyclohexane dimethanol) gives a polymer with a regular structure but a somewhat stiffer chain than PET. Such a semicrystalline polymer has a T_m of about 289°C compared with about 250°C for PET. In turn this gives, for the commercial 30% glass-filled grade (Valox 9731—General Electric), a Vicat B50 softening point of 270°C and a deflection temperature under load at 0.45 MPa of 275°C (both about 50°C higher than PET). Perhaps surprisingly the deflection temperature under 1.8 MPa load at 200°C is very similar to that for a typical PET compound.

More to be expected of a more hydrocarbon polymer than PET is a somewhat lower water absorption, typically about 70% that of PET. With appropriate flame retardants, grades can have a UL V-0 rating at 0.8 mm thickness.

Since PCT is sensitive to hydrolysis at the high moulding temperatures, it must be thoroughly dried before moulding for 4–6 h at 65–70°C in a desiccant dehumidifying drier. Typical melt temperatures for moulding are 295–310°C, and mould temperatures can range from 65 to 135°C, although for the important circuit board components temperatures of 95–120°C are used to reduce post-moulding shrinkage and optimise surface finish.

PCT may be used for the production of electronic and automotive components such as circuit board components, connectors, switches and relays, and alternator armatures and pressure sensors. The main application has been in the fabrication of surface-mount connectors that can withstand infrared reflow soldering operations.

25.8.1 Poly-(1,4-Cyclohexylenedimethyleneterephthalate-co-isophthalate)

In 1972 Eastman Kodak introduced a copolymer produced by reacting 1,4-cyclohexylene glycol with a mixture of isophthalic and terephthalic acids. Thus the polymer contains 1,4-cyclohexanedimethoxy units (I), terephthalic acid units (II) and isophthalic acid units (III) (*Figure 25.20*).

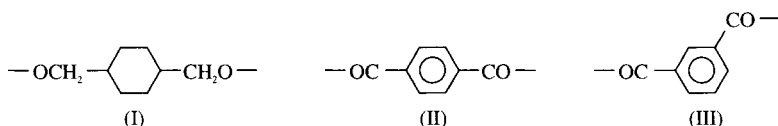


Figure 25.20

The copolyester was first marketed as Tenite Polyterephthalate 7DRO but is now sold as Kodar PETG.

Being irregular in structure the polymer is amorphous and gives products of high clarity. In spite of the presence of the heterocyclic ring the deflection temperature under load is as low as that of the poly(butylene terephthalates) and is also slightly softer. Some typical properties are given in *Table 25.9*.

Early interest in the material centred round the ability of the polymer to be thermoformed at draw ratios as high as 4:1 without blushing or embrittlement. Because of its good melt strength the material performs well during extrusion blow-moulding whilst the low moulding shrinkage facilitates injection moulding.

Table 25.9 Typical properties of the copolyester Kodar PETG

<i>Property</i>	<i>Units</i>	<i>Value</i>
Specific gravity	—	1.2
Transparency (film)	%	70–80
Deflection temperature (at 1.86 MPa stress)	°C	68
Yield strength	MPa	51.3
Elongation at break	%	210
Flexural modulus	MPa	2100
Rockwell hardness	R-scale	108
Impact strength (unnotched)		no break

A similar product is Kodar PETG 6703 in which one acid (terephthalic acid) is reacted with a mixture of glycols (ethylene glycol and 1,4-cyclohexylene glycol). A related glass-reinforced grade (Ektar PCTG) has also been offered.

25.9 HIGHLY AROMATIC LINEAR POLYESTERS

It has already been shown (e.g. Chapters 20 and 21) that the insertion of a *p*-phenylene into the main chain of a linear polymer increased the chain stiffness and raised the heat distortion temperature. In many instances it also improved the resistance to thermal degradation. One of the first polymers to exploit this concept commercially was poly(ethylene terephthalate) but it was developed more with the polycarbonates, polysulphone, poly(phenylene sulphides) and aromatic polyketones.

During the period of development of these materials work proceeded on heat-resistant polyesters. It was found, for example, that reaction of resorcinol with terephthalyl chloride gave a polymer that showed no signs of melting below 500°C (Figure 25.21).

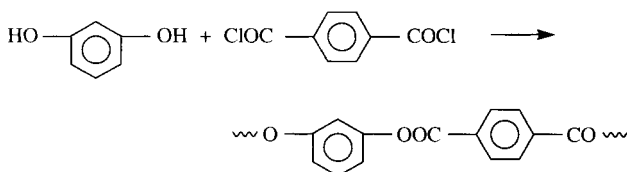


Figure 25.21

The polyester made by reacting hydroquinone with terephthalic acid also melted above 500°C. That from bis-phenol A and 4,4'-(2,2-butylidene)dibenzoic acid is said to be stable in nitrogen to above 400°C.

In the 1960s the Carborundum company introduced the polymer Ekonol P-3000. This was the polymer of *p*-hydroxybenzoic acid (I) (Figure 25.22), in practice produced by the self-ester exchange of its phenyl ester to prevent decarboxylation. A blend with PTFE, Ekonol T-4000, was also produced.

A number of related copolymers were also introduced. Ekkcel C-1000 contained the units (I), (II) and (III) whilst Ekkcel I-2000 contained the units (I), (IV) and (V) (Figure 25.22).

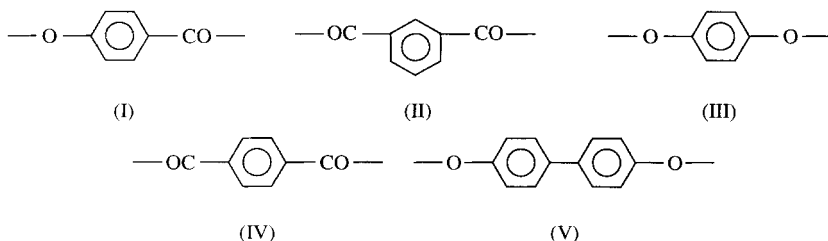


Figure 25.22

The homopolymer (I) (Figure 25.22) had an average molecular weight of 8–12 000. It is insoluble in dilute acids and bases and all solvents 'up to their boiling points'. The polymer also has a high level of thermal stability. The weight loss after 200 h at 260°C is 1% and at 400°C it is 1% per hour. The limiting oxygen index is about 37%. Some typical properties are given in Table 25.10.

The homopolymer is difficult to fabricate and has been shaped by hammering (like a metal), impact moulding and pressure sintering at 420°C and 35 MPa pressure. The copolymers are somewhat easier to fabricate. The difficulty in fabrication has severely limited the development of these polymers.

Table 25.10 Typical properties of commercial polyhydroxybenzoate and related copolymers

Property	Units	Homopolymer (Ekonol P-3000)	Copolymers	
			(Ekkcel C-1000)	(Ekkcel I-2000)
Specific gravity	—	1.45	1.35	1.40
Deflection temperature under load (1.86 MPa)	°C	>550	370	413
Tensile strength				
at 23°C	MPa		70	99
at 260°C	MPa		21	21
Flexural modulus				
at 23°C	MPa	510	3200	4900
at 260°C	MPa		880	1410
Water absorption (24 h)	%	0.02	0.04	0.025
Dielectric constant at 1 kHz	—	3.28	3.68	3.16

With a somewhat lower level of heat resistance but with many properties that make them of interest as engineering materials alongside the polycarbonates, polysulphones, poly(phenylene sulphides) and polyketones are the so-called *polyarylates* which are defined as polyester from bis-phenols and dicarboxylic acids.

One such material is the copolymer first marketed by the Japanese company Unitika in 1974 as U-Polymer and more recently by the Belgian company Solvay as Arylef and Union Carbide as Ardel. (Around 1986 the Union Carbide interest in Ardel, as well as in polysulphones, was taken over by Amoco.) Similar polyarylates have since been marketed by Hooker (Durel), Bayer (APE) and DuPont (Arylon). This is a copolyester of terephthalic acid, isophthalic acid and bis-phenol A in the ratio 1:1:2 (Figure 25.23).

The use of the two isomeric acids yields an irregular chain inhibiting crystallisation. This has two consequences:

- (1) The absence of a T_m allows the material to be processed at much lower temperatures than would be possible with a crystalline homopolymer using only one of the acids.
- (2) Unfilled polymer is transparent.

The high concentration of aromatic rings nevertheless assures a high T_g , variously quoted as being between 173 and 194°C. As with other polymers of

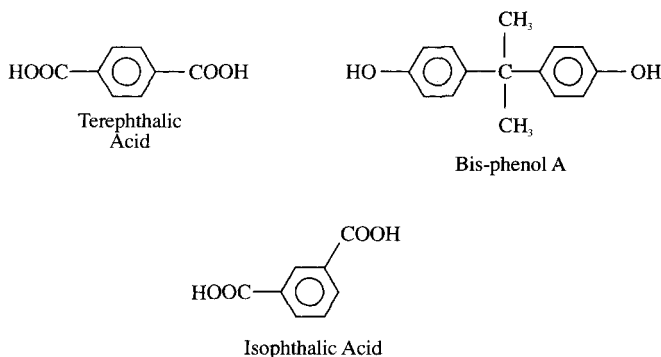


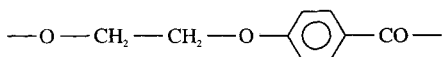
Figure 25.23

high C:H ratios the polymer is self-extinguishing, with a limiting oxygen index of 34 and a self-ignition temperature of 545°C. The Underwriters Laboratories gives it a V-0 classification. Typical properties are given in *Table 25.11*. Amongst specific characteristics that should be noted are the following:

- (1) The polymer has an impact strength between that of a polycarbonate and a polysulphone.
- (2) It shows an exceptionally high level of recovery after deformation that is exploited in several applications such as clips and snap fasteners.
- (3) The abrasion resistance is superior to that of polycarbonates.
- (4) The heat deflection temperature under load is equal to that of a polysulphone.
- (5) A somewhat low Underwriters' Laboratories Temperature Index rating of 120–130°C.
- (6) Some rather unusual reactions to ultraviolet light.

The aryl ester structure of polyarylates is also found in certain ultraviolet stabilisers such as resorcinol monobenzoate. Initially these compounds are not good ultraviolet stabilisers but on exposure they rearrange by means of the photo-Fries reaction to *o*-hydroxy benzophenone structures which offer good ultraviolet stabilisation. Similar rearrangements have been found to occur in polyarylates, and after rearrangement polyarylates have been found to have excellent ultraviolet stability, although the rearrangement causes some surface yellowing, precluding use in 'water-white' applications. Patents have been taken out (e.g. USP 4 259 458) for blending polyarylates with other polymers (such as PET) to improve the ultraviolet stability of the latter.

Of a somewhat lower level of heat resistance is poly(ethyleneoxy benzoate), which has the structure:



The material was marketed as a fibre in 1968 jointly by the Japanese companies Unitika and Mitsubishi as A-Tell. The polymer is about 41% crystalline, and has a specific gravity of 1.34, a T_m of 223°C and a T_g of 65°C. The fibres are somewhat silk-like in character.

Table 25.11 Principal characteristics of the polyarylate Arylef U100

<i>Properties</i>	<i>Methods of measurement</i>	<i>Values</i>
<i>General properties</i>		
Density	ASTM D 1505	1.21 mg/m ³
Water absorption 24 h at 23°C	ASTM D 570	0.26%
30 d at 23°C		0.71
Shrinkage on moulding	ASTM D 905	0.009 mm/mm
Refractive index n_D^{23}	ASTM D 542	1.61
<i>Mechanical properties</i>		
<i>Tensile</i>		
Tensile stress at yield		71 MPa
Elongation at yield	ASTM D 638	8%
Elongation at break		50
Elasticity modulus		2000 MPa
<i>Bending</i>		
Flexural strength	ASTM D 790	81 MPa
Bending modulus		2000 MPa
<i>Compression</i>		
Compressive strength	ASTM D 695	94 MPa
Modulus in compression		2050 MPa
<i>Impact strength</i>		
Notched Izod impact strength (3.2 mm bar)	ASTM D 256	220 J/m
Impact strength in tension	ASTM D 1822	260–360 kJ/m ²
<i>Hardness</i>		
Rockwell	ASTM D 785	R 126, M 95
<i>Thermal properties</i>		
Deflection temperature under load (1.8 MPa)	ASTM D 648	175°C
Coefficient of linear expansion (–30°C to +30°C)	ASTM D 696	$6.2 \times 10^{-5} \text{ K}^{-1}$
Specific heat 20–300°C		$1.3 \text{ kJ kg}^{-1} \text{ K}^{-1}$
>300°C		$3.4 \text{ kJ kg}^{-1} \text{ K}^{-1}$
Flammability	{ ASTM D 635 UL 94	SE V-O
Limiting oxygen index	ASTM D 2863	34
Temperature of self-ignition	ASTM D 1929	545°C
<i>Electrical properties</i>		
Dielectric strength	ASTM D 149	30 kV/mm
Dielectric constant 60 Hz		2.73
10 ³ Hz	ASTM D 150	2.71
10 ⁶ Hz		2.62
Volume resistivity at 23°C	ASTM D 257	$3 \times 10^{16} \Omega \text{ cm}$
Surface resistivity (0.03 mm film)	—	$>2 \times 10^{17} \Omega$

25.9.1 Liquid Crystal Polyesters

In Chapter 3 it was pointed out that certain rod-like polymers showed many of the attributes of liquid crystals in the melt. In particular, these molecules were oriented in shear to such an extent that interchain entanglement was small and the melts had a low viscosity. On cooling of the melt these rod-like molecules remained oriented, effectively self-reinforcing the polymer in the direction of flow. The essential differences in the properties of liquid crystal polymers

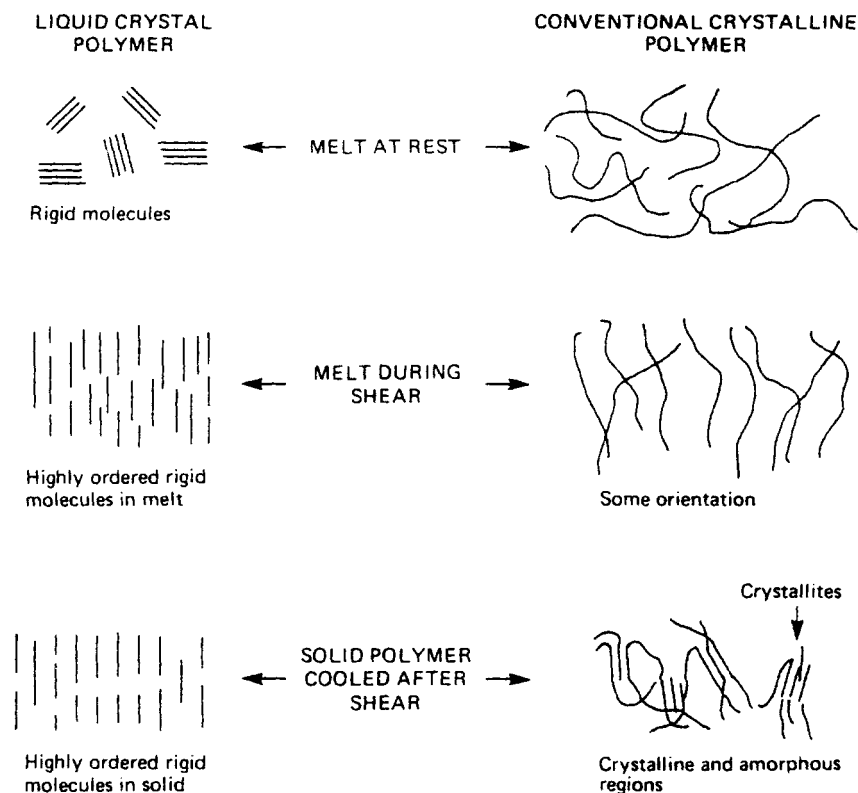


Figure 25.24. Difference in behaviour between liquid crystal polymers and conventional crystalline polymers in the melt at rest, during shear and when cooled after shearing

compared with conventional crystalline thermoplastics are schematically illustrated in Figure 25.24.

These liquid crystal polymers are generally prepared from monomers which are long, flat and fairly rigid along the major axis of the molecule, with the chain-extending linkages being either coaxial or parallel (e.g. ester and amide links). In particular, *p*-linked benzene rings tend to give a rod-like shape and are the predominant components of liquid crystal polymers.

For the liquid crystal polyesters the basic structural units are derived from such materials as *p*-hydroxybenzoic acid, terephthalic acid and hydroquinone. Some basic sequences from such materials are shown in Figure 25.25.

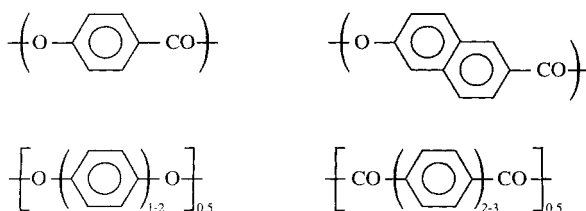


Figure 25.25. Typical sequences found in intractable liquid crystal polymers with $T_m > 400^\circ\text{C}$

However, momomers based on these units alone have extremely high melting points and are intractable. This has led to the use of a variety of techniques to produce more tractable materials which may be processed without degradation whilst retaining many of the features of liquid crystalline materials. These techniques include:

- (1) Frustrated chain packing: in this approach aromatic substituents are pendants attached to the main chain rings.
- (2) Incorporation of flexible aliphatic links, for example by copolymerising with ethylene glycol.
- (3) Incorporation of non-linear rigid links which lead to kinks in the structure. Some examples are illustrated in *Figure 25.26*.

Polymers based on these structures became available as Victrex SRP (ICI), Vectra (Hoechst) and Xydar (Amoco). It is reported that the Vectra materials are based on *p*-hydroxybenzoic acid and hydroxynaphthoic acid monomers, whilst Xydar is based on terephthalic acid, *p*-hydroxybenzoic acid and *pp'*-dihydroxybiphenyl. Whilst properties vary between grades, in general they possess the following outstanding properties:

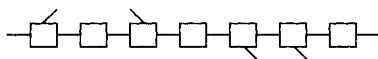
- (1) High continuous use temperatures with a UL thermal index around 215°C.
- (2) High heat distortion temperatures (over a range 170–350°C) for unfilled materials with some further increase with some types when filled with glass or carbon fibre.
- (3) Very low flammability with limiting oxygen indices in the range 35–50 and UL 94 V-0 ratings at as low a thickness as 0.4 mm in some instances, even without fibre reinforcement.
- (4) Low smoke emission (roughly comparable to that of a polycarbonate).
- (5) Very low coefficient of thermal expansion in the flow direction (0–15 cm/cm/°C) but correspondingly higher in the transverse direction (27–76 cm/cm/°C).
- (6) Much lower water absorption than some other heat-resisting thermoplastics such as polysulphones and PEEK (of the order of 0.1% absorption in 24 h at 23°C).
- (7) Excellent mechanical properties with very high values for tensile strength, flexural strength and modulus in the flow direction. This applies to unfilled materials and may be further enhanced by incorporation of fibrous fillers. Quoted data for these properties are in the following ranges:

Tensile strength 165–230 MPa (unfilled); 149–207 MPa (filled).
 Flexural strength 169–256 MPa (unfilled); 207–317 MPa (filled).
 Flexural modulus 9–15.2 GPa (unfilled); 15–24 GPa (filled).

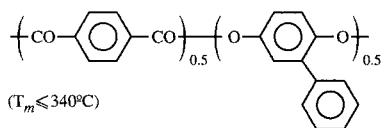
Such is the anisotropy that flexural modulus may be four times as high in the flow direction as in the transverse directions. This difference may be reduced by incorporating fillers such as glass fibre or mica.

- (8) Exceptionally high Izod impact strength of unreinforced grades, with one ICI grade having a quoted notched Izod figure as high as 931 J/m (approx. 18 ft lb/in notch). Fibre reinforcement reduces this figure. It should be stressed that these figures apply to Izod test pieces, where a high level of

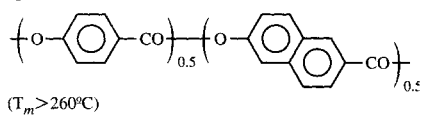
FRUSTRATED CHAIN PACKING



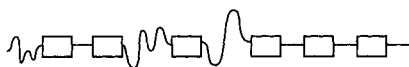
e.g.



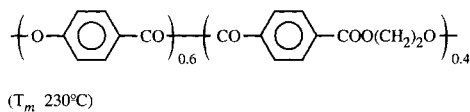
e.g.



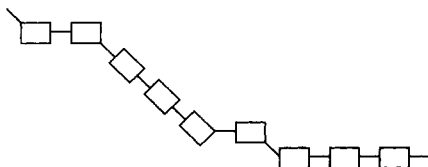
FLEXIBLE (ALIPHATIC) LINKS



e.g.



NON-LINEAR RIGID LINKS



e.g.

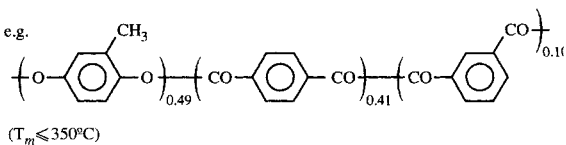


Figure 25.26. Techniques for reducing T_m of liquid crystal polyesters

orientation leads to high values. Quite different results might be expected on tests carried out on flat discs using a falling weight.

- (9) A rather high specific gravity of about 1.40 (unfilled).
- (10) Good electrical insulation properties with a high dielectric strength and good microwave transparency but with a low tracking resistance typical of aromatic polymers with a high C:H ratio in the structure.

The main disadvantages of these polymers are (in addition to the poor tracking properties):

- (1) Poor abrasion resistance of unfilled grades, although special filled grades are available with very good abrasion resistance.
- (2) Very high price, characteristic of very high performance materials.

The materials may be processed on conventional equipment with process temperatures usually below 350°C (and mould temperatures < 100°C). (In the case of Xydar, melt temperatures may be as high as 370–455°C and mould temperatures from 95 to 260°C). The melts have a low viscosity and this may even be exploited by blending some liquid crystal polymer into other engineering polymers (such as PEEK, PVC, nylons and polysulphones) to lower their viscosity and facilitate moulding of intricate sections. Good mould release, fast cycle times, very low mould shrinkage and very low warpage are claimed additional benefits of the material. The raw granules must, however, be thoroughly dried before moulding.

At the time of writing, liquid crystal polymers are in an early stage of exploitation. Potential uses that have been suggested include fibre optic sheathing, rigid data storage discs, moulded circuit boards, connectors and encapsulants. For electronic and fibre optic applications, the low coefficient of expansion is a particularly valuable property, with good mechanical properties, fire retardancy, good barrier properties and ease of processing also being of value. One unusual application has been the replacement of more brittle ceramic packing materials in distillation columns.

It was estimated that in 1987 about 25 companies were involved in the development of liquid crystal polymers, but by 1995 only Hoechst and Amoco were sharing the 3000 t.p.a. global market in the ratio of about 70 : 30.

25.10 POLYESTER THERMOPLASTIC ELASTOMERS

In Chapters 3 and 11 reference was made to thermoplastic elastomers of the tri-block type. The most well known consist of a block of butadiene units joined at each end to a block of styrene units. At room temperature the styrene blocks congregate into glassy domains which act effectively to link the butadiene segments into a rubbery network. Above the T_g of the polystyrene these domains disappear and the polymer begins to flow like a thermoplastic. Because of the relatively low T_g of the short polystyrene blocks such rubbers have very limited heat resistance. Whilst in principle it may be possible to use end-blocks with a higher T_g an alternative approach is to use a block copolymer in which one of the blocks is capable of crystallisation and with a T_m well above room temperature. Using what may be considered to be an extension of the chemical technology of poly(ethylene terephthalate) this approach has led to the availability of thermoplastic polyester elastomers (Hytrel—Du Pont; Arnitel—Akzo).

In a typical preparation dimethyl terephthalate is transesterified with a blend of butane-1,4-diol and a hydroxyl terminated polyether (polytetramethylene ether glycol: PTMEG) of a molecular weight in the range 600–3000. The stoichiometry is such that the formation of relatively long sequences of tetramethylene terephthalate (4GT) are produced which, unlike the polyether segments, have a high melting point. Since the 4GT segments segregate into rigid domains they are referred to as ‘hard’ segments whilst the polyether segments, for the opposite reason, are referred to as ‘soft’ segments. The basic reaction is illustrated by the equation given in *Figure 25.27*.

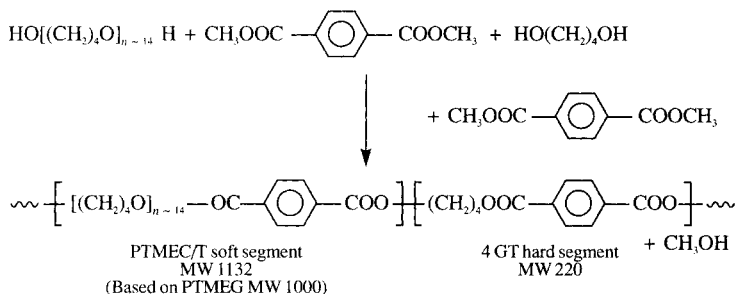


Figure 25.27

In a typical preparation a prepolymer is first prepared by ester exchange of the methyl ester of one or more dicarboxylic acids, usually dimethyl terephthalate, with a mixture of a polymeric diol (e.g. PTMEG) and a 50% excess of a short chain diol in the presence of an ester exchange catalyst. After removal of the methanol formed the reaction mixture is heated to 240–260°C and the pressure in the reaction vessel reduced to 1 mmHg or less. The excess diol is distilled off, this stage proceeding until the polymer melt viscosity no longer continues to increase, this stage taking about 2 hours.

With a typical \bar{M}_n of 25 000–30 000 the molecular size is low compared with most conventional covalently cross-linked elastomers. With such rubbers \bar{M}_n values of about 100 000 are desirable so that the effects of a significant amount of non-load-bearing chain ends do not occur. Such a problem does not arise in block copolymers terminated by hard segments.

In the case of the polycrystalline polyester thermoplastic rubbers the simple domain theory does not seem to apply. With these rubbers it would appear that they contain spherulitic structures consisting of 4GT radial lamellae with inter-radial amorphous regions that are mixtures of PTMEG soft segments and non-crystalline hard segments.

The polymers available range from those with a stiffness similar to that of polypropylene to that of a rather firm rubber. The harder grades have up to 84% of 4GT segments and a T_m of 214°C whilst the softest grades contain as little as 33% 4GT units and have a T_m of 163°C.

As polar polymers these rubbers have good oil and petrol resistance. They also exhibit a high resilience, good resistance to mechanical abuse, good flex fatigue resistance as well as a wider service temperature range than many general purpose rubbers. Some typical properties of three grades of polymer are given in *Table 25.12*. The polymers are soluble in *m*-cresol whilst those with less than

Table 25.12 Properties of Hytrel-type thermoplastic elastomers

Property	Units	4GT content (%)		
		33	58	76
Specific gravity	—	1.15	1.20	1.22
Melting point	°C	163	202	212
Glass transition	°C	-78	-50	-2
Brittle temperature	°C	<-70	<-70	<-70
Tensile strength	MPa	40	45	49
Elongation at break	%	810	760	510
10% modulus	MPa	3.7	10	17.2
100% modulus	MPa	8.1	15.1	20.1
Shore hardness		A92	D55	D63

60% of hard segments are also soluble in dichloromethane, chloroform and 1,1,1-trichloroethane.

Processing of these thermoplastic rubbers is quite straightforward providing that the raw compound is dry. Injection moulding is facilitated by the high crystallisation rates of the hard segments whilst the low viscosity at low shear rates, relative to many other rubbers, enables low shear processes such as rotational moulding, fluidised bed sintering and electrostatic spraying to be used.

In spite of their somewhat high price relative to most conventional rubbers these materials have become widely accepted as engineering rubbers in such applications as seals, belting, water hose and even low-pressure tyres.

25.11 POLY(PIVALOLACTONE)

For an aliphatic polyester, poly(pivalolactone) has a rather high T_m of 245°C and for such a T_m an unexpectedly low T_g of -10°C. It is also claimed to have good hydrolysis resistance for a polyester and this appears to be one of the reasons for its manufacture on an experimental scale by Shell with a view for use as both a fibre and as a thermoplastics moulding material.

Self-condensation of hydroxypivalic acid (also known as β -hydroxy- α,α -dimethylpropionic acid and as 2-hydroxy-1,1-dimethylpropionic acid) only yields low molecular weight polymers and it is more convenient to prepare the polymer from pivalolactone (also known as α,α -dimethyl- β -propiolactone) using tributylphosphine as an initiator (Figure 25.28).

The polymer has a regular structure and is therefore crystallisable. Three crystalline forms are known:

- (1) The α -form which forms on rapid crystallisation from the melt and which has a helical conformation.

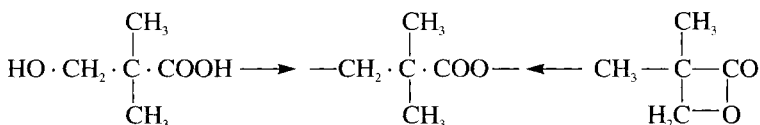


Figure 25.28

- (2) The β -form which crystallises more slowly than the α -form from the melt.
- (3) The γ -form which arises on stretching the polymer and which has an all-*trans*, i.e. a zig-zag, conformation.

Both the β - and the γ -forms revert to the α -form on annealing.

A 100% crystalline material has a density of 1.223 g/cm^3 at 20°C , a fully amorphous material a density of 1.097 g/cm^3 whilst samples cooled normally in a mould have a value of 1.19 g/cm^3 .

The polymer is liable to depolymerisation at temperatures just above T_m . In the case of pure polymer there is a tendency for the few spherulites to grow to sizes up to 1mm diameter. Spherulite size may be reduced by the use of nucleating agents and by fast cooling.

Fibres, film and moulded objects may be made from the polymer but properties are very dependent on morphology which is greatly affected by processing conditions and by subsequent annealing.

25.12 POLYCAPROLACTONES

Lactone rings are somewhat unusual amongst heterocyclic rings in that they may be opened by hydrolytic agents. It is perhaps rather surprising that this technique has only been recently developed for the manufacture of polyesters but polymers from ϵ -caprolactone and methyl- ϵ -caprolactone are now being evaluated in a number of areas since their introduction by Union Carbide in 1969. They may be prepared by ring-opening polymerisation with titanium catalysts and dihydroxy or trihydroxy initiators (*Figure 25.29*).

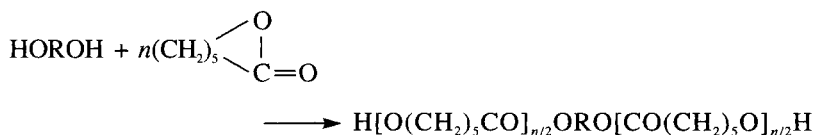


Figure 25.29

The initial commercial grades have been of comparatively low molecular weight (15 000–40 000) and the main lines of interest have been as precursors for polyurethanes (see Chapter 27) and as additives in other polymers. For example, it is claimed that up to 5% of a polycaprolactone improves the gloss and anti-blocking characteristics of low-density polyethylene film whilst the inclusion of up to 10% will improve the dyeability of polypropylene fibre. The materials are also being evaluated as polymeric plasticisers for PVC whilst 5–10% is claimed to give good gloss and low-profile characteristics to polyester laminating resins (see Section 25.3).

25.13 SURFACE COATINGS, PLASTICISERS AND RUBBERS

It has been estimated that in the United States somewhat over half of the surface coatings are of the polyester (alkyd) type.

These resins are produced by reacting a polyhydric alcohol, usually glycerol, with a polybasic acid, usually phthalic acid and the fatty acids of various oils such as linseed oil, soya bean oil and tung oil. These oils are triglycerides of the type shown in *Figure 25.30*. R_1 , R_2 and R_3 usually contain unsaturated groupings. The alkyd resins would thus have structural units, such as is shown in *Figure 25.31*.

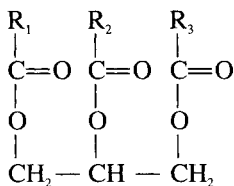


Figure 25.30

In modern manufacturing methods the oil is sometimes reacted directly with the glycerol to form a monoglyceride and this is then reacted with the acid to form the alkyd resin. When the resulting surface coating is applied to the substrate the molecules are substantially linear. However, in the presence of certain 'driers' such as lead soaps there is oxidative cross-linking via the unsaturated group in the side chain and the resin hardens.

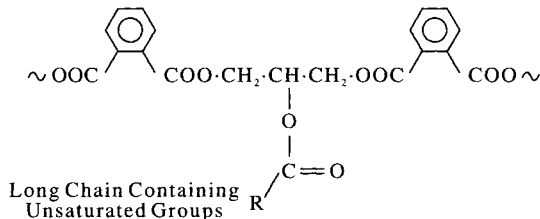


Figure 25.31

The alkyd resins are of value because of their comparatively low cost, durability, flexibility, gloss retention and reasonable heat resistance. Alkyd resins modified with rosin, phenolic resin, epoxy resins and monomers such as styrene are of current commercial importance.^{13,14}

The hardening process involved with the alkyd resins, because it involves air oxidation, is only satisfactory with thin coating films. This limitation has been circumvented by the use of *unsaturated polyester resins* for coating applications. These may be considered as developments of the laminating resins discussed in Section 25.2. The latter resins were, however, not altogether satisfactory because the phenomenon of air inhibition of cure (see page 683) became serious when the resin was used in an application where there was such a high surface/volume ratio. The use of additives such as hydrogenated castor oil and paraffin wax in quantities up to 0.5% is helpful but leads to two limitations. Firstly a thin layer of wax is formed at the resin-substrate interface, weakening the adhesive bond. Secondly the hardened film has a dull appearance which may require buffing if a gloss effect is needed.

This has led to chemical modification of the polyesters, in particular the introduction of allyl ether groups into the resins. Amongst the monomers figuring prominently in the literature are allyl glyceryl ether I, trimethylolpropane diallyl ether II (1,1-diallyloxypropanol) and pentaerythritol triallyl ether III (2,2,2-triallyoxyethanol), as shown in *Figure 25.32*.

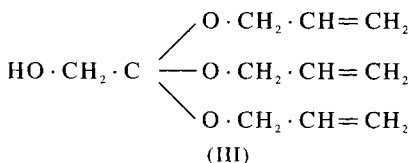
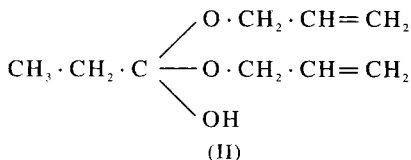
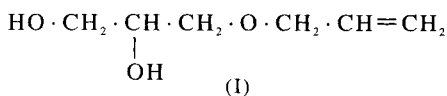


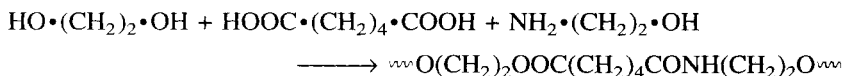
Figure 25.32

The resins are commonly cured by the use of peroxide with or without cobalt accelerators, depending on whether the hardening is to be carried out at room temperature or at some elevated temperature. Electron irradiation curing, which can be completed within a few seconds, has, however, been introduced for coatings on large flat surfaces such as plywood, chipboard and metal panels.

Whilst the unsaturated polyester coatings show high hardness, excellent clarity and good abrasion and chemical resistance their prime advantage is the ability to produce thick coatings. The main application area is in wood coating such as bedroom furniture and television cabinets and for steel coating in, for example, boat and bridge structures.

Low molecular weight liquid polyester resins are useful as plasticisers, particularly for PVC, where they are less volatile and have greater resistance to extraction by water than monomeric plasticisers. Examples of such plasticisers are poly(propylene adipate) and poly(propylene sebacate). In some cases monobasic acids such as lauric acid are used to control the molecular weight.

Cross-linkable rubbery polyesters have been produced but are now no longer produced. Rubbery polyester-amides were introduced by ICI under the trade name Vulcaprene as a leathercloth material but later were used primarily as leather adhesives and as flexible coatings for rubber goods. A typical polymer may be made by condensing ethylene glycol, adipic acid and ethanolamine to a wax with a molecular weight of about 5000.



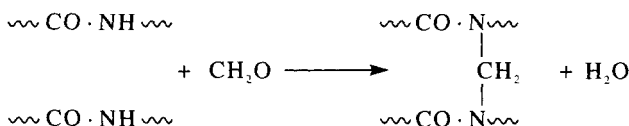


Figure 25.33

The chain length of the polymer is then increased by reacting the wax via the hydroxyl, amino or acid end groups with a di-isocyanate such as hexamethylene-di-isocyanate (see Chapter 27 for the appropriate reaction).

The rubbers were vulcanised by formaldehyde donors reacting across —NH—groups in the main chain (Figure 25.33).

References

1. BERZELIUS, J., *Rap. Ann. Progr. Sci. Physiq.*, **26** (1847)
2. LUSSAC, J. G., and PELOUZE, J., *Ann.*, **7**, 40 (1833)
3. BRYDSON, J. A., and WELCH, C. W., *Plastics* (London), **21**, 282 (1956)
4. SCOTT, K. A., and GALE, G. M., *Rubber and Plastics Research Association of Great Britain, Research Report 132* (September 1964)
5. MORGAN, P., *Glass Reinforced Plastics*, Iliffe, London, 3rd Edn (1961)
6. SONNERBORN, R. H., *Fibreglass Reinforced Plastics*, Reinhold, New York (1954)
7. DE DANI, A., *Glass Fibre Reinforced Plastics*, Newnes, London (1960)
8. LAWRENCE, J. R., *Polyester Resins*, Reinhold, New York (1960)
9. HAGEN, H., *Glasfaserverstärkte Kunststoffe*, Springer-Verlag, Berlin (1961)
10. RAECH, H., *Allylic Resins and Monomers*, Reinhold, New York (1965)
11. GREATREX, J. L., and HAYNES, I. E., *Brit. Plastics*, **35**, 340 (1962)
12. WATSON, M. T., *Soc. Plastics Engrs*, 1083 (October 1961)
13. MARTENS, C. R., *Alkyd Resins*, Reinhold, New York (1961)
14. PATTON, T. C., *Alkyd Resin Technology*, Interscience, New York (1962)
15. GOODMAN, I., and RHYS, J. A., *Polyesters, Vol. 1: Saturated Polymers*, Iliffe, London (1965)

Bibliography

- BJORKSTEN, J., *Polyesters and their Applications*, Reinhold, New York (1956)
- DE DANI, A., *Glass Fibre Reinforced Plastics*, Newnes, London (1960)
- GOODMAN, I., and RHYS, J. A., *Polyesters, Vol. 1: Saturated Polymers*, Iliffe, London (1965)
- HAGEN, H., *Glasfaserverstärkte Kunststoffe*, Springer-Verlag, Berlin (1961)
- HILL, R., *Fibres from Synthetic Polymers*, Elsevier, Amsterdam (1953)
- LAWRENCE, J. R., *Polyester Resins*, Reinhold, New York (1960)
- MARTENS, C. R., *Alkyd Resins*, Reinhold, New York (1961)
- MORGAN, P., *Glass Reinforced Plastics*, Iliffe, London, 3rd Edn (1961)
- PARKYN, B., LAMB, F., and CLIFTON, B. V., *Polyesters, Vol. 2: Unsaturated Polyesters and Polyester Plasticisers*, Iliffe, London (1967)
- PATTON, T. C., *Alkyd Resin Technology*, Interscience, New York (1962)
- PETUKHOV, B. V., *The Technology of Polyester Fibres*, Pergamon, Oxford (1963)
- RAECH, H., *Allylic Resins and Monomers*, Reinhold, New York (1965)
- SONNERBORN, R. H., *Fibreglass Reinforced Plastics*, Reinhold, New York (1956)
- WEATHERHEAD, R. G., *FRP Technology*, Applied Science, London (1980)

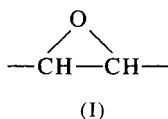
Reviews

- BREITENFELLNER, F. and KAINMÜLLER, T., *Kunststoffe*, **80** (10), 1121 (1990)
- CAESAR, H. M., *Kunststoffe*, **77**, 1004–9 (1987)
- CLAUSS, J. and MITCHELL, K., *Kunststoffe*, **86**, 1506–1508 (1996)
- DIETRICH, H. J., ZANDER, K. and LEHNERT, G., *Kunststoffe*, **86**, 1510–1512 (1996)
- FISCHER, W., GEHRKE, J. E., and REMPEL, D., *Kunststoffe*, **70**, 650–5 (1980)
- SCHIK, J. P., *Kunststoffe*, **70**, 1004–9 (1987)

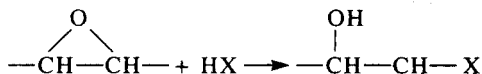
Epoxide Resins

26.1 INTRODUCTION

The epoxide resins (also widely known as epoxy resins and, occasionally, as ethoxyline resins) are characterised by the possession of more than one 1,2-epoxy group (I) per molecule. This group may lie within the body of the molecule but is usually terminal.



The three-membered epoxy ring is highly strained and is reactive to many substances, particularly by with proton donors, so that reactions of the following schematic form can occur:



Such reactions allow chain extension and/or cross-linking to occur without the elimination of small molecules such as water, i.e. they react by a rearrangement polymerisation type of reaction. In consequence these materials exhibit a lower curing shrinkage than many other types of thermosetting plastics.

There is, quite clearly, scope for a very wide range of epoxy resins. The non-epoxy part of the molecule may be aliphatic, cycloaliphatic or highly aromatic hydrocarbon or it may be non-hydrocarbon and possibly polar. It may contain unsaturation. Similar remarks also apply to the chain extension/cross-linking agents, so that cross-linked products of great diversity may be obtained. In practice, however, the commercial scene is dominated by the reaction products of bis-phenol A and epichlorohydrin, which have some 80–90% of the market share.

The commercial interest in epoxide (epoxy) resins was first made apparent by the publication of German Patent 676 117 by I G Farben¹ in 1939 which described liquid polyepoxides. In 1943 P. Castan² filed US Patent 2 324 483, covering the curing of the resins with dibasic acids. This important process was subsequently exploited by the Ciba Company. A later patent of Castan³ covered the hardening of epoxide resins with alkaline catalysts used in the range 0.1–5%. This patent, however, became of somewhat restricted value as the important amine hardeners are usually used in quantities higher than 5%.

In the early stage of their development the epoxy resins were used almost entirely for surface coating and developments in this field are to a large extent due to the works of S.O. Greenlee and described in a number of patents. These included work on the modification of epoxy resins with glycerol⁴, the esterification of the higher molecular weight materials with drying oil acids⁵ and reactions with phenolic⁶ and amino resins.⁷

Before World War II the cost of the intermediates for these resins (in most cases epichlorohydrin and bis-phenol A) would have prevented the polymers from becoming of commercial importance. Subsequent improvements in the methods of producing these intermediates and improved techniques of polymerisation have, however, led to wide commercial acceptance.

By the beginning of the 1980s world capacity for epoxide resins reached about 600 000 tonnes per annum but at this time plant utilisation was only about 50–60%. Thus with a global consumption of about 10 million tonnes per annum for thermosetting plastics, epoxide resins had a share of about 3%. Western Europe and the USA each had about 40% of the market and Japan a little over 10%. This situation has not greatly changed since then; but by the late 1990s the world market for epoxide resins had risen to about 750 000 t.p.a.

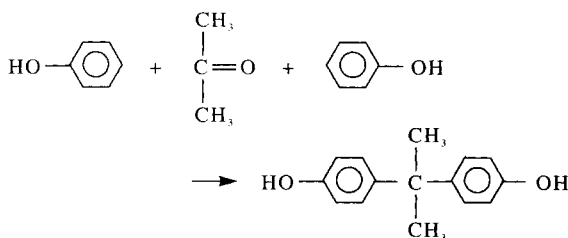
About half of epoxide resin production is used for surface coating applications, with the rest divided approximately equally between electronic applications (particularly for printed circuit boards and encapsulation), the building sector and miscellaneous uses. In tonnage terms consumption of epoxide–fibre laminates is only about one-tenth that of polyester laminates, but in terms of value it is much greater.

Whilst the properties of the cross-linked resins depend very greatly on the curing system used and on the type of resin, the most characteristic properties of commercial materials are their toughness, low shrinkage on cure, high adhesion to many substrates, good alkali resistance and versatility in formulation.

26.2 PREPARATION OF RESINS FROM BIS-PHENOL A

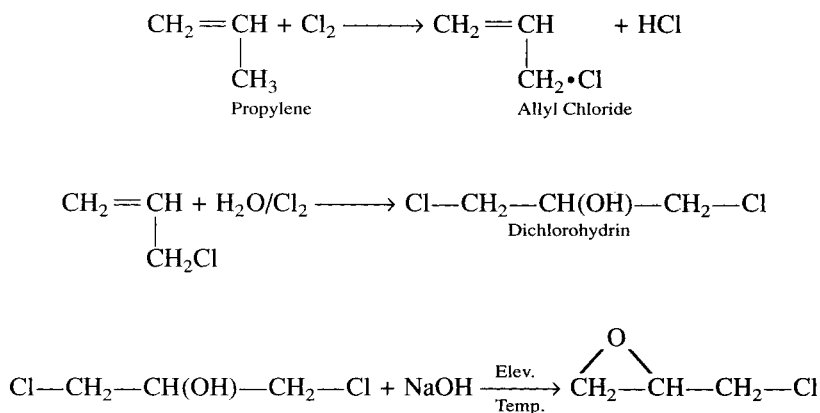
The first, and still the most important, commercial epoxide resins are reaction products of bis-phenol A and epichlorohydrin. Other types of epoxide resins were introduced in the late 1950s and early 1960s, prepared by epoxidising unsaturated structures. These materials will be dealt with in Section 26.4. The bis-phenol A is prepared by reaction of the acetone and phenol (*Figure 26.1*).

Since both phenol and acetone are available and the bis-phenol A is easy to manufacture, this intermediate is comparatively inexpensive. This is one of the reasons why it has been the preferred dihydric phenol employed in epoxide resins manufacture. Since most epoxide resins are of low molecular weight and because

*Figure 26.1*

colour is not particularly critical the degree of purity of the bis-phenol A does not have to be so great as when used in the polycarbonate resins. Bis-phenol A with a melting point of 153°C is considered adequate for the most applications whilst less pure materials may often be employed.

Epichlorohydrin, the more expensive compound is derived from propylene by the sequence of reactions shown in *Figure 26.2*.

*Figure 26.2*

It will noticed that the initial steps correspond with those used in the manufacture of glycerol. The material is available commercially at 98% purity and is a colourless mobile liquid.

Many of the commercial liquid resins consist essentially of the low molecular weight diglycidyl ether of bis-phenol A together with small quantities of higher molecular weight polymers. The formation of the diglycidyl ether is believed to occur in the manner shown in *Figure 26.3*, the hydrochloric acid released reacting with the caustic soda to form sodium chloride.

Although it would appear, at first glance, that diglycidyl ether would be prepared by a molar ratio of 2:1 epichlorohydrin-bis-phenol A, probability considerations indicate that some higher molecular weight species will be produced. Experimentally it is in fact found that when a 2:1 ratio is employed, the yield of the diglycidyl ether is less than 10%. Therefore in practice two to three

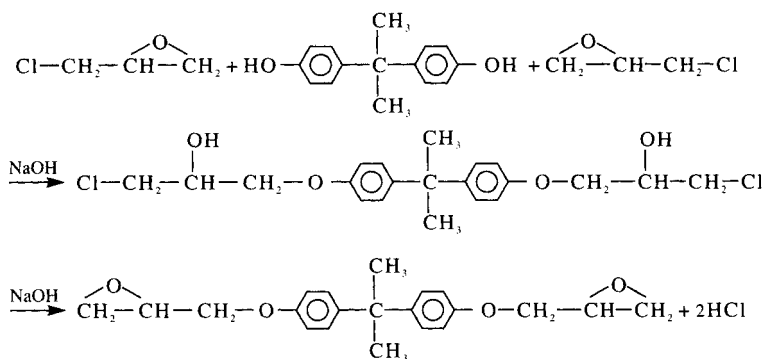


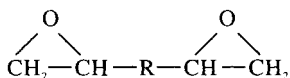
Figure 26.3

times the stoichiometric quantity of epichlorohydrin may be employed. A typical laboratory scale preparation⁸ is as follows:

'1 mole (228g) of bis-phenol A is dissolved in 4 moles (370g) of epichlorohydrin and the mixture heated to 105–110°C under an atmosphere of nitrogen. The solution is continuously stirred for 16 hours while 80g (2 moles) of sodium hydroxide in the form of 30% aqueous solution is added dropwise. A rate of addition is maintained such that reaction mixture remains at a pH which is insufficient to colour phenolphthalein. The resulting organic layer is separated, dried with sodium sulphate and may then be fractionally distilled under vacuum.'

The diglycidyl ether has a molecular weight of 340. Many of the well-known commercial liquid glycidyl ether resins have average molecular weights in the range 340–400 and it is therefore obvious that these materials are composed largely of the diglycidyl ether.

Higher molecular weight products may be obtained by reducing the amount of excess epichlorohydrin and reacting the more strongly alkaline conditions which favour reaction of the epoxide groups with bis-phenol A. If the diglycidyl ether is considered as a diepoxide and represented as



this will react with further hydroxyl groups, as shown in Figure 26.4.

It will be observed that in these cases hydroxyl groups will be formed along the chain of the molecule. The general formulae for glycidyl ether resins may thus be represented by the structure shown in Figure 26.5.

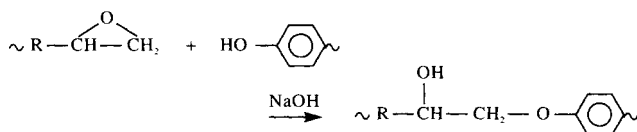


Figure 26.4

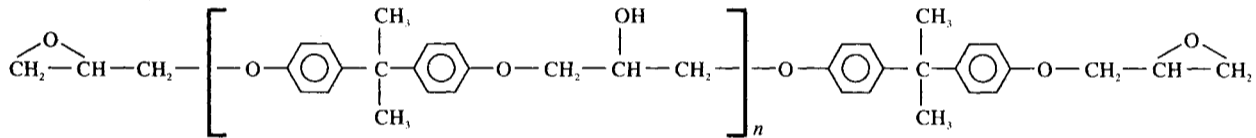


Figure 26.5

When $n = 0$, the product is the diglycidyl ether, and the molecular weight is 340. When $n = 10$ molecular weight is about 3000. Since commercial resins seldom have average molecular weights exceeding 4000 it will be realised that in the uncured stage the epoxy resins are polymers with a low degree of polymerisation.

Table 26.1 shows the effect of varying the reactant ratios on the molecular weight of the epoxide resins.⁹

Table 26.1 Effect of reactant ratios on molecular weights

<i>Mol. ratio epichlorohydrin/ bis-phenol A</i>	<i>Mol. ratio NaOH/ epichlorohydrin</i>	<i>Softening point (°C)</i>	<i>Molecular weight</i>	<i>Epoxide equivalent</i>	<i>Epoxy groups per molecule</i>
2.0	1.1	43	451	314	1.39
1.4	1.3	84	791	592	1.34
1.33	1.3	90	802	730	1.10
1.25	1.3	100	1133	862	1.32
1.2	1.3	112	1420	1176	1.21

It is important that care should be taken to remove residual caustic soda and other contaminants when preparing the higher molecular weight resins and in order to avoid the difficulty of washing highly viscous materials these resins may be prepared by a two-stage process.

This involves first the preparation of lower molecular weight polymers with a degree of polymerisation of about three. These are then reacted with bis-phenol A in the presence of a suitable polymerisation catalyst such that the reaction takes place without the evolution of by-products.¹⁰

The epoxide resins of the glycidyl ether type are usually characterised by six parameters :

- (1) Resins viscosity (of liquid resin)
- (2) Epoxide equivalent.
- (3) Hydroxyl equivalent.
- (4) Average molecular weight (and molecular weight distribution).
- (5) Melting point (of solid resin).
- (6) Heat distortion temperature (deflection temperature under load) of cured resin.

Resin viscosity is an important property to consider in handling the resins. It depends on the molecular weight, molecular weight distribution, chemical constitution of the resin and presence of any modifiers or diluents. Since even the diglycidyl ethers are highly viscous materials with viscosities of about 40–100 poise at room temperature it will be appreciated that the handling of such viscous resins can present serious problems.

The epoxide equivalent is a measure of the amount of epoxy groups. This is the weight of resin (in grammes) containing 1 gramme chemical equivalent epoxy. For a pure diglycidyl ether with two epoxy groups per molecule the epoxide

equivalent will be half the molecular weight (i.e. epoxide equivalent = 170). The epoxy equivalent is determined by reacting a known quantity of resin with hydrochloric acid and measuring the unconsumed acid by back titration. The reaction involved is



It is possible to correlate epoxy equivalent for a given class of resin with infrared absorption data.

The hydroxyl equivalent is the weight of resin containing one equivalent weight of hydroxyl groups. It may be determined by many techniques but normally by reacting the resin with acetyl chloride.

The molecular weight and molecular weight distribution may be determined by conventional techniques. As the resins are of comparatively low molecular weight it is possible to measure this by ebullioscopic and by end-group analysis techniques.

It is useful to measure the melting point of the solid resins. This can be done either by the ring and ball technique or by Durrans mercury method. In the latter method a known weight of resin is melted in a test tube of fixed dimensions. The resin is then cooled and it solidifies. A known weight of clean mercury is then poured on to the top of the resin and the whole assembly heated, at a fixed rate, until the resin melts and the mercury runs through the resin. The temperature at which this occurs is taken as the melting point.

The ASTM heat distortion temperature (deflection temperature under load) test may be used to characterise a resin. Resins must, however, be compared using identical hardeners and curing conditions.

Typical data for some commercial glycidyl ether resins are given in *Table 26.2*.

Table 26.2

<i>Resin</i>	<i>Average Mol. Wt.</i>	<i>Epoxide equivalent</i>	<i>Viscosity cP at 25°C</i>	<i>Melting point °C (Durrans)</i>
A	350-400	175-210	4-10 000	—
B	450	225-290	—	—
C	700	300-375	—	40-50
D	950	450-525	—	64-76
E	1400	870-1025	—	95-105
F	2900	1650-2050	—	125-132
G	3800	2400-4000	—	145-155

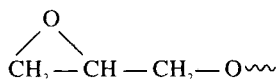
Solid resins have been prepared having a very closely controlled molecular weight distribution.¹¹ These resins melt sharply to give low-viscosity liquids. It is possible to use larger amounts of filler with the resin with a consequent reduction in cost and coefficient of expansion, so that such resins are useful in casting operations.

26.3 CURING OF GLYCIDYL ETHER RESINS

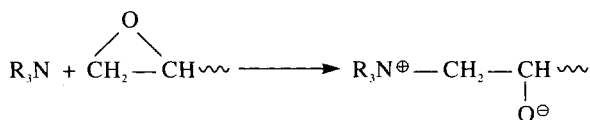
The cross-linking of epoxy resins may be carried out either through the epoxy groups or the hydroxy groups. Two types of curing agent may also be distinguished, catalytic systems and polyfunctional cross-linking agents that link the epoxide resin molecules together. Some systems used may involve both the catalytic and cross-linking systems.

Whilst the curing mechanisms may be quite complex and the cured resins too intractable for conventional analysis some indication of the mechanisms involved has been achieved using model systems.

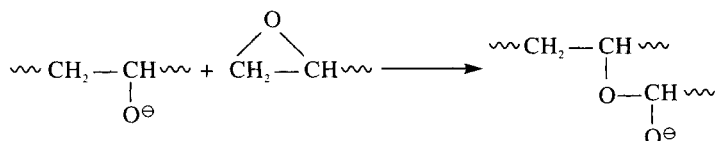
It has been shown in the course of this work¹² that the reactivity of the epoxy ring is enhanced by the presence of the ether linkage separated from it by a methylene link.



The epoxy ring may then be readily attacked not only by active hydrogen and available ions but even by tertiary amines. For example, with the latter it is believed that the reaction mechanism is as follows :



This ion may then open up a new epoxy group generating another ion which can in turn react with a further epoxy group.

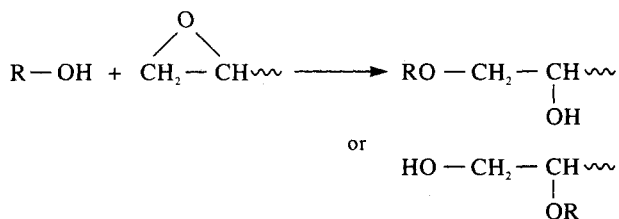


Since this reaction may occur at both ends of the molecule (in case of glycidyl ether resins) a cross-linked structure will be built up.

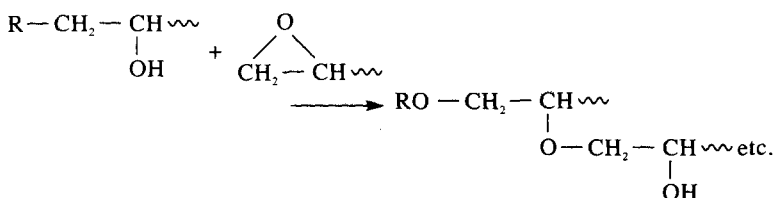
The overall reaction is complicated by the fact that the epoxy group, particularly when catalysed, will react with hydroxyl groups. Such groups may be present due to the following circumstances :

- (1) They will be present in the higher molecular weight homologues of the diglycidyl ether of bis-phenol A.
- (2) They may be introduced by the curing agent or modifier.
- (3) They will be formed as epoxy rings are opened during cure.
- (4) In unreacted phenol-type materials they are present as impurities.

The epoxy-hydroxyl reaction may be expressed as



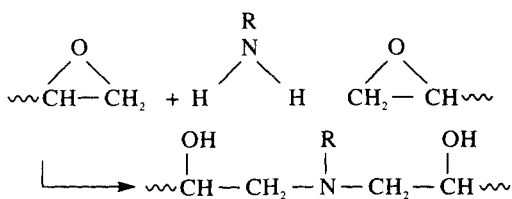
This product will contain new hydroxyl groups that can react with other epoxy rings, generating further active hydroxyl groups, e.g.



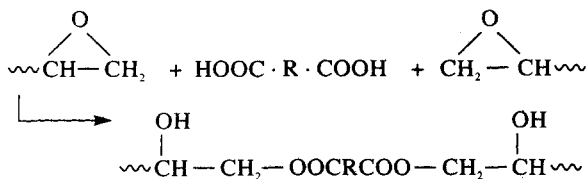
The predominance of one reaction over the other is greatly influenced by the catalyst system employed. Tertiary amine systems are often used in practice.

In addition to the catalytic reactions the resins may be cross-linked by agents which link across the epoxy molecules. These reactions may be via the epoxy ring or through the hydroxyl groups. Two examples of the former are:

(1) With amines

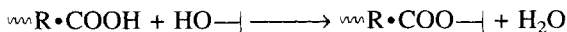


(2) With acids

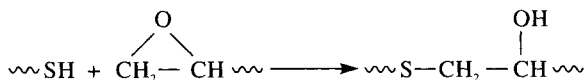


The reactions indicated above in fact lead only to chain extension. In practice, however, polyamines are used so that the number of active hydrogen atoms exceeds two and so cross-linkage occurs.

In the case of acids and acid anhydrides, reaction can also occur via the hydroxyl groups that are present, including those formed on opening of the epoxide ring.



Both amines and acid anhydrides are extensively used cross-linking agents. The resins may also be modified by reacting with other polymers containing hydroxyl or mercaptan groupings, e.g.



These various systems will be dealt with individually in the following sections.

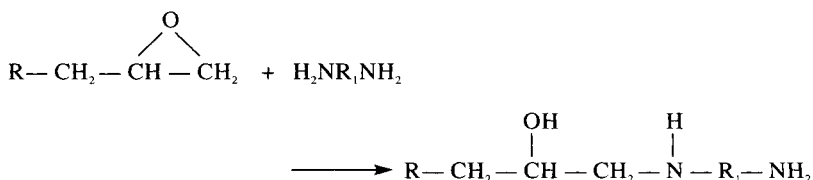
26.3.1 Amine Hardening Systems

As indicated in the preceding section, amine hardeners will cross-link epoxide resins either by a catalytic mechanism or by bridging across epoxy molecules. In general the primary and secondary amines act as reactive hardeners whilst the tertiary amines are catalytic.

Diethylenetriamine and *triethylenetetramine* are highly reactive primary aliphatic amines with five and six active hydrogen atoms available for cross-linking respectively. Both materials will cure glycidyl ether at room temperature. In the case of diethylenetriamine, the exothermic temperature may reach as high as 250°C in 200 g batches. With this amine 9–10 pts phr, the stoichiometric quantity, is required and this will give a room temperature pot life of less than an hour. The actual time depends on the ambient temperature and the size of the batch. With triethylenetetramine 12–13 pts phr are required. Although both materials are widely used in small castings and in laminates because of their high reactivity, they have the disadvantage of high volatility, pungency and being skin sensitisers. Properties such as heat distortion temperature (HDT) and volume resistivity are critically dependent on the amount of hardener used.

Similar properties are exhibited by *dimethylaminopropylamine* and *diethylaminopropylamine*, which are sometimes preferred because they are slightly less reactive and allow a pot life (for a 500 g batch) of about 140 minutes.

A number of modified amines have been marketed commercially. For example, reaction of the amine with a mono- or polyfunctional glycidyl material will give a larger molecule so that larger quantities are required for curing, thus helping to reduce errors in metering the hardener.



Higher heat distortion temperatures are achieved using 4,4'-methylenedianiline (diaminodiphenylmethane) and diaminophenyl sulphone, in conjunction with an accelerator, but this is at some expense to chemical resistance.

Many other amines are catalytic in their action. One of these, piperidine, has been in use since the early patents of Castan. 5–7 pts phr of piperidine are used to give a system with a pot life of about eight hours. A typical cure schedule is three hours at 100°C. Although it is a skin irritant it is still used for casting of larger masses than are possible with diethylenetriamine and diethylaminopropylamine.

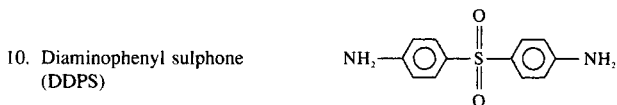
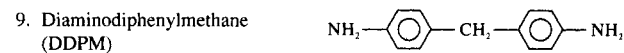
Tertiary amines form a further important class of catalytic hardeners. For example, triethylamine has found use in adhesive formulations. Also of value are the aromatic substituted tertiary amines such as benzyldimethylamine and dimethyldiaminophenol. They have found uses in adhesive and coating applications. A long pot life may be achieved by the use of salts of the aromatic substituted amines.

Typical amine hardeners are shown in Table 26.3 and their characteristics and behaviour are summarised in Table 26.4.

Table 26.3 Typical amine hardeners for epoxy resins

PRIMARY ALIPHATIC AMINES	
1. Diethylenetriamine (DET)	$\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH—CH}_2\text{—CH}_2\text{—NH}_2$
2. Triethylenetetramine (TET)	$\text{NH}_2\text{—(CH}_2\text{)}_2\text{—NH—(CH}_2\text{)}_2\text{—NH—(CH}_2\text{)}_2\text{—NH}_2$
3. Dimethylaminopropylamine (DMAP)	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{N—CH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2 \\ \diagup \\ \text{CH}_3 \end{array}$
4. Diethylaminopropylamine (DEAP)	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagdown \\ \text{N—CH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2 \\ \diagup \\ \text{C}_2\text{H}_5 \end{array}$
ALIPHATIC AMINE ADDUCTS	
5. Amine-glycidyl adducts e.g.	$\text{R—CH}_2\text{—CH—(OH)—CH}_2\text{—NH (CH}_2\text{)}_2\text{NH—(CH}_2\text{)}_2\text{—NH}_2$ from diethylenetriamine
6. Amine-ethylene oxide adducts e.g.	$\text{HO—CH}_2\text{—CH}_2\text{—NH—(CH}_2\text{)}_2\text{—NH—(CH}_2\text{)}_2\text{—NH}_2$
7. Cyanoethylation products e.g.	$\text{CN—CH}_2\text{—CH}_2\text{—NH—(CH}_2\text{)}_2\text{—NH—(CH}_2\text{)}_2\text{—NH}_2$
AROMATIC AMINES	
8. <i>m</i> -Phenylenediamine (MPD)	

Table 26.3 Continued



CYCLIC ALIPHATIC AMINES



TERTIARY AMINES

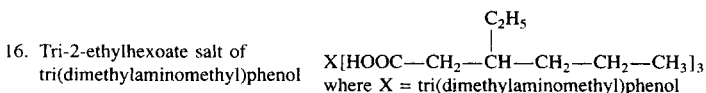
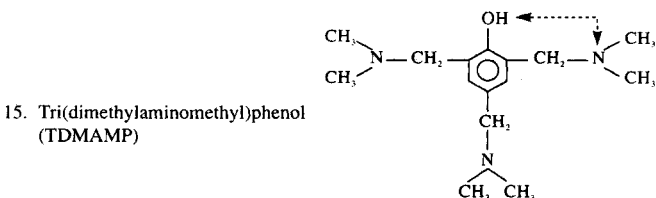
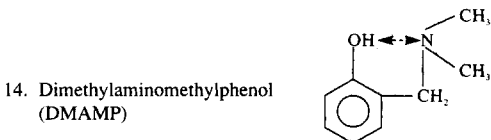
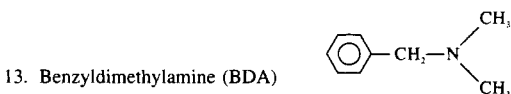
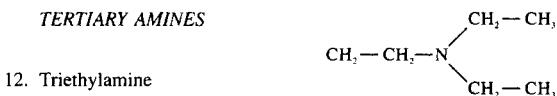


Table 26.4 Some characteristics of amine hardeners for use in low molecular weight glycidyl ether resins

<i>Hardener</i>	<i>Parts used per 100 pts resin</i>	<i>Pot life (500 g batch)</i>	<i>Typical cure schedule</i>	<i>Skin irritant</i>	<i>Max HDT cured resin (°C)</i>	<i>Features</i>	<i>Applications</i>
DET	10–11	20 min	room temp.	yes	110	cold curing	general purpose
DEAP	7	140 min	room temp.	yes	97	slightly slower than DET	general purpose
DET–glycidyl adduct	25	10 min	room temp.	yes	75	fast cure	adhesives laminating
DET–ethylene oxide adduct	20	16 min	room temp.	reduced	92	minimum irritation	—
DET–cyanoethylation adduct†	~37.5	60–80 min	*	yes	100	slower curing	—
MPD	14–15	>6 h	4–6 h at 150°C	yes	150	chemical resistance	laminates
DDPM	28.5	—	4–6 h at 165°C	yes	160	high HDT	laminates
DDPS	30	—	8 h at 160°C	yes	175	use with accelerator	laminates
Piperidine	5–7	8 h	3 h at 100°C	yes	75	—	general purpose
Triethylamine	10	7 h	room temp.	yes	—	—	adhesives
BDA	15	75 min	room temp.	yes	—	—	adhesives
TDMAMP	6	30 min	room temp.	yes	64	—	adhesive coatings
2-Ethyl hexoate salt of above	10–14	3–6 h	—	yes	—	long pot life	encapsulation

* 2 hours at 70°C, 3 hours at 100°C, 1 hour at 110°C

† Results are for highly substituted amines.

26.3.2 Acid Hardening Systems

The use of acid hardening systems for epoxy resins was first described in Castan's early patent but use was restricted in many countries until the consummation of cross-licensing arrangements between resin suppliers in 1956. Compared with amine-cured systems, they are less skin sensitive and generally give lower exotherms on cure. Some systems provide cured resins with very high heat distortion temperatures and with generally good physical, electrical and chemical properties. The cured resins do, however, show less resistance to alkalis than amine-cured systems. In practice acid anhydrides are preferred to acids, since the latter release more water on cure, leading to foaming of the product, and are also generally less soluble in the resin. Care must, however, be taken over storage since the anhydrides in general are somewhat hygroscopic.

The mechanism of anhydride hardening is complex but the first stage of reaction is believed to be the opening of the anhydride ring by an alcoholic hydroxyl group (or salt or a trace of water), e.g. *Figure 26.6*.

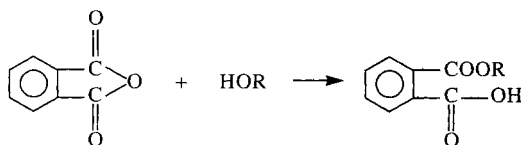


Figure 26.6

Hydroxyl groups attached to the epoxy resin would suffice for this purpose. Five further reactions may then occur.

- (1) Reaction of the carboxylic group with the epoxy group (*Figure 26.7*).

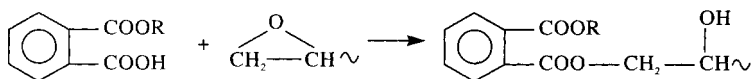


Figure 26.7

- (2) Etherification of the epoxy group by hydroxyl groups (*Figure 26.8*).

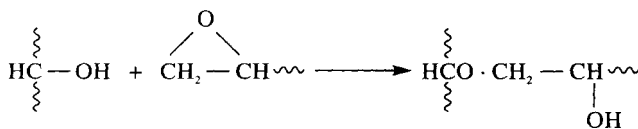


Figure 26.8

- (3) Reaction of the monoester with hydroxyl group (*Figure 26.9*).

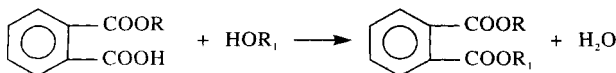


Figure 26.9

- (4) Hydrolysis of the anhydride to acid by the water released in (3).
 (5) Hydrolysis of the monoester with water to give acid and alcohol.

In practice it is found that reactions 1 and 2 are of greatest importance and ester and ether linkages occur in roughly equal amounts. The reaction is modified in commercial practice by the use of organic bases, tertiary amines, to catalyse the reaction.

The anhydrides are usually used at ratios of 0.85:1.1 moles anhydride carboxyl group per epoxy equivalent. Lower ratios down to 0.5:1 may, however, be used with some systems. The organic bases are used in amounts of 0.5–3%. These are usually tertiary amines such as α -methylbenzyl dimethylamine and *n*-butylamine.

Three classes of anhydride may be recognised, room temperature solids, room temperature liquids and chlorinated anhydrides.

Phthalic anhydride (Figure 26.10 I) is an important example of the first class of hardener. It has a molecular weight of 148 and about 0.6–0.9 equivalent is used per epoxy group. For the lower molecular weight bis-phenol resins this works out at about 35–45 phr. The hardener is usually added at elevated temperature of about 120–140°C. It will precipitate out below 60°C but will again dissolve on reheating.

The resin is slow curing with phthalic anhydride and a typical cure schedule would be 4–8 hours at 150°C. Longer cures at lower temperatures tend to improve the heat distortion temperatures and reduce the curing shrinkage. As with the amine hardeners the heat distortion temperature is very dependent on the amount of anhydride added and reaches a maximum at about 0.75 equivalent. Maximum heat distortion temperatures quoted in the literature are of the order of 110°C, a not particularly exceptional figure, and the hardener is used primarily for large castings where the low exotherm is particularly advantageous.

Hexahydrophthalic anhydride (Figure 26.10 II) (Mol. Wt. 154) has a melting point of 35–36°C and is soluble in the epoxy resin at room temperature. When 0.5% of a catalyst such as benzyl dimethylamine is used the curing times are of the same order as with phthalic anhydride. About 80 phr are required. In addition

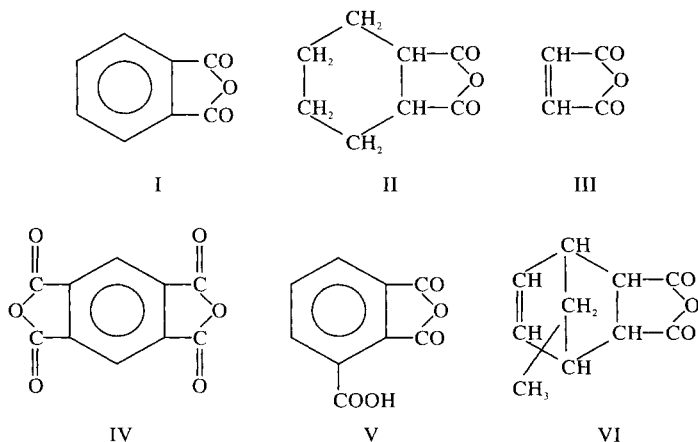


Figure 26.10

to the somewhat improved ease of working, the hardener gives slightly higher heat distortion temperatures ($\sim 120^{\circ}\text{C}$) than with phthalic anhydride. It is, however, more expensive. *Maleic anhydride* (Figure 26.10 III) is not usually used on its own because the cured resins are brittle, but it may be used in conjunction with pyromellitic dianhydride.

In order to obtain cured products with higher heat distortion temperatures from bis-phenol epoxy resins, hardeners with higher functionality have been used, thus giving a higher degree of cross-linking. These include *pyromellitic dianhydride* IV, and *trimellitic anhydride* V.

Heat distortion temperatures of resins cured with pyromellitic dianhydride are often quoted at above 200°C . The high heat distortion is no doubt also associated with the rigid linkages formed between epoxy molecules because of the nature of the anhydride. The use of these two anhydrides has, however, been restricted because of difficulties in incorporating them into the resin.

The methylated maleic acid adduct of phthalic anhydride, known as *methyl nadic anhydride* VI, is somewhat more useful. Heat distortion temperatures as high as 202°C have been quoted whilst cured systems, with bis-phenol epoxides, have very good heat stability as measured by weight loss over a period of time at elevated temperatures. The other advantage of this hardener is that it is a liquid easily incorporated into the resin. About 80 phr are used but curing cycles are rather long. A typical schedule is 16 hours at 120°C and 1 hour at 180°C .

Other anhydrides that have been used include *dodecenylsuccinic anhydride*, which imparts flexibility into the casting, and *chlorendic anhydride*, where flame-resistant formulations are called for.

Table 26.5 summarises the characteristics of some of the anhydride hardeners.

Table 26.5 Properties of some anhydrides used in low molecular weight diglycidyl ether resins

<i>Anhydride hardener</i>	<i>Parts used phr</i>	<i>Typical cure schedule</i>	<i>Physical form</i>	<i>Max. HDT of cured resin °C</i>	<i>Use</i>
Phthalic	35–45	24 h at 120°C	powder	110°C	casting
Hexahydrophthalic (+ accelerator)	80	24 h at 120°C	glassy solid	130°C	casting
Maleic	—	—	solid	—	secondary hardener
Pyromellitic (dianhydride)	26	20 h at 220°C	powder	290°C	high HDT
Methyl nadic	80	16 h at 120°C	liquid	202°C	high HDT
Dodecenylsuccinic (+ accelerator)		2 h at 100°C + 2 h at 150°C	viscous oil	38°C	flexibilising
Chlorendic	100	24 h at 180°C	white	180°C	flame retarding

In some instances it is desired to produce a more open network from epoxide resins that have been acid-cured. This may be achieved by the oligoesterdicarboxylic acids of general structure



26.3.3 Miscellaneous Hardener Systems

In addition to the amine, acid and anhydride hardeners many other curing agents have been made available. These include a number of amides that contain amine groups. Among them are the polyamides already considered in the section on flexibilisers and which form the basis of some domestic adhesive systems. Amongst the advantages of the system is the fact that roughly similar quantities of hardener and resin are required and since this is not too critical adequate metering can be done visually without the need for quantitative measuring aids. Also used with epoxide resins for adhesives is dicyanodiamide. Insoluble in common resins at room temperature, it is dissolved at elevated temperatures, forming the basis of a one-pack system.

Complexes of boron trifluoride and amines such as monoethylamine are of interest because of the very long pot lives possible. The disadvantages of these complexes are their hygroscopic nature and the corrosive effects of BF_3 liberated during cure.

Very high cure rates may be achieved using mercaptans.

26.3.4 Comparison of Hardening Systems

The number of hardening agents used commercially is very large and the final choice will depend on the relative importance of economics, ease of handling, pot life, cure rates, dermatitic effects and the mechanical, chemical, thermal and electrical properties of the cured products. Since these will differ from application to application it is understandable that such a wide range of material is employed.

As a very general rule it may be said that the amines are fast curing and give good chemical resistance but most are skin sensitive. The organic anhydrides are less toxic and in some cases give cured resins with very high heat distortion temperatures. They do not cross-link the resins at room temperature.

In addition to the considerable difference of the properties of the cured resins with different hardeners it must also be stressed that the time and temperatures of cure will also have an important effect on properties. As a very general rule, with increasing aliphatic amines and their adducts the time of cure and temperature of cure (up to 120°C at least) will improve most properties¹⁰.

26.4 MISCELLANEOUS EPOXIDE RESINS

In addition to the resins based on bis-phenol A dealt with in preceding sections there are now available a number of other resins containing epoxide groups. These can be treated in two main groups:

- (1) Other glycidyl ether resins
- (2) Non-glycidyl ether resins

26.4.1 Miscellaneous Glycidyl Ether Resins

Glycidyl ether resins are formed by reaction of epichlorohydrin with polyhydroxy compounds. In addition to the dominant use of bis-phenol A several other polyhydroxy compounds have been used. In particular there has been

increasing interest in the use of bis-phenol F. As made, this is a mixture of three isomers (*Figure 26.11* (Ia,b,c)). The resins are of a somewhat lower viscosity than the corresponding bis-phenol A materials. Hydrogenated bis-phenol A (known as bis-phenol H) (II) is also to show promise in resins with enhanced weathering characteristics. Other low molecular weight polyhydroxy compounds that have been used include glycerol (III) and the long chain bis-phenol from cashew nut shell oil (IV).

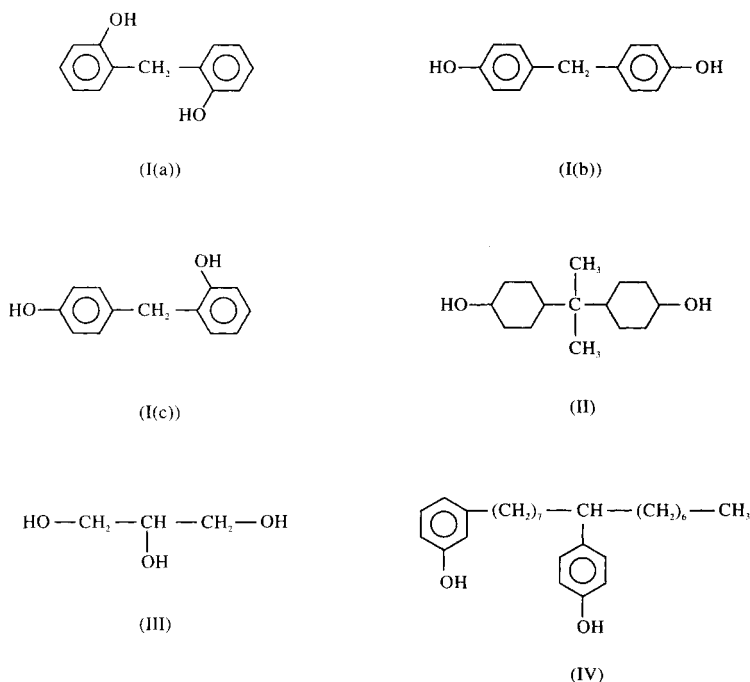


Figure 26.11

Novolak resins (Chapter 23) have also been epoxidised through their phenolic hydroxy groups. A wide variety of novolak resins may be used based on a range of different phenols, including cresols, ethylphenols, *t*-butylphenols, resorcinol, hydroquinone and catechol as well as phenol itself. The epoxide–novolak can also vary in its average molecular weight and in the number of phenolic hydroxy groups that have been reacted with epichlorohydrin. A typical epoxide–novolak resin would be as shown in *Figure 26.12*.

This molecule has a functionality of four. Commercial epoxide–novolak resins have functionalities between 2.5 and 6.

When cured with room temperature curing system these resins have similar thermal stability to ordinary bis-phenol A type epoxides. However, when they are cured with high-temperature hardeners such as methyl ‘nadic’ anhydride both thermal degradation stability and heat deflection temperatures are considerably improved. Chemical resistance is also markedly improved. Perhaps the most serious limitation of these materials is their high viscosity.

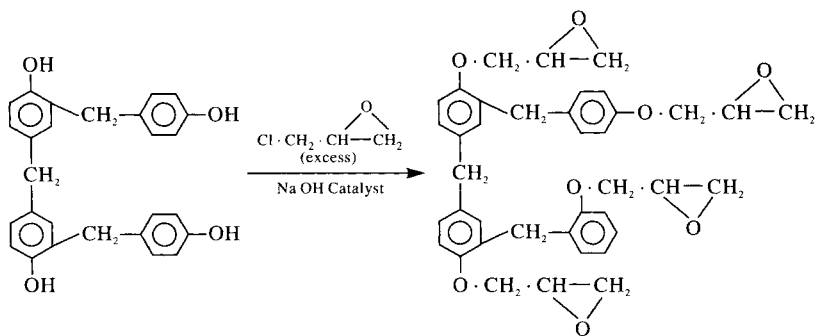


Figure 26.12

Their main applications have been in heat-resistant structural laminates, 'electrical' laminates resistant to solder baths, chemical-resistant filament-wound pipe and high-temperature adhesives.

Low-viscosity diglycidyl ether resins of undisclosed composition¹¹ have been marketed in the United States and in Britain. The materials are stated to be totally difunctional, i.e. free from monofunctional reactive diluents. The cured resins have properties very similar to those of the standard diglycidyl ether resins.

To produce resins of high heat distortion temperature it is important to have a high density of cross-linking and to have inflexible segments between the cross-links. This approach has been used with reasonable success using certain anhydride hardeners such as pyromellitic dianhydride and with the cyclic aliphatic resins (Section 26.4.2). Attempts have also been made to use glycidyl ether resins of higher functionality such as the tetrafunctional structure (Figure 26.13).

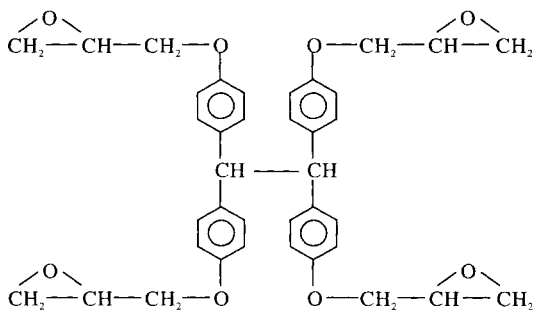


Figure 26.13

Because of the higher viscosity of such resins their use has been restricted to applications where they may be used in solution.

As a result of the demand for flame-resistant resins, halogenated materials have been marketed. A typical example is the diglycidyl ether of tetrachlorobisphenol A (Figure 26.14).

The resin is a semisolid and must be used either in solution form or as blends.

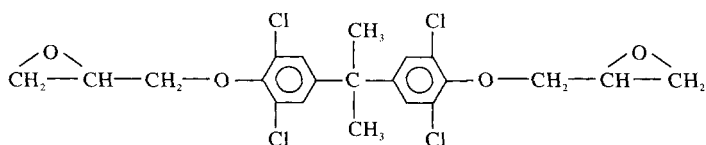


Figure 26.14

In practice the bromo analogue has been more widely used. This arises from a combination of two reasons. In the first instance the tetrabromo resin contains 48% halogen whilst the tetrachloro resin contains 30% halogen.

Secondly, whereas 26–30% chlorine is required to make the resin effectively fire retardant, only 13–15% of bromine is required. It is therefore possible to achieve a greater flexibility in formulation with the bromine resins, which may be blended with other resins and yet remain effectively fire retardant.

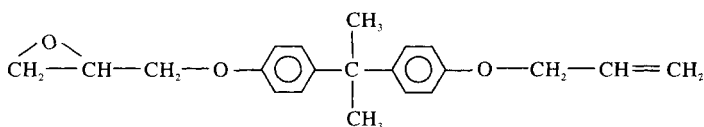


Figure 26.15

Mention may also be made of fixed diethers, some of which are unsaturated. These materials may be cured by a variety of mechanisms. An example is the allyl glycidyl mixed ether of bis-phenol A (Figure 26.15)

26.4.2 Non-Glycidyl Ether Epoxides

Although the first and still most important epoxide resins are of the glycidyl ether type, other epoxide resins have been commercially marketed in recent years. These materials are generally prepared by epoxidising unsaturated compounds using hydrogen peroxide or peracetic acid.



Such materials may be considered in two classes :

- (1) Those which contain a ring structure as well as an epoxide group in the molecule—the cyclic aliphatic resins.
- (2) Those which have an essentially linear structure on to which are attached epoxide groups—the acyclic aliphatic epoxide resins.

Cyclic aliphatic resins

Cyclic aliphatic epoxide resins¹¹ were first introduced in the United States. Some typical examples of commercial materials are shown in Table 26.6.

Table 26.6 Some commercially available cyclic-aliphatic epoxide resins

Chemical name	Commercial reference	Approximate structure	Physical state
1. 3,4-Epoxy-6-methyl-cyclohexylmethyl-3,4-epoxy-6-methyl-cyclohexanecarboxylate	Unox epoxide 201		liquid
2. Vinylcyclohexene dioxide	Unox epoxide 206		liquid
3. Dicyclopentadiene dioxide	Unox epoxide 207		Solid

Compared with standard diglycidyl ether resins, the liquid cyclic aliphatic resins are paler in colour and have a much lower viscosity. Whereas in general the cyclic aliphatic resins react more slowly with amines, there is less difference with acid anhydrides. *Table 26.7* provides data illustrating this point.

Table 26.7 Some properties of cyclic aliphatic resins

	Unox Epoxide 201	Unox Epoxide 206	Unox Epoxide 207	Standard diglycidyl ether
Appearance	pale straw liquid	water white liquid	white powder	straw liquid
Viscosity at 25°C (cP)	1200	7.7	—	10 500
Specific gravity	1.121	1.099	1.330	1.16
Epoxide equivalent	145	76	82	185
Hardening time (100°C) using aliphatic polyamine (h)	24	0.25	—	0.12
HHPA (h)	15	6.75	—	7.00
HHPA +0.5% BDA (h)	1.25	0.75	—	0.75

HHPA, hexahydrophthalic anhydride; BDA, benzyldimethylamine.

Because of the compact structure of the cycloaliphatic resins the intensity of cross-linking occurring after cure is greater than with the standard diglycidyl ethers. The lack of flexibility of the molecules also leads to more rigid segments between the cross-links.

As a consequence the resins are rather brittle. The high degree of cross-linking does, however, lead to higher heat distortion temperatures than obtained with the normal diglycidyl ether resins.

Heat aging resistance does not appear to be as good as with the bis-phenol A epoxide but outdoor weathering is said to be superior.

The cycloaliphatic resins also are clearly superior in arc resistance and arc track resistance. This has led to applications in the tension insulators, rocket motor cases and transformer encapsulation.

Because of their low viscosity the liquid cyclic aliphatic resins find use in injection moulding and extrusion techniques, as used for glass-reinforced laminates. They are also very useful diluents for the standard glycidyl ether resins.

Acyclic aliphatic resins

These materials differ from the previous class of resin in that the basic structure of these molecules consists of long chains whereas the cyclic aliphatics contain ring structures. Three subgroups may be distinguished, epoxidised diene polymers, epoxidised oils, and polyglycol diepoxides.

Typical of the epoxidised diene polymers are products produced by treatment of polybutadiene with peracetic acid. The structure of a molecular segment (*Figure 26.16*) indicates the chemical groupings that may be present.

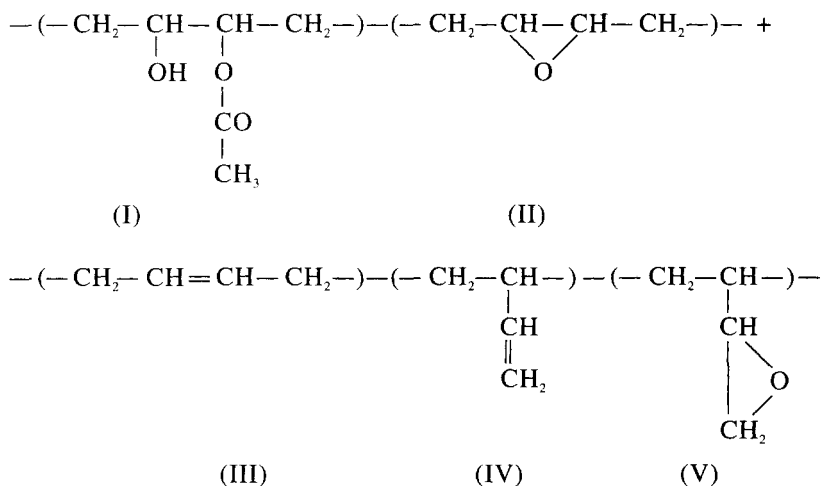


Figure 26.16

Residue (I) is a hydroxy-acetate segment produced as a side reaction during the epoxidising process, (II) is an epoxide group in the main chain, (III) is an unreacted segment, (IV) is an unreacted pendant vinyl group present through a 1:2 addition mechanism whilst (V) is an epoxidised derivative of the vinyl group.

The epoxidised polybutadiene resins available to date are more viscous than the diglycidyl ethers except where volatile diluents are employed. They are less reactive with amines but have a similar reactivity with acid anhydride hardeners. Cured resins have heat distortion temperatures substantially higher than the conventional amine-cured diglycidyl ether resins. A casting made from an epoxidised polybutadiene hardened with maleic anhydride and cured for two hours at 50°C plus three hours at 155°C plus 24 hours at 200°C gave a heat

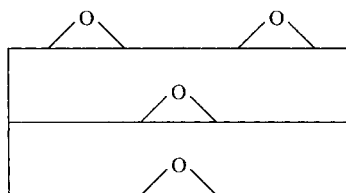
Table 26.8 Some properties of epoxidised polybutadiene resins

	A	B	C	Standard diglycidyl ether
Appearance	amber liquid	light yellow liquid	light yellow liquid	straw coloured liquid
Viscosity at 25°C (cP)	180 000	16 000	1500	10 500
Specific gravity	1.010	1.014	0.985	1.16
Epoxide equivalent	177	145	232	185
Hardening time (100°C) using				
(a) aliphatic amine (h)	1	1.3	1.7	0.12
(b) maleic anhydride (h)	1	1.25	1.25	1.5

* Contains about 23% volatile matter.

distortion temperature of 250°C. Some typical characteristics of the resins are given in *Table 26.8*.¹¹

Epoxidised drying oils have been available for several years as stabilisers for poly(vinyl chloride). They may be considered to have the skeletal structure shown in *Figure 26.17*.

*Figure 26.17*

The number of epoxy groups per molecule will vary but for modified soya bean oils there are an average of about four whereas there are about six for epoxidised linseed oils.

As with the other non-glycidyl ether resins the absence of the ether oxygen near to the epoxide group results in low reactivity with amine hardeners whereas activity with acid anhydride proceeds at reasonable rates.

The epoxidised oils are seldom used in a cross-linked form as the products are rather soft and leathery. Exceptions to this are their occasional use as diluents for more viscous resins and some applications in adhesive formulations.

The polyglycol diepoxides, which are used as reactive flexibilisers, are considered in the next section.

Nitrogen-containing epoxide resins

There has been recent interest in a number of epoxide resins containing nitrogen. Prominent amongst these is triglycidyl isocyanurate (*Figure 26.18 (a)*). This material is unusual in that it is marketed in crystalline form. Because of its trifunctional nature it yields higher T_g than bis-phenol A resins with corresponding hardeners. The resins are also reputed to have good oxidation and tracking resistance.

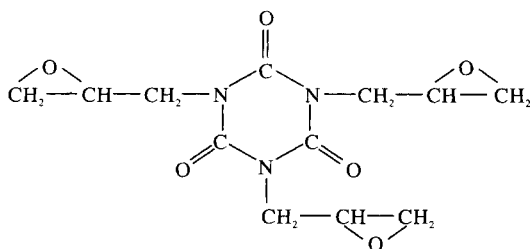


Figure 26.18 (a)

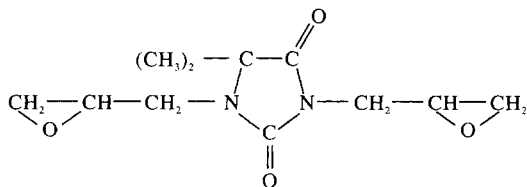


Figure 26.18 (b)

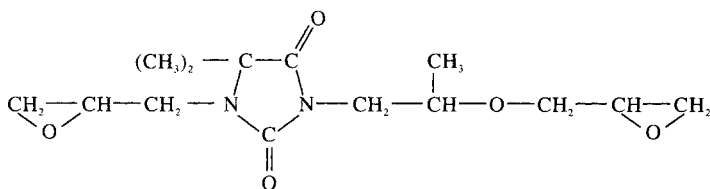


Figure 26.18 (c)

Rather similar are the 5,5-dimethylhydantoin derivatives shown in *Figure 26.18* (b, c). These resins are said to confer improved weathering resistance but also exhibit higher water absorption. Another trifunctional material is *p*-glycidyl-oxy-*N,N*-diglycidylaniline. This has been recommended for adhesive systems in conjunction with benzophenonetetracarboxylic acid dianhydride, which is a room temperature curing agent in this case.

26.5 DILUENTS, FLEXIBILISERS AND OTHER ADDITIVES

For a number of purposes the unmodified epoxide resins may be considered to have certain disadvantages. These disadvantages include high viscosity, high cost and too great a rigidity for specific applications. The resins are therefore often modified by incorporation of diluents, fillers, and flexibilisers and sometimes, particularly for surface coating applications, blended with other resins.

Diluents are free-flowing liquids incorporated to reduce the resin viscosity and simplify handling. At one time hydrocarbons such as xylene were used for this purpose but, being non-reactive, were lacking in permanence. Today, reactive diluents such as phenyl glycidyl ether (*Figure 26.19*) (I), butyl glycidyl ether (II) and octylene oxide (III) are employed. Since, however, they are more volatile than the resin, care must be used in vacuum potting applications.

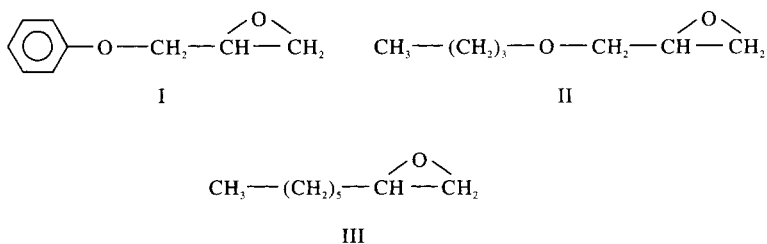


Figure 26.19

The diluents tend to have an adverse effect on physical properties and also tend to retard cure. Many are also skin irritants and must be used with care. For this reason they are seldom used in amounts exceeding 10 phr.

Fillers are used in tooling and casting application. Not only do they reduce cost but in diluting the resin content they also reduce curing shrinkage, lower the coefficient of expansion, reduce exotherms and may increase thermal conductivity. Sand is frequently used in inner cores whereas metal powders and metal oxide fillers are used in surface layers. Wire wool and asbestos are sometimes used to improve impact strength.

In order to increase the flexibility, and usually, in consequence, the toughness of the resins, plasticisers and flexibilisers may be added. Non-reactive plasticisers such as the conventional phthalates and phosphates have proved unsuccessful. Monofunctional materials, which in some cases also act as reactive diluents, have been used but are not of great importance.

More interest has been shown in polymeric flexibilisers, particularly the low molecular weight polyamides from dimer acid (see Chapter 18), the low molecular weight polysulphides (Chapter 19), polyamines and the polyglycol diepoxides.

The low molecular weight polyamides are interesting in that they are not only flexibilisers but that they also act as non-irritating amine hardeners, reaction occurring across amine groups present. A certain amount of latitude is allowable in the ratio of polyamide to epoxy resin but the optimum amount depends on the epoxy equivalent of the epoxide resin and the amine value of the polyamide. (The amine value is the number of milligrams of potassium hydroxide equivalent to the base content of 1 gram polyamide as determined by titration with hydrochloric acid). The polyamides are highly viscous and must be used in resin solutions or at elevated temperatures.

Elevated temperatures are necessary for cure and the chemical resistance of the laminates is inferior to those from unmodified resins. Because of problems in handling, the polyamides have found only limited use with epoxy resins, mainly for coating and adhesive applications.

The low molecular weight polysulphides have found somewhat greater use. Of general structure HS—R—SH and with molecular weights of approximately 1000 they will react with the epoxy group to cause chain extension but not cross-linking. The normal hardeners must therefore be employed in the usual amounts (Figure 26.20).

The polysulphides used are relatively mobile liquids with viscosities of about 10 poise and are thus useful as reactive diluents. They may be employed in any ratio with epoxide and products will range from soft rubbers, where only polysulphides are employed, to hard resins using only epoxide.

The amine flexibilisers may be used in two ways :

- (1) Where allowance is made for the reactivity of the hardener.
- (2) Where the reactivity of the hardener is ignored.

Progressive replacement of amine hardener by a low-viscosity flexibiliser will reduce mix viscosity, increase pot life and reduce the heat distortion temperature of the cured system. Higher impact strengths are achieved using approximately equivalent amounts of hardener and flexibiliser.

Using flexibilisers in addition to the usual amount of hardener, very flexible products may be obtained.

Although in many respects they are similar to the liquid polysulphides, the amine flexibilisers differ in three important respects:

- (1) They reduce the reactivity of the system rather than increase it.
- (2) They are compatible with a different range of room temperature hardeners.
- (3) They have a low level of odour.

Table 26.10¹³ compares the effect of the above classes of flexibiliser.

Table 26.10 Influence of flexibilisers on epoxy resins

	Difunctional amine			Polysulphide			Polyamide	
Flexibiliser	—	25	25	50	25	50	43	100
Epoxy resin	100	100	100	100	100	100	100	100
Amine hardeners	20	13.2	20	20	20	20	—	—
Pot life (1 lb) (min)	20	69	44	76	13	6	150	140
Viscosity (25°C)(cP)	3700	1070	870	490	—	—	210 000	210 000
Flexural strength (lbf/in ²)	16 000	14 400	17 710	—	15 300	—	10 700	11 670
(MPa)	110	99	122	—	105	—	73	80
Compressive yield stress (lbf/in ²)	15 000	13 900	14 330	—	12 300	—	12 800	10 700
(MPa)	103	96	98	—	85	—	88	73
Impact strength (ft lb ^{1/2} in notch)	0.7	0.82	1.03	8.0	0.5	1.7	0.3	0.32
Heat distortion temperature (°C)	95	44	40	<25	53	32	81	49

Yet another approach to the production of flexible epoxide resin-based systems is to modify the epoxide resin itself. There are now available polyglycol diepoxides of the general structure in Figure 26.22 where *n* is in the range 2–7.

Used alone they give soft compositions and they are usually used in blends with other epoxide resins. Compared with unmodified rigid resins the blends

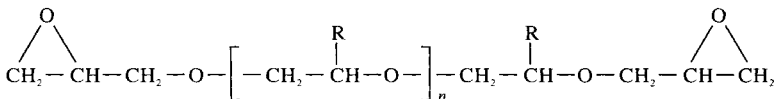


Figure 26.22

have a greater toughness and elongation at break when cured whilst the uncured resins have a lower viscosity. They have been used for laminating safety glass to television tubes, in encapsulation applications subjected to extensive thermocycling and in tooling.

26.6 STRUCTURE AND PROPERTIES OF CURED RESINS

Since the characteristic grouping of the resins discussed in this chapter largely disappears on cross-linking it is difficult to make simple generalisations relating structure to properties.

Being cross-linked, the resin will not dissolve without decomposition but will be swollen by liquids of similar solubility parameter to the cured resin. The chemical resistance is as much dependent on the hardener as on the resin since these two will determine the nature of the linkages formed. The acidic hardeners form ester groups which will be less resistant to alkalis.

The main skeleton of the resins themselves has generally good chemical resistance

The thermal properties of the resin are dependent on the degree of cross-linking, the flexibility of the resin molecule and the flexibility of the hardener molecule. Consequently the rigid structures obtained by using cycloaliphatic resins or hardeners such as pyromellitic dianhydride will raise the heat distortion temperatures.

The resins are somewhat polar and this is reflected in the comparatively high dielectric constant and power factor for an insulating material.

26.7 APPLICATIONS

The epoxide resins are used in a large number of fields, including in surface coatings, in adhesives, in potting and encapsulation of electronic components, in tooling, for laminates in flooring and to a small extent in moulding powders and in road surfacing.

The encapsulation of electrical components provides an interesting extension to the use of plastics materials as insulators. Components of electronic systems may be embedded in a single cast block of resin (the process of encapsulation). Such integrated systems are less sensitive to handling and humidity and in the event of failure the whole assembly may be replaced using seldom more than a simple plugging-in operation. Encapsulation of miniaturised components has proved invaluable, particularly in spacecraft.

The formulation of encapsulating systems involves a great deal of attention. In order to achieve adequate wetting and impregnation the resin viscosity must be low. Since the encapsulation operation is often carried out under vacuum it is also necessary that the mix be free of volatile components. Exothermic heat and shrinkage on cure may damage or affect the characteristics of the components to be potted. The coefficient of thermal expansion should be brought as near to that of the components as possible by judicious use of fillers. Alternatively the system used can be made more ductile by the use of the flexibiliser such as polysulphide resin. It is also important that components of the mix do not react with any of the materials forming the electronic components. Finally the cost should be at the minimum possible to give a satisfactory formulation.

Systems based on the epoxide resins may be provided which are closer to these requirements than can be obtained in other ways. The polyester resins are very restricted because of their high shrinkage, the corroding influence of polyester formulations on copper and on the volatility of components. There is, however, some application of flexible polyurethanes where good damping qualities are of importance. The low shrinkage and simplicity of fabrication make epoxide resins admirably suited for a number of tooling applications. Patterns, jigs, metal shaping moulds and vacuum forming moulds are frequently made from these materials. Since many of these products are quite large in bulk it is important that low exotherm curing systems are used. A reduction in exotherm is also achieved by using large quantities of fillers which in addition may substantially lower the cost. Large mouldings are often made by a two-stage process. The inner surfaces of the casting mould are covered with about a $\frac{1}{2}$ in deep layer of plasticine or some similar material. The residual space is then filled with a sand-resin-hardener mixture. When this has hardened it is removed, and the plasticine stripped from the mould and the resin sand core. The core is then replaced in its original position, leaving a gap where there was previously the layer of plasticine. This gap is then filled with a resin mixture containing a fine filler and allowed to harden.

The choice of filler depends on the end use. Metal fillers will improve machineability, hardness and thermal conductivity but may in some cases inhibit cure.

As mentioned in the introduction, epoxide resin laminates are much less important in tonnage terms than those for polyesters. However, in terms of value the epoxide laminates are significant.

Compared with the polyesters the epoxide resins generally have better mechanical properties and, using appropriate hardeners, better heat resistance and chemical resistance, in particular, resistance to alkalis.

The laminates are employed mainly where an intermediate degree of heat stability is required which does not justify the use of the more expensive silicone and other laminates considered in Chapter 29. They have additional advantages over the silicones in their ease of forming by wet lay-up techniques and the greater strength of the laminates.

Epoxide resin laminates are of particular importance in the aircraft industry. It has been stated that the Boeing 757 and 767 aircraft use 1800 kg of carbon fibre/epoxide resin composites for structural purposes per aeroplane. The resin has also been used with Aramid fibres for filament-wound rocket motors and pressure vessels. The AV-18 fighter aircraft is also said to be 18% epoxide resin/carbon fibre composite. The resins are also widely used both with fibres and with honeycomb structures for such parts as helicopter blades.

Epoxide resins reinforced with carbon and Aramid fibres have been used in small boats, where it is claimed that products of equal stiffness and more useable space may be produced with a 40% saving in weight over traditional polyester/glass fibre composites. Aramid fibre-reinforced epoxide resins have been developed in the United States to replace steel helmets for military purposes. Printed circuit board bases also provide a substantial outlet for epoxide resins. One recent survey indicates that over one-quarter of epoxide resin production in Western Europe is used for this application. The laminates also find some use in chemical engineering plant and in tooling.

Perhaps rather surprisingly recent competition has come more from thermoplastics than from other thermosetting materials. The thermoplastics in question

are the highly aromatic polymers with their high heat deflection temperatures, high thermal index, low flammability and low smoke emission. Amongst such materials, the polyether ether ketones and polyetherimides are particularly noteworthy.

The properties of the laminates will depend on a number of factors, of which the following are the most important:

- (1) Resin used.
- (2) Hardener used.
- (3) Fillers and modifiers used.
- (4) Type of reinforcement.
- (5) Resin content of laminate.
- (6) Curing conditions.

Since these factors can have a considerable influence on properties it is difficult to give typical figures. *Table 26.11* shows some quoted figures for glycidyl ether resin cured with diaminophenylmethane. The laminates were pressed at 400 lbf/in² (2.75 MPa) for one hour at 160°C and post-cured for eight hours at 60°C.

Table 26.11 Mechanical properties of epoxy-glass cloth laminates

	<i>Resin A Mol. Wt. 1000</i>	<i>Resin B Mol. Wt. 1500</i>
Tensile strength (10 ³ lbf/in ²)	52–59	61–66
(MPa)	360–410	420–450
Tensile modulus (10 ⁶ lbf/in ²)	2.9–3.4	3.5–4.0
(MPa)	20 000–24 000	24 500–28 000
Flexural strength (10 ³ lbf/in ²) 25°C	80–85	95–100
127°C	69–74	70–75
(MPa) 25°C	550–585	650–690
127°C	475–510	482–517
Flexural modulus (10 ⁶ lbf/in ²) 25°C	3.6–3.9	4.4–4.6
(MPa)	24 800–26 900	30 300–31 700

The electrical properties will also depend on the above factors as well as on the test conditions, in particular temperature, test frequency and humidity. *Table 26.12* quotes ranges for figures quoted in the literature for various electrical properties.

Table 26.12 Electrical properties of laminates

<i>Property</i>	<i>Unit</i>	<i>Range of values</i>
Power factor	—	0.008–0.04
Dielectric constant	—	3.4–5.7
Dielectric strength	kV/cm	100–220
Volume resistivity	Ω m	10 ¹⁶ –10 ¹⁸

Moulding powders based on epoxy resins have been available on a small commercial scale for several years. Their particular advantages are the very low shrinkage on cure and the high fluidity developed during the moulding operation. This makes them particularly suitable for moulding thin sections round relatively large metal inserts and for moulding around delicate pins and inserts. Although some commercial grades are glass fibre filled their low viscosity in the molten state allows them to be transfer moulded without difficulty.

The finished mouldings have high dimensional stability, low water absorption and good resistance to tracking. They also exhibit good heat resistance and mouldings are said to have withstood temperatures of 200°C without undue deterioration.

The application of the moulding powders is limited by their cost, which is greater than that of general purpose phenolics. Main end uses have been for electronic applications, where good electrical properties and heat resistance are required, particularly in mouldings containing inserts.

The composition of an epoxide moulding material will greatly depend on the specific application, and this has been discussed at length.¹⁴ The resin may be of the epoxide novolac type and there will also be present hardeners, fillers (such as silica), a silane coupling agent, pigment, flame retardant and a wax release agent.

One limitation of epoxide moulding compositions is their short shelf life (typically 1–3 months), which necessitates strict stock control. The compounds may be compression, transfer or injection moulded, although compression moulding is preferred for long-fibre grades.

When compression moulding, it is common to pellet and either preheat or preplasticise the material before moulding to about 80–100°C. Standard material is typically moulded at 150–200°C at 5–20 MPa moulding pressure with curing times of about 80 seconds. Long-fibre grades require about twice the pressure and somewhat longer cure times. Transfer moulding, with variable speed transfer rams, is very useful for electronic encapsulation and requires transfer pressures of 10–50 MPa but with curing times of less than one minute for standard grades. Injection moulding of epoxides has the advantage over other thermosetting moulding compositions in that thick-wall components can be produced using very short cycle times (20–40 seconds). They are also useful in that mouldings are comparatively insensitive to moderate levels of overcure, making it easier to produce mouldings of varying section. The low melt viscosity is beneficial for moulding round, delicate inserts, but these should be preheated before being put into the mould to prevent cracking around inserts.

Some properties of a typical grade of epoxy moulding powder are given in *Table 26.13*.

The largest single end use of epoxide resins, accounting for over 50% of production, is for surface coatings. They may be blended with other resins such as alkyds, amino-resins and phenolics or they may be esterified by heating with resin acids or fatty acids. They may be used in solution form or more commonly as solventless coatings, either liquid resins or powders, the latter being applied by fluid bed or electrostatic spray technique. As a class the epoxides therefore have great versatility and this, combined with excellent adhesion, good chemical resistance and flexibility, has led to many industrial applications.

The excellent adhesion, high cohesion, low shrinkage on cure, absence of volatile solvents and low creep of the resins have led to important applications as adhesives, particularly for metal-to-metal and metal-to-plastics bonding. As with

Table 26.13 Properties of a typical epoxide moulding composition (BS 771 Test Methods where applicable)

<i>Property</i>	<i>Units</i>	<i>Value</i>
Specific gravity	—	1.8–2.1
Flexural strength	10 ³ lbf/in ² (MPa)	13–19 90–130
Mould shrinkage	cm/cm	<0.002
After-shrinkage 48 h at 105°C	%	negligible
Water absorption	mg	5–10
Dielectric constant 800 Hz	—	4.5–5.5
10 ⁶ Hz	—	4.5–5.0
Power factor 800 Hz	—	0.01–0.02
10 ⁶ Hz	—	0.01–0.02
Volume resistivity	Ω m	10 ¹⁶ –10 ¹⁷

the surface coating there is a diversity of possible formulations available, selection being dependent on the requirements of the end-product.

The resins have also found use in a number of other directions. The use of the resins in floorings and road surfacings is somewhat spectacular. In spite of the high initial cost, such floorings have excellent chemical resistance and resistance to wear. The resins are claimed to be of particular value at road junctions and roundabouts, where severe wear is experienced, but where repairs and maintenance operations need to be kept to a minimum because of the resultant disruption in the flow of traffic.

Epoxide resins are available in a powder form that contains a suitable hardening system. The powder may be used for coating metals by fluidised bed or by electrostatic spraying techniques. Unlike with nylon and polyolefin powder coatings it is necessary to bake the coating in order to cure the resin. The powder coating are particularly useful for application of thick film to parts of a complicated or irregular shape and have good chemical and electrical resistance. The coatings are much harder and adhere more strongly to the substrate than the older more well-established thermoplastic powders. The electrostatic spraying of epoxide powders to form surface coatings presents an important challenge to the usual methods using solutions.

References

1. *German Patent* 676,117
2. *US Patent* 2,324,483
3. *US Patent* 2,444,333
4. *US Patent* 2,582,985
5. *US Patent* 2,456,408
6. *US Patent* 2,521,911: *US Patent* 2,521,912
7. *US Patent* 2,528,399: *US Patent* 2,528,360
8. *US Patent* 2,467,171
9. *US Patent* 2,575,558
10. LEE, H., and NEVILLE, K., *Epox Resins in their Application and Technology*, McGraw-Hill, New York (1957)
11. LEWIS, R. N., *Brit. Plastics*, **35**, 580 (1962)
12. SCHECHTER, J., WYNSTRA, L., and KURKJY, R. P., *Ind. Eng. Chem.*, **48**, 94 (1956)
13. LEWIS, R. N., from *Plastics Progress 1959* (Ed. P. Morgan), Iliffe, London. p. 37 (1960)
14. GOOSEY, M. T., *Plastics for Electronics* (Chapters 5 and 6), Elsevier Applied Science, London (1985)

Bibliography

- BRUINS, P. F. (Ed.), *Epoxy Resin Technology*, Wiley, New York (1968)
- GOOSEY, M. T., *Plastics for Electronics* (Chapters 5 and 6), Elsevier Applied Science, London (1985)
- LEE, H., and NEVILLE, K., *Epoxy Resins in their Application and Technology*, McGraw-Hill, New York (1957)
- LEE, H., and NEVILLE, K., *Handbook of Epoxy Resins*, McGraw-Hill, New York (1967)
- MAY, C. A., and TANAKA, Y. (Eds), *Epoxy Resins: Chemistry and Technology*, Marcel Dekker, New York (1973)
- POTTER, W. G., *Epoxide Resins*, Iliffe, London (1970)
- SKEIST, L., *Epoxy Resins*, Reinhold, New York (1958)

Reviews

- BATZZER E. H., and LOHSE, F., *Kunststoffe*, **66**, 637–41 (1976)
- GARDZIELLA, A., *Kunststoffe*, **86**, 1566–1578 (1996)
- LOHSE, F., and BATZER, E. H., *Kunststoffe*, **70**, 690–4 (1980)
- KUNZE, W., *Kunststoffe*, **77**, 1047–9 (1987)
- MÖCKEL, J., *Kunststoffe*, **80**, 1177–80 (1990)

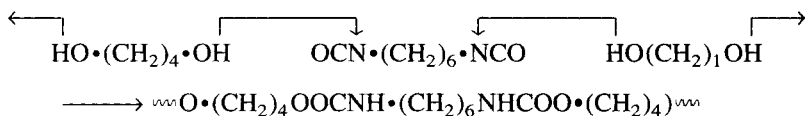
Polyurethanes and Polyisocyanurates

27.1 INTRODUCTION

The reaction of an isocyanate and an alcohol results in the formation of a urethane.



By the same reaction polyhydroxy materials will react with polyisocyanates to yield polyurethanes. For example, the reaction between 1,4-butanediol and hexamethylenedi-isocyanate is shown below:



This particular polymer is a fibre-forming material (Perlon U). Although in many respects this reaction resembles the formation of polyesters and polyamides it is not a condensation reaction but involves a transfer of hydrogen atoms and thus may be considered as an example of rearrangement polymerisation.

Although the first polyurethanes were similar to that shown above, several polymers currently used contain many linkages in addition to the urethane group. Because of this the term polyurethane is now generally extended to cover all the complex reaction products of isocyanates and polyhydroxy compounds (the latter frequently known in this context as polyols).

Commercial development of the polyurethanes arose from the work of German chemists attempting to circumvent the Du Pont patents on nylon 66. O. Bayer and his team of chemists were able to produce fibre-forming polymers by reacting aliphatic di-isocyanates and aliphatic diols (glycols). Subsequent work resulted in the production of useful products by using polymeric hydroxyl-containing compounds such as polyesters to give rubbers, foams, coatings and adhesives.

Whilst initial development was primarily in the fields of fibres and rubbers, the presence of polyurethanes at about sixth position in the production league tables is largely due to the widespread use of foam materials. By 1980 global consumption was of the order of 3×10^6 tonnes per annum.

Since 1980, partly due to the maturity of markets and partly due to the advent of legislation aimed at reducing fire risks, particularly in furniture, annual growth rates have not always been positive. Furthermore statistics for polyurethane production and consumption are somewhat unreliable. Nevertheless it was estimated in one trade journal that in 1998 global polyurethane production was as high as 5×10^6 t.p.a. with Europe and North America each consuming about one-third of global output, Latin America 10% and the Pacific Rim 25%. Particularly noteworthy was the rapidly growing Chinese demand for polyurethanes from about 100 000 t.p.a. to 500 000 t.p.a. during the course of the 1990s. Another trade journal predicted in 1998 that in the year 2000 global production would be of the order of 9×10^6 t.p.a.

The market is dominated by flexible foam applications (43% in the United States) and rigid and semi-rigid foam (29%). Cast elastomers (4%) and RIM elastomers (3%) have only specialised outlets. The remaining sizeable 21% of the market cover such diverse uses as thermoplastic rubbers, surface coatings, adhesives, sealants and synthetic leathers.

27.2 ISOCYANATES

The first isocyanates were produced by Wurtz¹ in 1849 by reacting organic sulphates with cyanic acid salts.



Most commercial methods are based on the phosgenation of amines and their salts, a route first described by Hentschel² in 1884. Only a few isocyanates are used commercially and the most important are:

- (1) 80:20 mixtures of 2,4-tolylene di-isocyanate with 2,6 tolylene di-isocyanate (80:20 TDI) and their derivatives.
- (2) A 65:35 mixture of the above (65:35 TDI).
- (3) 'Diphenylmethane' di-isocyanates (MDI).
- (4) Naphthylene di-isocyanate.
- (5) Hexamethylene di-isocyanate and its derivatives.
- (6) Triphenylmethane-*pp'p''*-triyl tri-isocyanate.
- (7) p-Phenylene di-isocyanate.

These materials are all liquids.

The TDI mixtures are produced by a series of reactions starting from toluene. The first stage is the nitration of the toluene to yield 2-nitrotoluene and 4-nitrotoluene in roughly equal proportions. These can be further nitrated, the 4-isomer yielding only 2,4-dinitrotoluene and 2-nitrotoluene both the 2,4- and the 2,6-dinitro compound (*Figure 27.1*).

If toluene is dinitrated without separation a mixture of about 80% 2,4-dinitrotoluene and 20% 2,6-dinitrotoluene is obtained. Nitration of separated 2-nitrotoluene will yield a mixture of approximately 65% of the 2,4- and 35% of

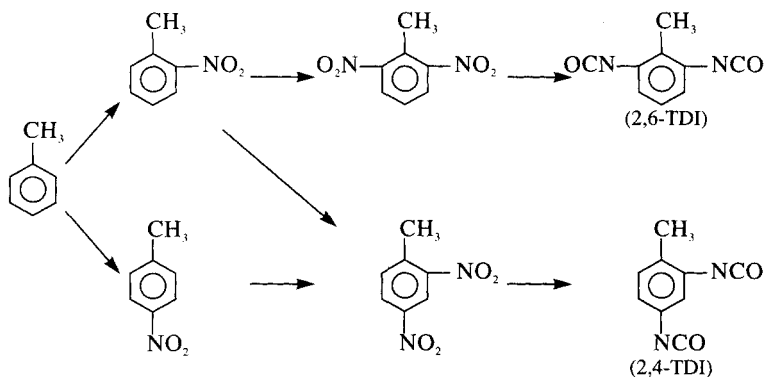
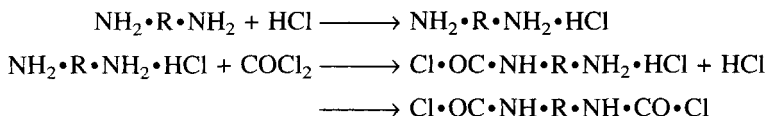


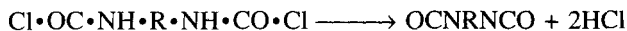
Figure 27.1

the 2,6-isomer. Both mixtures are used for the manufacture of commercial isocyanates.

The next stage is the reduction of the nitro compounds to amines using such reagents as iron dust and water. The resultant amines are then reacted with phosgene. A number of variations in the phosgenation process have been described in the literature.³⁻⁵ The general method is to react a solvent slurry of the appropriate amine hydrochloride with phosgene at about 140°C, typical solvents being toluene, *o*-dichlorobenzene and nitrobenzene. The initial reactions are primarily



The carbamoyl chloride formed may then be decomposed more or less simultaneously with the initial phosgene-amine reaction to produce diisocyanate. A urea may be formed as the result of side reactions.



In one projected commercial modification of the process the phosgenation stage is replaced by one in which the nitro compounds are reacted with CO and an alcohol to form a urethane. This is then split to form an isocyanate in the second step.

1,5-Naphthylene diisocyanate, important in the production of certain rubbers, can be prepared by a similar route starting from naphthalene. Hexamethylene diisocyanate is prepared from hexamethylenediamine, an intermediate readily available because of its large-scale use in polyamide manufacture. It is, however, less reactive than either TDI or MDI and also more toxic. In the presence of certain catalysts, including those based on tin compounds, the activity may be comparable to that of TDI. In order to reduce the toxicity a higher molecular weight derivative made by reacting the hexamethylene diisocyanate with water can be used (Figure 27.2).

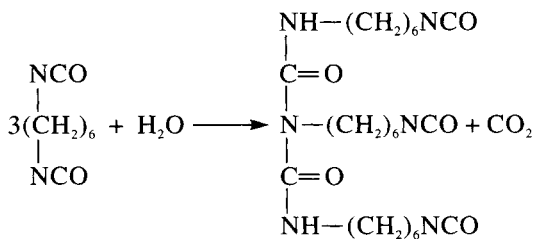


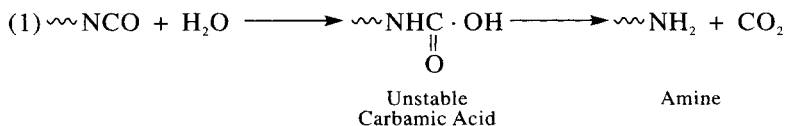
Figure 27.2

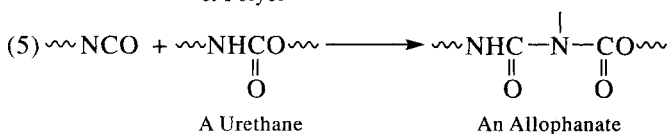
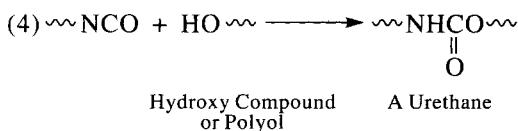
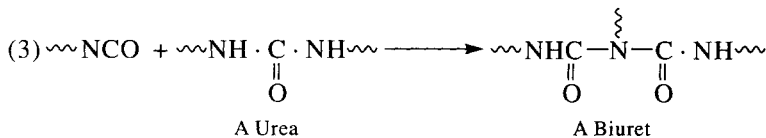
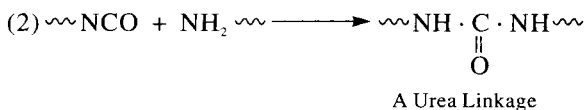
This tri-isocyanate is reported to impart good light stability and weather resistance in polyurethane coatings and is probably the most widely used aliphatic isocyanate. A number of other aliphatic polyisocyanates have been introduced recently in attempts to produce polyurethanes with improved light stability. Amine derivatives of diphenylmethane are made by reacting aniline or toluidines with formaldehyde. These can lead to a mixture of di-isocyanates, the 'diphenylmethane di-isocyanates' (MDIs) of commerce. Triphenylmethane-*pp'p'*-triyl tri-isocyanate is produced from leucorosanine.

For environmental reasons there has been interest in methods for manufacturing isocyanates without the use of phosgene. One approach has been to produce diurethanes from diamines and then to thermally cleave the diurethanes into diisocyanates and alcohols. Although this method has been used for the production of aliphatic diisocyanates such as hexamethylene diisocyanate and isophorone diisocyanate, for economic reasons it has not been adopted for the major aromatic isocyanates MDI and TDI.

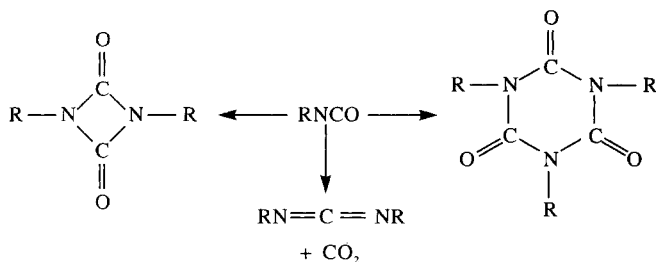
Isocyanates are toxic materials and care should be exercised in their use. Their main effect is on the respiratory system and as a result people exposed to them may suffer from sore throats, bronchial spasms and a tightness of the chest. The greatest troubles are usually associated with people having a history of bronchial troubles. Other individuals, once sensitised by the reagents, will react to the slightest trace in the atmosphere. Isocyanates may also affect the skin and the eyes. The respiratory effects of the isocyanates are directly related to their volatility. The most volatile and hence the most difficult to use is hexamethylene di-isocyanate but this is rarely used in the manufacture of foams. The TDI mixtures are rather less volatile but should be used in well-ventilated conditions. Where it is desired to produce rigid foam *in situ* in a building between cavity walls or about a ship's cold storage hold then the even less volatile diphenylmethane di-isocyanates are to be preferred. Isocyanates are so reactive that they do not survive in finished products such as foams and there is no evidence that these products contain any toxic residues.

Isocyanates are highly reactive materials and enter into a number of reactions with groups containing active hydrogen. The reactions of most importance in the formation of polyurethanes are:





In addition, isocyanates may, under appropriate conditions, react with themselves to give dimers, trimers (isocyanurates) and carbodi-imides.



Not only are these reactions of importance in the development of the cross-linked polyurethane networks which are involved in the manufacture of most polyurethane products but many are now also being used to produce modified isocyanates. For example, modified TDI types containing allophanate, urethane and urea groups are now being used in flexible foam manufacture. For flexible integral foams and for reaction injection moulding, modified MDIs and carbodi-imide MDI modifications are employed.

The significance of these reactions will be discussed with the various types of product.

27.3 FIBRES AND CRYSTALLINE MOULDING COMPOUNDS

As previously mentioned the initial research on polyurethanes was directed towards the preparation of fibre-forming polymers. Many polyhydroxy compounds and many di-isocyanates were used and the melting points of some of the more linear aliphatic polyurethanes produced are given in *Table 27.1*.

Table 27.1

<i>No. of carbon atoms in Di-isocyanate</i>	<i>Glycol</i>	<i>Melting point (°C)</i>
4	4	190
4	6	180
4	10	170
5	4	159
6	3	167
6	4	183
6	5	159
6	9	147
8	4	160
8	6	153
12	12	128

These figures in many ways resemble those of the aliphatic polyamides. Both types of polymer are capable of hydrogen bonding and in both types the greater the distance between amide or urethane links the lower the melting point, provided there is an even number of carbon atoms between the characteristic groupings. Both polyamides and polyurethanes with an odd number of methylene groups in the repeating unit have lower melting points than the polymer with one more, intermediate, carbon atom (i.e. an even number of carbon atoms).

Although 4,4-polyurethane has the highest melting point this material was not produced commercially because of the difficulty of obtaining tetramethylene diisocyanate with the desired degree of purity. The polymer with the next highest melting point, 6,4-polyurethane, the reaction product of hexamethylene diisocyanate and butane-1,4-diol, was thus chosen for commercial production by German chemists during World War II because of the availability of the isocyanate.

The polymer may be prepared by running the isocyanate into the glycol while the temperature is raised slowly to near 200°C. The reaction is exothermic and carried out under a blanket of nitrogen. The polymers produced have a molecular weight of 10 000–15 000 and after filtration may be melt spun into fibres.

Compared with nylon 66 fibres, the polyurethane fibres (known as Perlon U) have a tensile strength at the higher end of the range quoted for nylon 66, they are less prone to discolouration in air, are more resistant to acid conditions and they have a lower moisture absorption. On the debit side they are less easy to dye, are hard, wiry and harsh to handle and have too low a softening point for many applications. They are currently of little importance but have found some use in bristles, filler cloths, sieves and a few other miscellaneous applications.

The linear polyurethanes used to make fibres can also be used as thermoplastics and may be processed by injection moulding and extrusion techniques. A number of grades are available varying in hardness, softening point, water absorption and other properties. That with the highest melting point is based on 6,4-polyurethane but those with lower melting points are copolymers in which about 10–15% of the butanediol-1,4-diol is replaced by another diol such as hexamethylene glycol or methylhexamethylene glycol. The processing characteristics are very similar to the nylons, in particular the low melt viscosity

requires the use of nylon-type injection nozzles. The polymers start to decompose at about 220°C and care should be taken to prevent overheating.

The properties of the polyurethane moulding compositions are also very similar to nylon 66. The greatest difference in properties is in water absorption, the 6,4-polyurethane absorbing only about $\frac{1}{5}$ of that of nylon 66 under comparable conditions. This results in better dimensional stability and a good retention of electrical insulation properties in conditions of high humidity. Resistance to sulphuric acid is somewhat better than with nylon 66 but both types of polymer are dissolved by phenols and formic acid.

There is little call for these thermoplastics materials (marketed as Durethan U, Farbenfabriken Bayer) since they are about twice the price of nylons 66 and 6. Where a thermoplastic for light engineering purposes is required with a low water absorption, nylon 11, acetal resins and, in certain instances, polycarbonates are cheaper and, usually, at least as satisfactory.

Whilst the crystalline fibres and their thermoplastic counterparts are no longer of importance, elastic polyurethane fibres, commonly known as *spandex* fibres, are of significance. These will be considered further in Section 27.4.1.

27.4 RUBBERS

It was pointed out in Chapters 3 and 4 that rubbers are substantially amorphous polymers with glass transition temperatures below their service temperature. The greatest degree of elasticity is obtained with highly flexible segments, generally low intermolecular forces and little or no crystallinity. In order to reduce creep and high compression set it is usual to lightly cross-link the polymers. For high tensile strength, tear resistance and abrasion resistance the above requirements for high elasticity and resilience may require some modification; in particular, some ability to crystallise is often desirable.

By careful formulation it is possible to produce polyurethane rubbers with a number of desirable properties. The first rubbers were prepared by Pinten⁶ in Germany in about 1940. Known as I-Gummi, they were produced by reacting a polyester with a di-isocyanate. These products had a high tensile strength and abrasion resistance but low tear strength and poor low-temperature properties. Subsequently the variables in the formulation were systematically investigated by Bayer, Müller and co-workers⁷ and this led to the advent of the Vulkollan rubbers.

Today three types of solid polyurethane rubber may be recognised, namely:

- (1) Cast polyurethane rubbers.
- (2) Millable gums.
- (3) Thermoplastic polyurethane rubbers.

The cellular materials discussed in Section 27.5 may also be considered as polyurethane rubbers, but because of their importance are treated separately.

27.4.1 Cast Polyurethane Rubbers

These material may be subdivided into four groups:

- (1) Unstable prepolymer systems.
- (2) Stable prepolymer systems.

- (3) Quasi-prepolymer systems.
- (4) One-shot systems.

Unstable prepolymer systems

These systems are dominated by the Vulkollan materials, which remain of importance because of their excellent load-bearing and, for a polyurethane, excellent heat-resisting characteristics.

The starting point in the preparation of these rubbers is a polyester prepared by reacting a glycol such as ethylene or propylene glycol with adipic acid. This is then reacted with an excess of a bulky di-isocyanate such as 1,5-naphthylene diisocyanate (Figure 27.3).

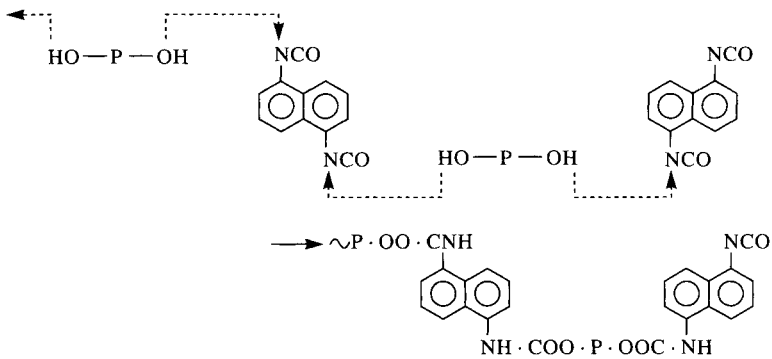


Figure 27.3

The molar excess of di-isocyanate is about 30% so that the number of polyesters joined together is only about 2–3 and the resulting unit has isocyanate end groups. A typical structure, with P for polyester groups, U for urethane and I for isocyanates would be



The resulting 'prepolymer' can then be chain extended with water, glycols or amines by linking cross terminal isocyanate groups (Figure 27.4).

The water reaction evolves carbon dioxide and is to be avoided with solid elastomers but is important in the manufacture of foams. These reactions cause chain extension and by the formation of urea and urethane linkages they provide sites for cross-linking, since these groups can react with free isocyanate or terminal isocyanate groups to form biuret or allophanate linkages respectively (Figure 27.5).

Where urea and urethane groups are present in the polymer chain in approximately equal amounts most branch points are biuret since the urea group reacts faster than urethane links. For branching and cross-linking to occur it is essential to have a slight excess of isocyanates over the glycol or amine chain extender so that isocyanate groups are available for formation of biuret and allophanate linkages. The degree of cross-linking can to some extent be controlled

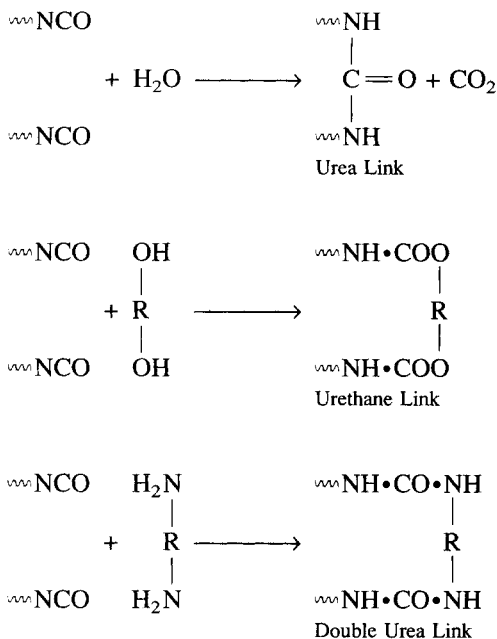


Figure 27.4

by adjusting the amount of excess isocyanate, whilst more highly cross-linked structures may be produced by the use of a triol in the initial polyester.

In their classical researches Bayer and Müller⁷ investigated the effect of the isocyanate type on the properties of the finished product. They found that 'bulky' aromatic isocyanates such as 1,5-naphthylene di-isocyanate and diphenylmethane di-isocyanates gave products of much higher tear strength and tensile strength than were obtained with either hexamethylene di-isocyanate or TDI. Various polyesters were also prepared and, as a result, it was found that poly(ethylene adipate), with a molecular weight of about 2000 and which allowed a moderate amount of crystallisation, gave the best balance of desirable properties in the product. A variety of chain extenders were also investigated. It was found that extenders which were 'bulky' and tended to 'stiffen' the rubber molecules gave the highest modulus and tear strength whereas extenders with

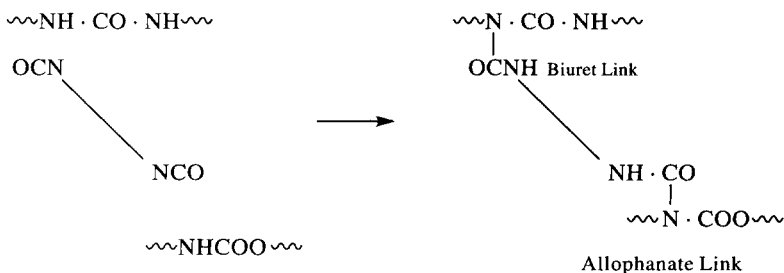


Figure 27.5

flexible linkages gave the greatest elasticity. Aromatic diamines are examples of the first class and thiodiethylene glycol the latter.

Somewhat unexpected results are obtained when the degree of cross-linking is increased by incorporating triols in the original polyester. In contrast to results with hydrocarbon rubbers the greater the degree of cross-linking the lower is the tensile strength and tear resistance but the higher the elasticity. This effect is believed to be due to the fact that in rubbers of the Vulkollan type much of the strength of the material is derived from secondary forces, hydrogen bonding in particular. Cross-linking not only interferes with the effectiveness of such secondary forces but it also restricts crystallisation. Corroborating evidence for this is that at elevated temperatures, where secondary forces are greatly reduced, the more highly cross-linked polymers are rather stronger. The fact that the chain consists of blocks of hard polyurethane segments separated by soft polyol segments is also a contributing factor.

One inherent weakness of Vulkollan-type materials is their susceptibility to hydrolysis. Life in a humid environment may, however, be doubled by the incorporation of 2 pphr (parts per hundred resin) of a carbodiimide.

Stable prepolymer systems

A serious disadvantage of the Vulkollan system is the necessity to use the prepolymer almost immediately after manufacture. In 1958 Du Pont introduced Adiprene C prepolymers (now marketed by Uniroyal). In this case the polyol was the polyether polytetramethylene glycol with tolylene diisocyanate as the isocyanate, the latter ingredient providing the key to the storage stability. Somewhat inferior products were obtained by using glycols as extenders, with better results being obtained using amines such as 3,3'-dichloro-4,4'-diaminodiphenyl methane (MOCA), although concern about the toxicity of this additive has led to the search for alternative materials.

More recently, storage systems based on MDI have become available which pose less of a health hazard than MDI/MOCA systems. Both polyethers and polyesters are used, with glycols being the usual chain extenders.

Both TDI/MOCA and MDI/diol prepolymer systems are of importance for harder grades of printer's rollers and the wear-resisting applications such as pipes, pumps and impellers used in the mining and quarrying industries.

In the late 1990s high quality elastomers were produced using *p*-phenylene diisocyanate (PPDI) but because of its high vapour pressure it has to be used in a prepolymer formulation.

Quasi-prepolymer systems

In these systems the prepolymer is prepared with an excess of isocyanate to give an isocyanate-terminated molecule. This is then reacted with unreacted glycol and other ingredients. The disadvantage of this system is that component streams are of similar volume and viscosity, this facilitating both metering and mixing. The system is used mainly for the manufacture of microcellular products.

One-shot systems

Because of their importance in foam manufacture, one-shot systems are dealt with in more detail in Section 27.5. With solid materials the systems are used for

the manufacture of soft rollers for the printing industry. Cold-curing systems of this type are also used for such diverse applications as cable jointing and potting compounds, and moulds for precast concrete.

27.4.2 Millable Gums

One disadvantage of the prepolymer systems is that they cannot be processed by the conventional methods of rubber technology. This resulted in the development of several materials which could be handled on standard rubber machinery. One example is Urepan 600 (formerly Desmophen A), marketed by Bayer. With these materials the isocyanate is reacted with a slight excess of polyester so that terminal hydroxyl groups are produced in the prepolymer. The prepolymers are rubber-like gums which may be compounded on two-roll mills with other ingredients. They may be cured by addition of a di-isocyanate or preferably a 'latent di-isocyanate', that is a substance which changes into an active isocyanate during moulding operations. This technique is reminiscent of the use of 'hexa' in phenolic resins and latent acid catalysts with the aminoplastics.

Another approach has been adopted by the Du Pont Company with Adiprene C. This is a urethane-type polymer with unsaturated groups in the polymer. Because of the unsaturation the polymer may be vulcanised with sulphur, the standard vulcanising agent of the rubber industry. This is a clear-cut example of a product being modified to suit the processor rather than that of a processor adapting himself to meet new products. Whereas Adiprene C has poor tensile strength when unfilled, the use of carbon black leads to appreciable reinforcement (as is the case with SBR and to some extent natural rubber).

27.4.3 Properties and Applications of Cross-linked Polyurethane Rubbers

Polyurethane rubbers in general, and the Vulkollan types in particular, possess certain outstanding properties. They can have higher tensile strengths than any other rubber and have excellent tear and abrasion resistance. They tend to have a high hardness and a low resilience and in fact may be regarded as somewhat intermediate between conventional rubbers and flexible thermoplastics. The urethane rubbers also show outstanding resistance to ozone and oxygen (features lacking with the diene-rubbers) and to aliphatic hydrocarbons. Reversible swelling occurs with aromatic hydrocarbons. One disadvantage of the materials is that hydrolytic decomposition occurs with acids, alkalis and the prolonged action of water and steam.

Some typical properties of a Vulkollan-type polyurethane cast rubber and a black-reinforced polyurethane rubber processed by conventional techniques are compared with black-reinforced natural and nitrile rubbers in *Table 27.2*.⁸

Urethane rubbers have found steadily increasing use for oil seals, shoe soles and heels, fork-lift truck tyres, diaphragms, chute linings and a variety of mechanical applications. Fabric coatings resistant to dry cleaning are a recent development. In many of these applications high elasticity is not an important prerequisite so that the polyurethane rubbers must be compared not only with other rubbers but also with a variety of thermoplastics.

Table 27.2 Comparison of properties of polyurethane, nitrile and natural rubbers

	<i>Polyurethane raw rubber + black</i>	<i>Polyurethane casting rubber</i>	<i>Natural rubber + black</i>	<i>Nitrile rubber + black</i>
Tensile strength (MPa)	38	37	24.8	20.7
Elongation (%)	640	700	460	363
Resilience (%)	56	69	64	46
Hardness (BS°)	86	86	66	74
Tear strength (MPa)	7.2	10.8	10	5.6
Abrasion resistance (Du Pont test) cm ³ loss	15	16	128	70
Swell in				
aliphatic hydrocarbon (%)	3	6	150	3
aromatic hydrocarbon (%)	77	79	200	141
trichloroethylene (%)	95	120	330	152
lubricating oil (%)	0	0	330	0

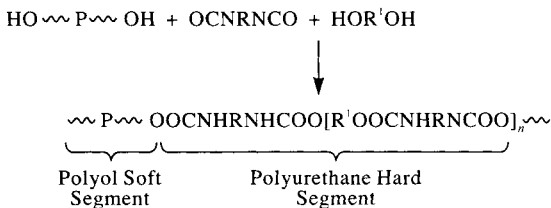
If a branched polyol, usually either castor oil or a simple polyester, is heated with an isocyanate but without chain extenders soft and weak rubbery products are obtained with very low resilience. These materials are useful for encapsulation of electronic components and for printer rollers.

The millable gums are today of limited importance for two reasons:

- (1) Their properties are not generally as good as the cast rubbers.
- (2) It is generally more convenient to use the thermoplastic polyurethane rubbers discussed in Section 27.4.4 for those applications where a cast process is not appropriate.

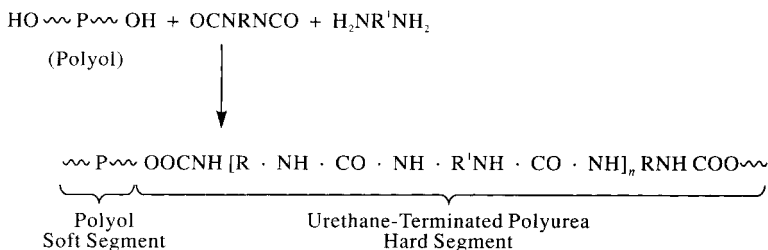
27.4.4 Thermoplastic Polyurethane Rubbers and Spandex Fibres

When polyols, di-isocyanates and glycols are reacted together as described in the previous section they do in fact tend to produce block copolymers as can be seen from the following reaction mechanism:



Since there are likely to be many more glycol molecules than polyol molecules present it is likely that the segment within the bracket will be repeated several times to form a block. Providing that R and R' are small and regular the polyurethane segment will show high intersegment attraction. This may include hydrogen bonding. Furthermore the segments may be able to crystallise.

Similar reactions occur when an amine is used instead of a glycol as chain extender:



With these polymers 'hard' blocks with T_g s well above normal ambient temperature are separated by 'soft' blocks which in the mass are rubbery in nature. This is very reminiscent of the SBS triblock elastomers discussed in Chapter 11 and even more closely related to the polyether-ester thermoplastic elastomers of the Hytrel type described in Chapter 25.

In a typical manufacturing process a prepolymer is first produced by reacting a linear polyester with terminal hydroxyl groups, or a similar polyether with molecular weights in the range 800–2500, with an excess of di-isocyanate (usually of the MDI type) to give an isocyanate-terminated polyol prepolymer plus free (unchanged) isocyanate. This blend is then reacted with a chain extender, usually a glycol such as 1,4-butane glycol, to give a polymer with hard polyurethane segments whose block length depends on the extent of excess isocyanate (and corresponding stoichiometric glycol). It is possible that an excess of isocyanate may react with urethane groups in the chain to produce allophanate cross-links. These do not, however, destroy the thermoplastic nature of the polymers because of their thermal lability, breaking down on heating and reforming on cooling. However, where amines have been used as chain extenders urea groups are produced and these on reaction with excess isocyanate give the more stable biuret cross-links.

Several materials designated as thermoplastic polyurethanes have been introduced onto the market but many of them are slightly cross-linked and this may be increased permanently by a post-curing operation after shaping. One product may, however, be regarded as truly thermoplastic (Estane by Goodrich).

The thermoplastic rubbers have properties similar to those of the cast polyurethane rubbers but, because of the absence of covalent cross-links, have rather higher values for compression set, a common problem with thermoplastic rubbers. Their main uses are for seals, bushes, convoluted bellows and bearings.

One particular form of thermoplastic polyurethane elastomers is the elastic fibre known as *spandex* fibre. Like the usual thermoplastic rubbers these materials consist of hard and soft segments but to qualify for the term *spandex* by the US Federal Trade Commission the polymer used should contain at least 85% of segmented polyurethane. The first commercial material of this type was introduced by Du Pont in 1958 (Lycra). Several other similar materials have since been introduced including Dorlastan (Bayer), Spanzelle (Courtaulds) and Vyrene (US Rubber).

Both polyethers and polyesters may be used as polyols. For example, Du Pont use polytetrahydrofuran for Lycra whilst US Rubber originally used a polyester of molecular mass of about 2000 obtained by condensing adipic acid with a mixture of ethylene and propylene glycols. A polyether-based mixture was used for Vyrene 2 introduced in 1967. All the polyols have terminal hydroxyl groups.

Reaction of these polyols with an excess of isocyanate yields isocyanate terminated materials which are then chain extended by an amine such as hydrazine (NH₂NH₂) or ethylenediamine. The fibre is usually spun from solution in dimethylformamide.

Spandex fibres, because of their higher modulus, tensile strength and resistance to oxidation, as well as their ability to be produced at finer deniers, have made severe inroads into the natural rubber latex thread market. They have also enabled lighter weight garments to be produced. Staple fibre blends with non-elastic fibres have also been introduced.

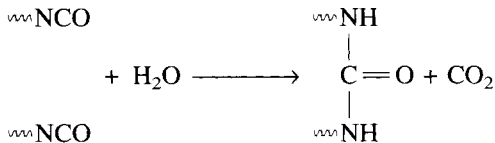
27.5 FLEXIBLE FOAMS

Whereas the solid polyurethane rubbers are speciality products, polyurethane foams are widely used and well-known materials.

In many respects the chemistry of these foams is similar to that of the Vulkollan-type rubbers except that gas evolution reactions are allowed to proceed concurrently with chain lengthening and cross-linking. Although volatile liquids are also used with rigid foams and for low-density flexible foams, the gas for flexible foam is usually carbon dioxide produced during reaction of the polyol, isocyanate and other additives. The earliest foams were produced by using polyesters containing carboxyl groups. These reacted with isocyanates thus



However, subsequent polyesters were produced with low carboxyl values and gas evolution occurred by the reaction already mentioned when discussing the Vulkollans, that between isocyanate and water



The isocyanate group may be terminal on a polyester chain or may be part of the unchanged di-isocyanate. The density of the product, which depends on the amount of gas evolved, can be reduced by increasing the isocyanate content of the reaction mixture and by correspondingly increasing the amount of water to react with the excess isocyanate (that is excess over that required for chain extension and cross-linking).

Polyurethane foams may be rigid, semi-rigid or flexible. They may be made from polyesters, polyethers or natural polyols such as castor oil (which contains approximately three hydroxyl groups in each molecule). Three general processes are available known as one-shot, prepolymer or quasi-prepolymer processes. These variations lead to 27 basic types of product or process, all of which have been used commercially. This section deals only with flexible foams (which are made only from polyesters and polyethers). Since prepolymers and

quasi-prepolymer processes are no longer important with polyesters, the four following types only will be considered here:

- (1) One-shot polyesters.
- (2) Polyether prepolymers.
- (3) Polyether quasi-prepolymers.
- (4) One-shot polyethers.

27.5.1 One-shot Polyester Foams

Until the late 1950s most flexible foams were based on polyester resins. These foams were developed in Germany during World War II and became known as 'Moltopren'. The polyesters commonly have a molecular weight of about 2000 and are commonly produced from adipic acid and a glycol such as diethylene glycol together with a small proportion of a trifunctional ingredient such as trimethylol propane. They are viscous liquids rather similar to polyester laminating resins.

One variation in polyester intermediates that has roused some interest are those prepared by a ring-opening polymerisation of ϵ -caprolactone and methyl- ϵ -caprolactones with titanium catalysts and diol and triol initiators (*Figure 27.6*).

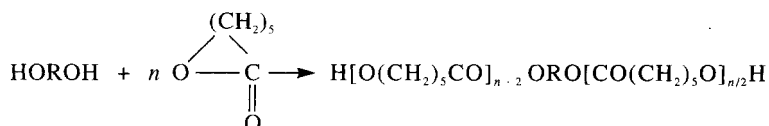


Figure 27.6

Foams may be produced from these resins by addition of 65:35 TDI, water, a catalyst, an emulsifier, a structure modifier and paraffin oil which helps to control pore size and prevents splitting of the foams.

Amongst the catalysts described in the literature may be mentioned dimethylbenzylamine, dimethylcyclohexylamine, diethylaminoethanol, *N*-alkylmorpholines and the adipic acid ester of *N*-diethylaminoethanol. A number of proprietary products of undisclosed composition have also been successfully employed. Emulsifiers include sulphonated castor oil and structure modifiers such as ammonium oleate and silicone oils.

The bulk of flexible foam is produced in block (slab stock) form using machines of the Hencke type or some simple modification of it. In this machine polyester and isocyanate are fed to a mixing head which oscillates in a horizontal plane. The other ingredients, known as the 'activator mixture', are then injected or bled into the isocyanate-polyester blend and the whole mixture is vigorously stirred and forced out of the base of the mixing head. The emergent reacting mixture runs into a trough which is moving backwards at right angles to the direction of traverse of the reciprocating head. In this way the whole of the trough is evenly covered with the reacting mass, which has frequently foamed within a minute or so of issuing from the mixing head. The principle of the Hencke machine is illustrated in *Figure 27.7*.

Because of the drag effect of the side-walls of the trough on the expanding and cross-linking foam the process as described above gives a domed block. Hence

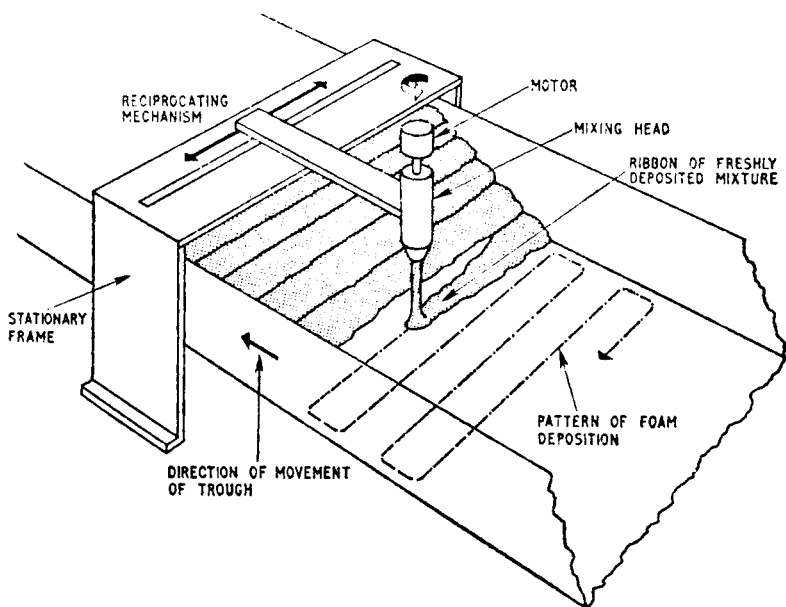


Figure 27.7. Principle of the Henecke machine (Farbenfabrik Bayer). (After Phillips and Parker⁴)

when the block is sliced up into sheet and slab there is an undesirable level of scrap. To some extent the fraction of scrap is reduced by increasing the block size. Over the years block sizes have been increased and widths of 2.20 m and heights of 1.2 m are produced although this is more common with polyether rather than polyester foams.

Much effort has been expended to try and produce flat-top foams. In one process polyethylene sheets placed along the side-walls of the trough rise with the foam. In another technique the reactants are metered from the mixing head into a fixed trough in which partial expansion takes place. The foaming material is then drawn over a weir by a moving band of paper and then drawn down a slope so that the top surface maintains a constant level as the material expands.

In another variation of the process, the foaming mix is fed to the bottom of a cylinder and the foaming mixture is pushed upwards (the Vertifoam process). The mass of material above the reacting foam can be used to control density, whilst in addition volatiles and gases find it more difficult to escape from the system. The solidified cylinder of foam may then be sliced horizontally into large discs.

Both the Henecke process and the variations described above are today widely used in conjunction with polyether polyols, discussed in the next three sections.

Foam may be made from such *polycaprolactones* by reaction with polyisocyanates in the presence of tin catalysts.

27.5.2 Polyether Prepolymers

As will be discussed later, flexible polyester foams are not altogether satisfactory for upholstery applications and in the 1950s the attention of American chemists turned to the use of polyethers. These materials could be obtained more cheaply than the polyesters but the products were less reactive and with the catalyst

systems then available could not be directly converted into foams by a one-shot process. As a result a prepolymer technique, reminiscent of that used with Vulkollan and which had already been used with certain polyesters, was developed.

In this process the polyether is reacted with an excess of isocyanate to give an isocyanate-terminated prepolymer which is reasonably stable if kept in sealed tins in dry conditions. If water, catalysts and other ingredients are added to the product a foam will result. Where linear polyethers are used it is found that this foam has rather poor load-bearing and cushioning properties and where this is important a low molecular weight triol, such as glycerol or trihydroxymethylpropane, is added to the polyether before reaction with isocyanate. This will then provide a site for chain branching. Alternatively a small amount of water could be added to the system. This would react with terminal isocyanate groups, which link up to produce a urea link as mentioned previously. This urea group is more reactive than a urethane link and reacts with isocyanates to give a biuret link as a site for chain branching. It is important that carbon dioxide evolved in the isocyanate-water reaction be allowed to escape and also that the reaction is kept down so that premature foaming does not occur.

Although prepolymer processes have become less important with the advent of the one-shot process they have certain advantages. Because there is less exotherm large blocks of foam can often be produced, there is often a greater flexibility in design of compounds, the reduced amount of free isocyanate reduces handling hazards and there is some evidence⁹ that two-stage foams have slightly better cushioning properties. On the other hand prepolymers have limited stability, are often rather viscous to handle, and do involve an extra process.

27.5.3 Quasi-prepolymer Polyether Foams

This process, which is intermediate between the prepolymer and one-shot process, is useful where prepolymers are too viscous, where the resin does not easily adapt itself to one-shot processes and where the equipment available is more suitable for two-part systems. In principle a polyol is reacted with a large excess of isocyanate so that the prepolymer formed is of low molecular weight and there are a large number of free isocyanate groups. This product is then reacted at the time of foaming with additional hydroxyl compound, water and catalyst to produce the foam. The additional hydroxyl compound may be a polyol or a simple molecule such as ethylene glycol or glycerol which has the additional function of a viscosity depressant. The system has the advantage of flexibility and of having low-viscosity components, but as with one-shot foams there are problems with high exotherms and with a high free isocyanate content. Quasi-prepolymer systems (also known as semi-prepolymer systems) are based on both polyesters, and polyethers are of interest in shoe soling; the former are most wear resistant and the latter the easiest to process.

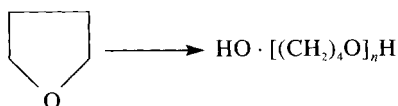
27.5.4 Polyether One-shot Foams

The one-shot polyethers now form the bulk of the flexible polyurethane foam now being manufactured. This is a result of the favourable economics of polyethers, particularly when reacted in a one-shot process, and because the polyethers generally produce foams of better cushioning characteristics. A typical formulation for producing a one-shot polyether foam will comprise

polyol, isocyanate, catalyst, surfactant and blowing agent and these will be considered in turn.

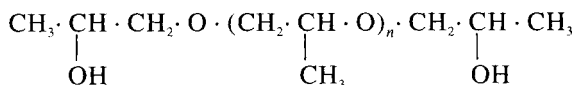
A variety of polyethers have been used and may be enumerated in their order of development as follows:

- (1) Polymers of tetrahydrofuran introduced by Du Pont as Teracol in 1955:



These polyethers produced good foams but were rather expensive.

- (2) Polymers of ethylene oxide, cheaper than the tetrahydrofuran polymers, were found to be too hydrophilic for successful use.
- (3) Propylene oxide polymers are less hydrophilic and also lower in cost and may be prepared by polymerising the oxide in the presence of propylene glycol as an initiator and a caustic catalyst at about 160°C. They have the general structure



The secondary hydroxyl groups of these poly(oxypropylene) glycol diols are less reactive than the primary hydroxyl groups of the earlier polyesters. At the time of the introduction of these polyethers, the catalysts then available were insufficiently powerful for one-shot processes to be practical and so these polymers have been used primarily in prepolymer processes.

- (4) Block copolymers of ethylene oxide and propylene oxide, less hydrophilic than poly(oxyethylene) glycol and more reactive than the propylene oxide polymers, were introduced by Wyandotte Chemical (USA) under the trade name Pluronic.
- (5) Today most polyether polyols are based on propylene oxide, usually in conjunction with 10–15% of ethylene oxide. Reaction is typically carried out at about 100°C at 2–3 atm. pressure using KOH as a catalyst. It is desirable that the polyether is branched and of a moderate molecular weight so that there is a level of cross-link density more typical of an elastomer rather than a rigid thermosetting plastic. The use of such branched polymers also confers better load-bearing characteristics for the foam as compared to foam made from unbranched polyol. Branching is brought about by initiating the reaction with a trifunctional material such as trihydroxymethylpropane, hexane-1,2,6-triol or, most commonly, glycerol. (It will be shown later that, for rigid foams, initiators of higher functionality are used whereas for thermoplastic rubbers difunctional initiators (to give an essentially linear polymer) are employed.)

Where only propylene oxide is used the resultant polymers will be of the following general type:



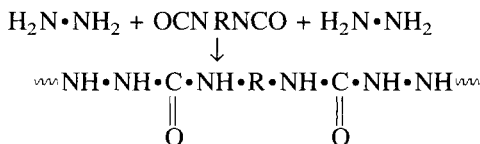
Molecular weights are usually in the range 3000–6000.

For the bulk of domestic upholstery applications the polyol used is made by co-feeding propylene oxide with the minor component of ethylene oxide. On statistical considerations, the bulk of the end groups will derive from the propylene oxide and thus be *secondary hydroxyls*. Higher reactivity may be achieved by the process known as *tipping* to give *tipped polyols*. In this process a propylene oxide homopolymer is grafted with a short block of ethylene oxide units to form a block copolymer which will have *primary hydroxyl* end groups. Such tipped polyols tend to be preferred for higher quality applications such as automotive moulding trim.

- (6) There is an increasing market for higher resilience foams using the so-called *polymer polyols*. Amongst the earliest to become established were suspensions of styrene-acrylonitrile copolymer in the polyol. A variation involved some grafting of SAN, either instead of or in addition to the use of a suspension.

In the 1990s this approach became more common in order to ensure sufficient compressive strength with the trend to lower bulk densities. Furthermore the proportion of SAN to polyol has been increased to about 40%. This may lead to serious stability problems and care must be taken to control the size and distribution of the particles and prevent agglomeration. Polymer polyols using polystyrene as the polymer component have recently become available (Postech-Shell) and are claimed to exhibit good stability, low viscosity and less discolouration as well as providing price advantages.

In a further variation developed by Bayer, hydrazine (NH_2NH_2) is dissolved in the polyol and then allowed to react during the foaming stage with some of the 80/20 TDI present. This is of the form of reaction (2) shown in Section 27.2 and this leads to a polyurea of general form:



This remains as a fine dispersion in the foam.

In a yet further variation of the process developed by Shell, diethanolamine ($\text{HOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$) is used instead of hydrazine and this leads to what is referred to as a polyurethane/polyurea suspension.

The second largest component of a foam formulation is the isocyanate. 80:20 TDI is found to be the most suitable of the various isocyanates available and was, for many years, used almost exclusively.

In recent years there has been some substitution of TDI by MDI derivatives. One-shot polyether processes became feasible with the advent of sufficiently powerful catalysts. For many years tertiary amines had been used with both polyesters and the newer polyethers. Examples included alkyl morpholines and triethylamine. Catalysts such as triethylenediamine ('Dabco') and 4-dimethylaminopyridine were rather more powerful but not satisfactory on their own. In the late 1950s organo-tin catalysts such as dibutyl tin dilaurate and stannous octoate were found to be powerful catalysts for the chain extension reactions. It was found that by use of varying combinations of a tin catalyst with a tertiary amine

(which catalyse both the gas evolution and chain extension reaction) it was possible to produce highly active systems in which foaming and cross-linking reactions could be properly balanced. Although stannous octoate is more susceptible to hydrolysis and oxidation than dibutyl tin dilaurate it does not cause such rapid aging of the foam, a problem with organometallic catalysts, and thus it is somewhat more popular.

During the 1990s concern increased about the odour and volatility of amino catalysts, particularly in enclosed spaces such as automobiles. Odourless low volatility (and hence low-fogging) catalysts based on salt-like or ionic carboxylates containing active amine centres became available. Another approach was to incorporate amine groups into the polymer to provide a built-in rather than a free-standing catalyst.

Surface active agents are important components of foam formulations. They decrease the surface tension of the system and facilitate the dispersion of water in the hydrophobic resin. In addition they can aid nucleation, stabilise the foam and control cell structure. A wide range of such agents, both ionic and non-ionic, has been used at various times but the success of the one-shot process has been due in no small measure to the development of the water-soluble polyether siloxanes. These are either block or graft copolymers of a polydimethylsiloxane with a polyalkylene oxide (the latter usually an ethylene oxide-propylene oxide copolymer). Since these materials are susceptible to hydrolysis they should be used within a few days of mixing with water.

The water present reacts with isocyanate to produce carbon dioxide and urea bridges. The more the water present (together with a corresponding additional amount of isocyanate) the more the gas evolved and the more the number of active urea points for cross-linking. Thus the foams of lower density do not necessarily have inferior load-bearing characteristics. When soft foams are required a volatile liquid such as fluorotrichloromethane may be incorporated. This will volatilise during the exothermic reaction and will increase the total gas present but not increase the degree of cross-linking.

The use of CFCs such as fluorotrichloromethane became quite widespread, particularly as for many years the material was believed to cause few toxic and environmental problems. However, evidence that such materials were damaging the ozone layer became substantial and the use of such materials is to be discouraged and is illegal in many countries. To some extent CFCs have been substituted by methylene chloride (also illegal in some countries) and other fluoro compounds, but these too may prove to be environmentally unacceptable. For this reason there has been increased dependence on the use of the isocyanate-water reaction to generate sufficient carbon dioxide to give products of the required density.

In some cases it may be desired to increase the cross-link density and hence the rigidity independently of the isocyanate-water reaction. Compounds such as glycerol, pentaerythritol and various amines have been employed as additional cross-linking agents.

Formulations should be based on stoichiometric considerations. Based on a knowledge of the hydroxyl value of the polyol the amount of isocyanate necessary to cause chain growth should be calculated. The gas evolved will depend on the water content and additional isocyanate must be incorporated corresponding to the water present. When the isocyanate used equals the theoretical amount the system is said to have a TDI index of 100. In practice a slight excess of isocyanate is used (TDI index 105–110) to ensure complete

reaction and to make available some free isocyanate for the biuret and allophanate reactions. A typical formulation would be

Polyether triol	100
80:20 TDI	40
Water	3
Triethylenediamine	0.5
Stannous octoate	0.3
Silicone block copolymer	1.0

Commercial formulations may also include other additives. Prominent amongst these are anti-aging additives (including tetravalent tin compounds, mercaptans and organic phosphites), fillers, colorants and cell regulators. In the last class may be mentioned solvents such as dimethylformamide which lead to reticulated foams with no cell membranes and agents such as lecithin and water-soluble silicone oils which can lead to cell structures resembling those of natural sponges.

The use of flame retardants has become increasingly important. They were originally primarily of concern for institutional bedding, but the increased number of domestic fatalities due to fires has led to mandatory use of fire retardant in flexible foams in a number of countries. In this connection it is to be noted that a substantial proportion of fatalities involving fires with polyurethane foams was due to inhalation of toxic substances arising from burning of the polymer rather than through individuals being burnt to death. In the late 1980s melamine (see Chapter 24) became the preferred fire retardant, being used at levels of 10–30 pts per 100 pts polyol for domestic applications but at levels up to 100 pphp polyol for institutional applications such as hospitals, nursing homes and aircraft. It may be used with 5–10 pphp polyol of a liquid fire retardant such as, preferably, ammonium polyphosphate trichlorethyl phosphate or trichlorpropyl phosphate. Organobromo compounds are also sometimes used but these can introduce toxic hazards.

For the most rigorous specifications it may be necessary to use expanded graphite as a flame-retarder but its use can pose other difficulties.

Most foam is produced on machines based on the Henecke process but in many cases it is necessary to have at least four streams to the mixing head; e.g. polyol and fluorocarbon (if any); isocyanate; water, amine, silicone; and tin catalyst. Reaction is carried out with slightly warmed components and foaming is generally complete within a minute of the mixture emerging from the head. Although slab stock flexible foam remains the largest single outlet for polyurethane materials, directly moulded foam now claims some 30% of the market. Such direct moulding may be carried out for the following reasons:

- (1) Where it is required to use metal or other inserts for fastening of upholstery elements or coverings.
- (2) Where the shape of the product is complex and it is difficult to cut this readily from slab stock.
- (3) Where it is uneconomic, because of scrap, to cut from slabstock.

Such conditions are particularly prevalent in the car industry where moulded foam is used for chair backs, chair seats, head restraints and knee strips. The furniture industry also widely uses moulded products.

There are also two variants of the direct foam moulding process: the so called hot moulding process and the cold moulding process.

For hot moulding somewhat more reactive polyethers with a higher proportion of primary hydroxyl groups are used than for slab stock foams. These are then reacted with TDI and most of the foaming is brought about by the isocyanate–water reaction (they are said to be ‘water blown’) rather than by fluorocarbons although these may be used as supplementary blowing agents.

Cold-curing foams use polyethers of somewhat higher molecular weight (~4500–6000) and which have a higher proportion of primary hydroxyls than are used for hot moulding. In addition the isocyanates used have a functionality greater than 2, this being achieved by the use of modified isocyanates.

Typical hot moulding requires mould residence times of about 12 minutes at 150°C, and cold moulding 5–8 minutes at 40–60°C. Whilst cold-cure foams have greater flexibility leading to greater comfort when sitting down onto the seat the hot-cure foams have greater load-bearing capacity and this is often associated with better damping of vehicle vibrations by the seat. In general, in comparison with coil-less spring constructions, all-foam seats give more reliable support to the user over a wide variety of driving situations, can, by good design, avoid high load concentrations which could affect blood circulation in the skin and in addition considerably reduce the transmission of vehicle vibrations.

27.5.5 Properties and Applications of Flexible Foams

Flexible polyurethane foams are resilient open-cell structures. Compared with foams from natural rubber and SBR latex they are less inflammable and have better resistance to oxidation and aging. The major interest of flexible polyurethane foams is for cushioning and other upholstery materials and for this reason the load–compression characteristics are of importance. People differ considerably in their opinions as to what constitutes an ideal cushioning material and, as a result, manufacturers have tended to try to reproduce the characteristics of natural rubber latex foam which has become widely accepted as a cushioning material. The early polyester foams unfortunately did not correspond well in their load–deflection characteristics for, although they had an initially high modulus, they tended to collapse or ‘bottom out’ above a certain loading. Thus in many applications the foam became essentially a solid piece of rubber. In addition the foam showed a slow recovery from compression and a pronounced hysteresis loop in the load–compression curve. Later polyether foams tended to be much more in line with latex foam but with a slightly greater damping capacity which in many instances may be considered a desirable feature. *Figure 27.8* shows typical load–compression curves for latex, PVC and polyurethane foams.

In addition to freedom from ‘bottoming out’, most people prefer a seat which effectively provides a soft surface with a firm interior. One measure of the relationship between such surface softness and inner support is the *sag factor* or *support factor*. In one commonly used test this is obtained by dividing the force required to compress a foam by 65% of its height by the force needed to obtain 25% sample compression. This generally increases with density but is typically <2.5 for a conventional slabstock foam but >2.5 for a high-resilience foam.

Today polyether foam with a density of less than half that of rubber latex foam is widely used as a cushioning material. Polyester foams, although tending to be more expensive, continue to have a number of outlets, particularly where a high initial modulus is desirable. In addition to miscellaneous upholstery applications

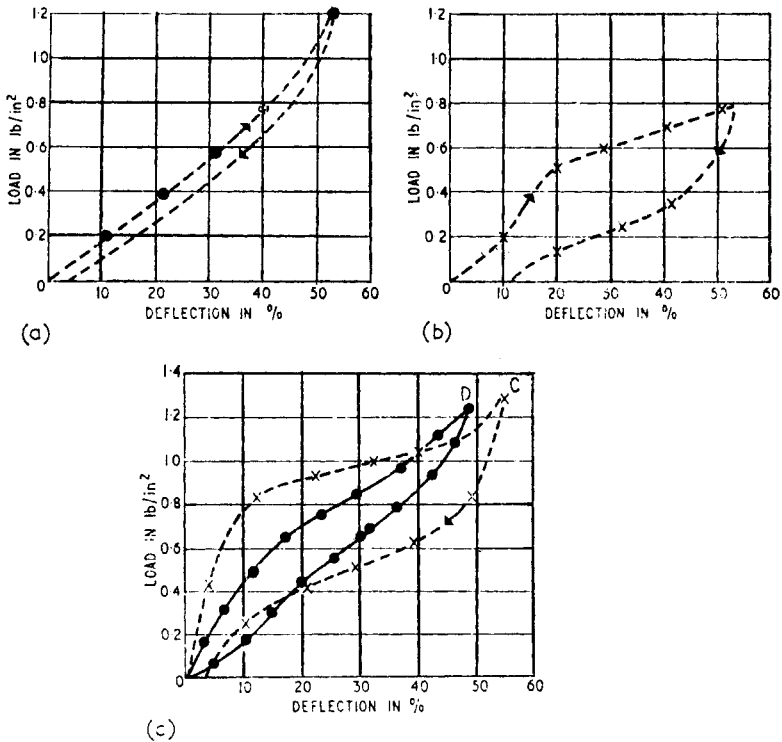


Figure 27.8. Typical load-deflection curves for (a) latex, (b) flexible PVC, (c) polyester polyurethane (curve C) and polyether polyurethane foams (curve D). Shell Chemical Co.)

polyester foams are useful as 'foam back', that is a foam backing in order to stiffen or shape some softer fabric. Examples include car door and roof trim, quilting, shoulder pads and coat interlinings. Amongst the many miscellaneous uses for both types of foam are paint rollers, sponges, draught excluders and packaging for delicate equipment.

Polyurethane foams do, however, suffer from one serious disadvantage. Unless modified they burn with copious evolution of smoke and toxic by-products, which has led to a number of fatal fires, particularly in domestic accommodation. To some extent the problem may be reduced by suitable upholstery covering, but as mentioned on p. 775 a number of countries have now made mandatory the use of fire retardant additives. At the time of writing there is considerable activity in the development of new safer systems, particularly in the use of amino materials such as melamine as additives. Further developments may also be expected in the near future.

27.6 RIGID AND SEMI-RIGID FOAMS¹⁰

The flexible foams discussed in the previous section have polymer structures with a low degree of cross-linking. If polyols of higher functionality, i.e. more hydroxyl groups per molecule, are used, tougher products may be obtained and in the case of material with a sufficiently high functionality rigid foams will result.

As with the flexible foams the early products were invariably based on polyesters, but more trifunctional alcohols such as glycerol or trihydroxymethylpropane was added to the initial polyester reaction mixture. These materials could then be reacted with isocyanate, catalyst, water and emulsifying agent in the presence of a flame retarder such as tri- β -chloroethyl phosphate. Although TDI was used initially, the increasing use of rigid foams for *in situ* applications led to the development of less volatile and subsequently less unpleasant isocyanates such as the diphenylmethane di-isocyanates. These foams can be produced without difficulty using one-shot techniques either on large factory-installed machines of the Henecke type or alternatively on small portable equipment. In most systems the reaction is rather slower than with the flexible foam and conditions of manufacture rather less critical. In the United States prepolymer and quasi-prepolymer systems corresponding to those discussed under flexible foam were developed, largely to reduce the hazards involved in handling TDI on portable equipment in places where there were severe ventilation problems.

As with the flexible foams there has been a shift to the use of polyethers. These are largely adducts based either on trifunctional hydroxy compounds, on tetrafunctional materials such as pentaerythritol or a hexafunctional material such as sorbitol. Ethylene diamine and, it is understood, domestic sugar are also employed. Where trifunctional materials are used these are of lower molecular weight (~500) than with the polyethers for flexible foams in order to reduce the distance between hydroxyl groups and hence increase the degree of cross-linking.

In the 1990s novel polyols included polyether-esters, which provided good prerequisites for flame retardancy in rigid foams and polyether carbonates with improved hydrolysis stability.

Formulations for one-shot polyether systems are similar to those used for flexible foams and contain polyether, isocyanate, catalyst, surfactant and water. Trichloroethyl phosphate is also often used as a flame retardant. As with polyesters, diphenylmethane di-isocyanate is usually preferred to TDI because of its lower volatility. Tertiary amines and organo-tin catalysts are used as with the flexible foams but not necessarily in combination. Silicone oil surfactants are again found to be good foam stabilisers. Volatile liquids such as trichlorofluoromethane have been widely used as supplementary blowing agents and give products of low density and of very low thermal conductivity.

Halocarbons have the further advantage of reducing the viscosity of the reaction mixture and, where used as the main blowing agent instead of the carbon dioxide produced by the isocyanate-water reaction, cheaper foams are obtained since less isocyanate is used. The reader should, however, note the comments made about the use of chlorofluorocarbons and their effect on the ozone layer made in Section 27.5.4.

While melamine is widely used in flexible foams as a fire-retardant, trichlorophenyl phosphate has been the preferred agent for use in rigid foams. However, the introduction of specifications stipulating halogen-free additives has led to a search for alternatives such as halogen-free phosphorus esters, red phosphorus and ammonium polyphosphate.

In addition to one-shot processes, quasi-prepolymer systems are used commercially with rigid polyether foams. The quasi-prepolymer is commonly produced using excess TDI rather than diphenylmethane di-isocyanate. Since the former isocyanate is light in colour and the latter dark, quasi-prepolymer foams

are usually lighter in colour. The quasi-prepolymer systems are also more tolerant to variations in processing conditions and often less careful control of the process can be tolerated.

Products intermediate to the flexible and rigid foams may be obtained from castor oil (a trihydroxyl molecule), synthetic triols of moderate molecular weight and polyesters with a moderate amount of trifunctional hydroxyl compound in the structure. Current practice, however, is to use tipped polyols of the type used for flexible foams with MDI. Semi-rigid foams are used for such purposes as crash pads, car steering wheels and packaging equipment.

Although some rigid foams are used in sandwich constructions for aircraft and building structures the major interest of rigid foams has been in the field of thermal insulation. In such application the foams encounter competition from polystyrene and U-F foams. With both the polystyrene and the polyurethane foams there has been intensive development in recent years leading to improved products of lower cost. The polystyrene foams have the economic advantage of being made from cheaper starting materials, can be produced successfully at lower densities (1 lb/ft^3 (0.016 g/cm^3) instead of 1.3 lb/ft^3 (0.021 g/cm^3) for polyurethane foam) and are generally less friable. One particular advantage of polyurethanes is that they may be formed *in situ* and themselves act as an adhesive to most cavity surrounds or skins. At the present time where it is necessary only to lay a piece of foam in position, expanded polystyrene is cheaper. Where, however, it is necessary to bond the foam on to the skin material, such as in a sandwich construction, the cost of the adhesives necessary with polystyrene makes a substantial addition to the overall cost. The relative economics of the two materials will therefore depend very much on the end use in question.

For materials of equivalent density water-blown polyurethanes and the hydrocarbon-blown polystyrene foams have similar thermal conductivities. This is because the controlling factor determining the conductivity is the nature of the gas present in the cavities. In both of the above cases air, to all intents and purposes, normally replaces any residual blowing gas either during manufacture or soon after. Polyurethane foams produced using fluorocarbons have a lower thermal conductivity ($0.12\text{--}0.15 \text{ Btu in ft}^{-2} \text{ h}^{-1} \text{ }^\circ\text{F}^{-1}$) ($0.017\text{--}0.022 \text{ W/mK}$) because of the lower conductivity of the gas. The comparative thermal conductivities for air, carbon dioxide and monofluorotrichloromethane are given in *Table 27.3*.

Except where the foam is surrounded by a skin of relatively impermeable material, it would be expected that the blowing gas would diffuse out and be replaced by air and that the thermal conductivities of the foams would increase until they approached that of expanded polystyrene of similar density. Whilst this

Table 27.3

Gas	Thermal conductivity	
	(Btu in $\text{ft}^{-2} \text{ h}^{-1} \text{ }^\circ\text{F}^{-1}$)	(W/mK)
Air	0.168	0.024
CO ₂	0.102	0.015
CCl ₃ F	0.058	0.008

is true of foams which generate carbon dioxide it is found that this does not happen when fluorocarbons are used. In this case diffusion of the fluorocarbon proceeds very slowly and it appears that an equilibrium is eventually reached when the ratio of air to fluorocarbon in the cell is about 1:1. For this reason fluorocarbon-blown foams have ultimate thermal conductivities significantly lower than those of CO₂-blown foams or expanded polystyrene of similar densities.

Foam density is largely a function of the concentration of blowing agents. There has been a strong development towards the use of less expanded, i.e. higher density rigid cellular polyurethanes. This includes not only the so-called structural foams for 'simulated wood' but also unexpanded solid materials used for brush handles and gun stocks. This range is clearly indicated in *Table 27.4*.¹¹

Table 27.4¹¹ Typical applications of cellular rigid polyurethanes and polyisocyanurates

Density range		Typical application
lb/ft ³	g/cm ³	
1.0–1.7	0.016–0.027	1. <i>In situ</i> packaging 2. Flower arrangements
1.7–6.0	0.027–0.096	1. <i>In situ</i> insulation of (a) refrigerators (e) chemical plant (b) deep freezers (f) houses (c) cold stores (g) building panels (d) ships 2. Buoyancy goods 3. Chair shells
6.0–10.0	0.098–0.16	1. Moulded insulation using self-skinning properties, e.g. refrigerators 2. Decorative mouldings, e.g. wood beams
10–30	0.16–0.48	1. Decorative applications (a) imitation wood (b) picture frames
30–60	0.48–0.96	1. Structural plastics mouldings (a) furniture of all kinds (b) car body parts (c) TV, radio and loudspeaker cabinets (d) brush handles and gun stocks
75 unexpanded	1.2	1. As above

27.6.1 Self-skinning Foams and the RIM Process

For many applications it is desirable that the surface of a foam moulding be non-porous and have a good finish. It is particularly desirable that in these cases both the cellular core and the skin be produced in one moulding step. This is best achieved by using a system employing a volatile blowing agent such as chlorotrifluoromethane or methylene dichloride rather than a 'water blown' system involving the evolution of carbon dioxide on reaction of isocyanate and water.

A critical factor is the boiling temperature of the blowing agent and its relationship to the temperature of the walls of the mould and of the reacting mixture. There should be sufficient exotherm to vaporise the blowing agent in the centre of the reacting material but the mould walls should be sufficiently cool to

condense the blowing agent in the reaction mixture close to the walls. In addition porosity near the wall can largely be suppressed under the correct moulding conditions by the pressure exerted internally on the skin by the vapour pressure developed in the core. Success in operating the process clearly requires close control over the metering of the raw materials and of mould temperatures. In respect of the latter, metal moulds with their good conductivity are preferred to moulds from such materials as epoxide resins.

The successful development of self-skinning foam technology is largely due to the process originally known as reaction casting but which has more commonly become known as *reaction injection moulding* (RIM) (or the German equivalent RSG). In this process the reaction components are metered into a reaction chamber adjacent to the mould cavity, and the reacting mixture then flows into the cavity. Mixing in the reaction chamber, which may have a capacity in the range 0.3–4 cm³, is brought about by injecting the components towards each other at high speed from opposite sides of chamber so that *impingement* or *counter-current* mixing takes place. At this stage turbulence is encouraged. Such a static impingement system also allows precise temperature control by the ability to continually recycle material except when it is being mixed. It is also self-cleaning and there are few moving parts. Typical mould temperatures are in the range 40–60°C.

Advantages of the RIM process over conventional injection moulding include:

- (1) Low plant investment.
- (2) Low process energy.
- (3) Low clamping pressures required—thus allowing production of very large mouldings.
- (4) Variations in thickness without sink marks due to presence of an internal pressure caused by the entrapped gases.
- (5) Low product densities.

Disadvantages include the facts that painting of the moulding is often necessary to obtain a good finish, and the difficulty in using any cross-linked waste.

The RIM process was originally developed for the car industry for the production of bumpers, front ends, rear ends, fascia panels and instrument housings. At least one mass-produced American car has RIM body panels. For many of these products, however, a number of injection moulding products are competitive, including such diverse materials as polycarbonate/PBT blends and polypropylene/EPDM blends. In the shoe industry the RIM process has been used to make soling materials from semi-flexible polyurethane foams.

Interest in the RIM process appears to have abated somewhat in the 1990s. Nevertheless, nearly 100 000 tonnes of polyol and polyisocyanate were consumed for this application in the USA alone in 1993.

The *reinforced reaction injection moulding* (RRIM) process is a development of RIM in which reinforcing fillers such as glass fibres are incorporated into the polymer. One advantage of such a system is to reduce the coefficient of thermal expansion, and with a 40–50% glass fibre content the coefficient is brought into line with those of metals.

One specific wish of the RIM technologist is the extension of the system to produce fast-running vehicle tyres and some progress has been made in this direction. One approach to overcome current problems, such as a low heat

distortion temperature and too soft a compound, has been the development of glass, fibre-filled materials produced by the 'reinforced RIM' technique.

27.7 COATINGS AND ADHESIVES

A wide range of polyurethane-type products has become available in recent years for coating applications. These include simple solutions of linear polyurethanes, two-pot alkyd-isocyanate and polyether-isocyanate systems and a variety of prepolymer and adduct systems. The coatings can vary considerably in hardness and flexibility and find use mainly because of their toughness, abrasion resistance and flexibility. Uses include metal finishes in chemical plant, wood finishes for boats and sports equipment, finishes for rubber goods and rain-erosion-resistant coatings for aircraft. One type of coating is potentially competitive with PVC leathercloth. Both alkyd-di-isocyanate and adduct-di-isocyanate compositions may be coated on to fabrics from solutions of controlled viscosity and solids content. Such coated fabrics are soft, flexible and, unlike PVC leathercloth, free from plasticisers.

Many isocyanates have good adhesive properties and one of them, triphenylmethane-*pp'p''*-triyl tri-isocyanate, has been successfully used for bonding of rubber. Isocyanates are, however, rather brittle and somewhat limited in application. Somewhat tougher products are obtained from adhesives involving both polyols and isocyanates, i.e. polyurethane-type materials. The major application of these materials to date is in the boot and shoe industry.

27.8 POLYISOCYANURATES

Whilst rigid closed-cell polyurethanes are excellent thermal insulators they do suffer from a limited and often unsatisfactory level of fire resistance, even in the presence of phosphorus-containing and halogen-containing fire retardants. Considerable promise is now being shown by the polyisocyanurates, which are also based on isocyanate chemistry.

These materials not only have a good resistance to burning and flame spread but are also able to withstand service temperatures of up to 150°C. At the same time polyisocyanurate foams have the very good hydrolytic stability and low thermal conductivity associated with rigid polyurethane foams.

The underlying reaction for polyisocyanurate formation is the trimerisation of an isocyanate under the influence of specific catalysts (*Figure 27.9*).

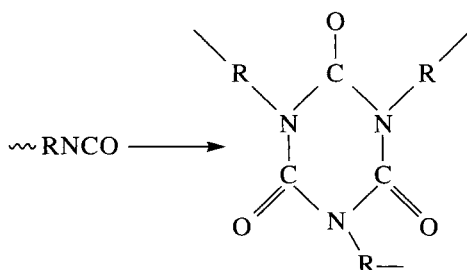


Figure 27.9

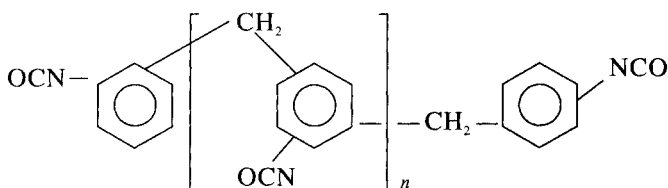


Figure 27.10

The most commonly used isocyanate is a modified form of MDI. Such polymeric forms may be prepared, for example, by reacting phosgene with formaldehyde-aniline condensates which have average functionalities of between 2 and 7 and may be represented by the formula given in Figure 27.10.

Polymeric MDIs, which are also used in polyurethane foams, usually have a lower reactivity than the monomeric material but are also less volatile. The polyisocyanurate produced from this material will be of the type shown in Figure 27.11.

Amongst the catalysts used on the polymerisation-trimerisation reactions are alkali metal phenolates, alcoholates and carboxylates and compounds containing *o*-(dimethylaminomethyl)phenol subgroups. Fluorocarbons such as trichlorofluoromethanes are used as the sole blowing agents in the absence of any isocyanate-water reaction.

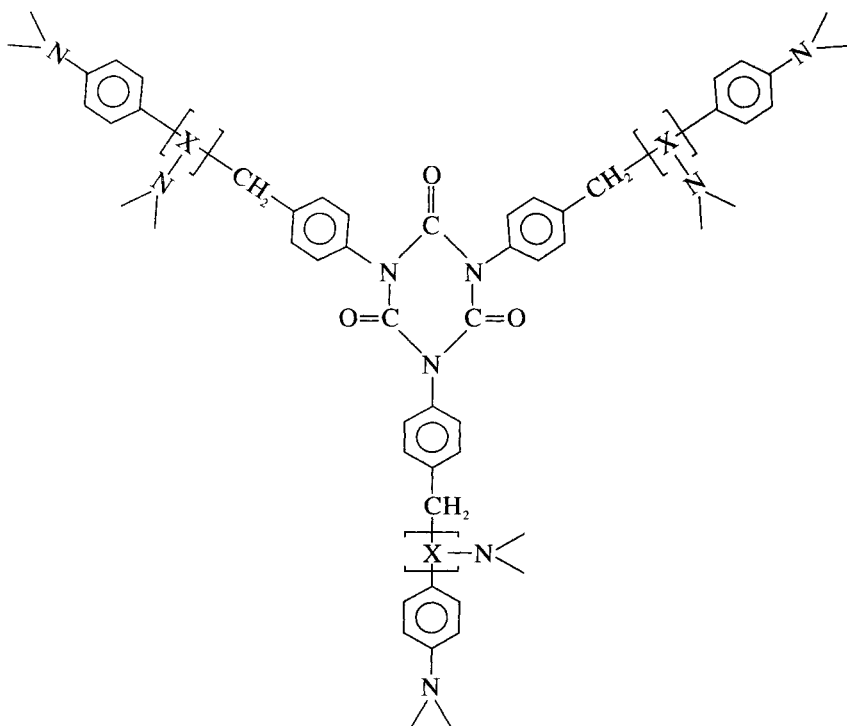


Figure 27.11

Because of the high cross-link density of polyisocyanurates as prepared above, the resultant foams are brittle, so that there has been a move towards polyisocyanurate-polyurethane combinations. For example, isocyanurate-containing polyurethane foams have been prepared by trimerisation isocyanate-tipped TDI-based prepolymers. The isocyanurate trimerising reaction has also been carried out in the presence of polyols of molecular weight less than 300 to give foams by both one-shot and prepolymer methods.

An alternative route involves the reaction of 1,2-epoxides with isocyanates to yield poly-2-oxazolidones (Figure 27.12).

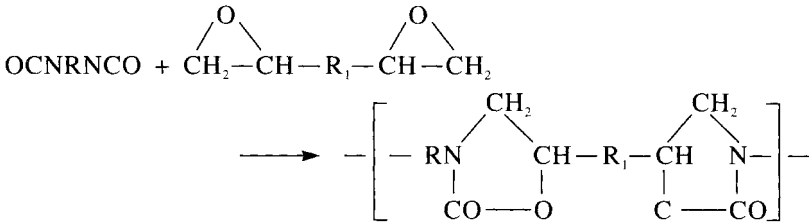


Figure 27.12

Whilst reaction can take place in the absence of catalysts it is more common to use such materials as tetra-alkylammonium halides and tertiary amines such as triethylenediamine. A major side reaction leads to the production of isocyanurate rings, particularly in the presence of tertiary amines.

The conventional polyisocyanurate may be prepared with a two-component system using standard polyurethane foaming equipment. It is usual to blend isocyanate and fluorocarbon to form one component whilst the activator or activator mixture form the second component.

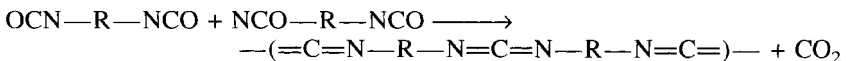
Typical properties of isocyanurate foam are given in Table 27.5.

Table 27.5 Typical properties of polyisocyanurate foams

Density	2.1–3.0 lb	38–48 kg/m ³
Compression strength	20–40 lbf/in ²	0.14–0.28 MPa
Shear strength	15–35 lbf/in ²	0.10–0.24 MPa
Initial K value	0.115 BTU in ft ⁻² h ⁻¹ °F ⁻¹ at 32°F	0.17 W/mK at 0°C
Equilibrium K value	0.16 units	0.24
Resistance to elevated temperature distortion (DIN 53424)		200°C

27.9 POLYCARBODI-IMIDE RESINS

Besides trimerisation, leading to the production of polyisocyanurates, isocyanates can react with each other to form polycarbodi-imides with the simultaneous evolution of carbon dioxide:



When this is carried out in suitable solvents at temperatures in the range 75–120°C, soluble products will be obtained. Polymeric MDI is usually used as the isocyanate component and this results in a stiff chain molecule. One such product is reported to have a T_g of 200–220°C.

In the absence of solvents and with suitable catalysts the evolution of carbon dioxide simultaneously with the polycarbodi-imide formation gives rise to a foamed product. These foams are cross-linked because of reactions between carbodi-imide groups and free isocyanate groups. Raw materials for such foams are now available from Bayer (Baymid).

The polymers combine a high level of flame retardancy with good thermal insulation and sound absorption characteristics. Densities are somewhat high (16–20 kg/m³).

Amongst applications reported are underfloor footfall sound insulation, thermal insulation between cavity walls and pipe insulation.

27.10 POLYURETHANE-ACRYLIC BLENDS

Over the years many blends of polyurethanes with other polymers have been prepared. One recent example¹² is the blending of polyurethane intermediates with methyl methacrylate monomer and some unsaturated polyester resin. With a suitable balance of catalysts and initiators, addition and rearrangement reactions occur simultaneously but independently to give *interpenetrating polymer networks*. The use of the acrylic monomer lowers cost and viscosity whilst blends with 20% (MMA + polyester) have a superior impact strength.

27.11 MISCELLANEOUS ISOCYANATE-BASED MATERIALS

Because of their great versatility there continues to be a steady stream of developments of polymers made by reaction of isocyanates.¹³ In addition to the materials discussed in this chapter there are, to name but three, the polyureas, the polyoxazolidinones and polybenzoxazinediones.

There is also growing interest in multi-phase systems in which hard phase materials are dispersed in softer polyether diols. Such hard phase materials include polyureas, rigid polyurethanes and urea melamine formaldehyde condensates. Some of these materials yield high-resilience foams with load deflection characteristics claimed to be more satisfactory for cushioning as well as in some cases improving heat resistance and flame retardancy.

Aqueous dispersions of polyurethanes have also become available which may be used instead of solutions in organic solvents for such applications as leather treatment, adhesives and surface coatings.

The polycarbamylsulphonates are water-soluble reactive bisulphite adducts of polyisocyanates and are being investigated as possible materials to render woollen fabrics crease-resistant.

References

1. WURTZ, A., *Ann.*, **71**, 326 (1849)
2. HENTSCHEL, W., *Ber.*, **17**, 1284 (1884)
3. SAUNDERS, J. H., and FRISCH, K. G., *Polyurethanes—Chemistry and Technology: Pt 1—Chemistry*, Interscience, New York (1962)

4. PHILLIPS, L. N., and PARKER, D. B. V., *Polyurethanes—Chemistry, Technology and Properties*, Iliffe, London (1964)
5. ARNOLD, R. G., NELSON, J. A., and VERBANC, J. J., *Chemistry of Organic Isocyanates*, Du Pont Bulletin HR-2 (1–20–56)
6. PINTEN, H., *German Patent, Appl. D–90*, 260 (March 1942)
7. BAYER, O., MÜLLER, F., PETERSEN, S., PIEPENBRINK, H. F., and WINDEMUTH, E., *Angew. Chem.* **62**, 57 (1950); *Rubber Chem. Technol.*, **23**, 812 (1950)
8. HAMPTON, H. A., and HURD, R., *Trans. Plastics Inst.*, **29**, 204 (1961)
9. BUIST, J. M., *Trans. Plastics Inst.*, **29**, 100 (1962)
10. FERRIGNO, T. H., *Rigid Plastics Foams*, Reinhold, New York (1963)
11. BALL, C. W., BALL, L. S., WALKER, M. G., and WILSON, W. J., *Plastics & Polymers*, **40**, 290 (1972)
12. KIRCHER, K., and PIPER, R., *Kunststoffe*, **68**, 141 (1978)
13. ELIAS, H.-NG., and VOHWINKEL, F., Chapter 13 in *New Commercial Polymers—2*, Gordon and Breach, New York, London (1986)

Bibliography

- BRYDSON, J. A., *Rubbery Materials and their Compounds*, Elsevier Applied Science, London (1988).
- BUIST, J. M. (Ed.), *Developments in Polyurethanes—1*, Elsevier Applied Science, London (1978)
- DOMBROW, B. A., *Polyurethanes*, Reinhold, New York (1957)
- DUNNOLS, J., *Basic Urethane Foam Manufacturing Technology*, Technomics, Westport, Conn. (1979)
- FERRIGNO, T. H., *Rigid Plastics Foams*, Reinhold, New York, 2nd Edn (1967)
- FRISCH, K. C., 'Recent Advances in the Chemistry of Polyurethanes', *Rubb. Chem. Technol.*, **45** 1442–1466 (1972)
- FRISCH, K. C., Recent Developments in Urethane Elastomers and Reaction Injection Moulded (RIM) Elastomers, *Rubber Chem. Technol.*, **53**, 126 (1980)
- FRISCH, K. C. and REEGAN, S. L., *Advances in Urethane Science and Technology* (Vols. 1, 1972; 2, 1973; 3, 1974; 4, 1976; 5, 1976; 6, 1978; 7, 1979), Technomics, Westport, Conn.
- FRISCH, K. C., and SAUNDERS, J. H., *Plastic Foams*, Pt 1, Marcel Dekker, New York (1972)
- HARROP, D. J., Chapter 5 in *Developments in Rubber Technology—3* (Eds WHELAN, A. and LEE, K. S.), Applied Science, London (1982)
- HEALY, T. T. (Ed.), *Polyurethane Foams*, Iliffe, London (1964)
- LEE, L. J. Polyurethane Reaction Injection Moulding, *Rubber Chem. Technol.*, **53**, 542 (1980)
- MECKEL, W., GOYERT, W., and WIEDER, W., Chapter 2 in *Thermoplastics Elastomers* (Eds LEGGE, N. R., HOLDEN, G., and SCHROEDER, H. E., Hanser, München (1987)
- PHILLIPS, L. N., and PARKER, D. B. V., *Polyurethanes—Chemistry Technology and Properties*, Iliffe, London (1964)
- SAUNDERS, J. H., and FRISCH, K. C., *Polyurethanes—Chemistry and Technology*; Pt 1—Chemistry; Pt 2—Technology, Interscience, New York (1962)
- WHELAN, A., and BRYDSON, J. A. (Eds), *Developments with Thermosetting Plastics*. (Chapter 6 by A. Barnatt and Chapter 7 by J. B. Blackwell). Applied Science, London (1974)
- Bayer-Polyurethanes*, Handbook produced by Bayer AG, English language edition (1979)

Technical Reviews

- UHLIG, K., and KOHORST, J., *Kunststoffe*, **66**, 616–24 (1976)
- PALM, R., and SCHWENKE, W., *Kunststoffe*, **70**, 665–71 (1980)
- MILLS, R., *Kunststoffe*, **77**, 1036–8 (1987)
- LÜDKE, H. *Kunststoffe*, **86**, 1556–1564 (1996)

Furan Resins

28.1 INTRODUCTION

The furan or furane resins mainly find use because of their excellent chemical and heat resistance. In the past they have mainly been used in applications peripheral to the plastics industry such as foundry resins, for chemically resistant cements and for binders. Recent developments have facilitated their use in laminates for chemical plant.

28.2 PREPARATION OF INTERMEDIATES

The two intermediates of commercial furan resins are furfural and furfuryl alcohol. Furfural occurs in the free state in many plants but is obtained commercially by degradation of hemicellulose constituents present in these plants. There are a number of cheap sources of furfural, and theoretical yields of over 20% (on a dry basis) may be obtained from both corn cobs and oat husks. In practice yields of slightly more than half these theoretical figures may be obtained. In the USA furfural is produced in large quantities by digestion of corn cobs with steam and sulphuric acid. The furfural is removed by steam distillation.

Furfural is a colourless liquid which darkens in air and has a boiling point of 161.7°C at atmospheric pressure. Its principal uses are as a selective solvent used in such operations as the purification of wood resin and in the extraction of butadiene from other refinery gases. It is also used in the manufacture of phenol-furfural resins and as a raw material for the nylons. The material will resinify in the presence of acids but the product has little commercial value.

Catalytic hydrogenation of furfural in the presence of copper chromite leads to furfuryl alcohol, the major intermediate of the furan resins (*Figure 28.1*).

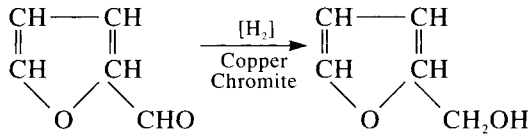


Figure 28.1

The alcohol is a mobile liquid, light in colour, with a boiling point of 170°C. It is very reactive and will resinify if exposed to high temperatures, acidity, air or oxygen. Organic bases such as piperidine and *n*-butylamine are useful inhibitors.

28.3 RESINIFICATION

Comparatively little is known of the chemistry of resinification of either furfuryl alcohol or furfural.

It is suggested that the reaction shown in *Figure 28.2* occurs initially with furfuryl alcohol.

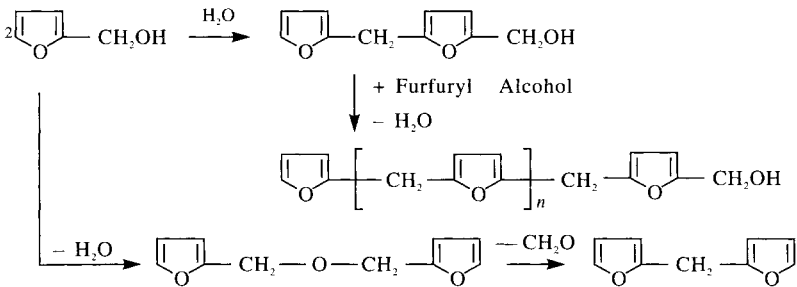


Figure 28.2

The liberation of small amounts of formaldehyde has been detected in the initial stage but it has been observed that this is used up during later reaction. This does not necessarily indicate that formaldehyde is essential to cross-linking, and it would appear that its absorption is due to some minor side reaction.

Loss of unsaturation during cross-linking indicates that this reaction is essentially a form of double bond polymerisation, viz *Figure 28.3*.

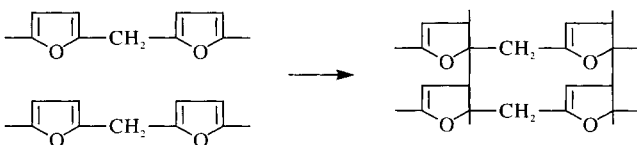


Figure 28.3

This reaction, like the initial condensation, is favoured by acidic conditions and peroxides are ineffective.

The polymerisation of furfural is apparently more complex and less understood.

For commercial use a partially condensed furan resin is normally prepared which is in the form of a dark free-flowing liquid. Final cure is carried out *in situ*.

The liquid resins are prepared either by batch or continuous process by treating furfuryl alcohol with acid. Initially the reaction mixture is heated but owing to the powerful exothermic an efficient cooling system is necessary if cross-linking is to be avoided. Water of condensation is removed under vacuum and the reaction stopped by adjusting the pH to the point of neutrality. Great care is necessary to prevent the reaction getting out of hand. This may involve, in addition to efficient cooling, a judicious choice of catalyst concentration, the use of a mixture of furfuryl alcohol and furfural which produces a slower reaction but gives a more brittle product and, possibly, reaction in dilute aqueous solution.

The resins are hardened *in situ* by mixing with an acidic substance just before application. A typical curing system would be four parts of toluene-*p*-sulphonic acid per 100 parts resin. The curing may take place at room temperature if the resin is in a bulk form but elevated temperature cures will often be necessary when the material is being used in thin films or coatings.

28.4 PROPERTIES OF THE CURED RESINS

The resins are cross-linked and the molecular segments between the cross-links are rigid and inflexible. As a consequence the resins have an excellent heat resistance, as measured in terms of maintenance of rigidity on heating, but are rather brittle.

Cured resins have excellent chemical resistance. This is probably because, although the resins have some reactive groupings, most of the reactions occurring do not result in the disintegration of the polymer molecules. Therefore, whilst surface layers of molecules may have undergone modification they effectively shield the molecules forming the mass of the resin. The resins have very good resistance to water penetration.

Compared with the phenolics and polyesters the resins have better heat resistance, better chemical resistance, particularly to alkalis, greater hardness and better water resistance. In these respects they are similar to, and often slightly superior to, the epoxide resins. Unlike the epoxides they have a poor adhesion to wood and metal, this being somewhat improved by incorporating plasticisers such as poly(vinyl acetate) and poly(vinyl formal) but with a consequent reduction in chemical resistance. The cured resins are black in colour.

28.5 APPLICATIONS

The principal applications for furan resins are in chemical plant. Specific uses include the lining of tanks and vats and piping and for alkali-resistant tile cements. The property of moisture resistance is used when paper honeycomb structures are treated with furan resins and subsequently retain a good compression strength even after exposure to damp conditions.

Laminates have been prepared for the manufacture of chemical plant. They have better heat and chemical resistance than the polyester-epoxide-phenolic- or aminoplastic-based laminates but because of the low viscosity of the resins were not easy to handle. Because they were also somewhat brittle, furan-based laminates have been limited in their applications.

This situation may be expected to change somewhat with the advent of new polymers of greater viscosity (375–475 cP) ($37.5\text{--}47.5\text{ N s/m}^2$) and generally easier handling qualities. Whilst patents (e.g. Ger. Pat. 1927 776) describe polymeric blends of UF and furane resins as being suitable for such laminating it has been stated that the commercially available polymers (e.g. Quacorr RP100A—Quaker Oats Co.) are basically furfuryl alcohol polymers not modified by PF or UF resins. They are cured by modified acid catalysts, giving a rather more gentle cure than the earlier catalyst systems.

Furane resin-chopped strand mat laminates have tensile strengths in excess of $20\,000\text{ lbf/in}^2$ (140 MPa), a heat distortion temperature of about 218°C and good fire resistance.

Not only does the material have excellent resistance to burning but smoke emission values are reported to be much less than for fire-retardant polyester resin. The laminates are being increasingly used in situations where corrosion is associated with organic media, where corrosion is encountered at temperatures above 100°C as in fume stacks and where both fire retardance and corrosion resistance are desired as in fume ducts.

One other substantial development of the 1960s was the use of ureaformaldehyde-furfuryl alcohol materials as foundry resins, particularly for 'hot-box' operations. The furfuryl alcohol component of the resin is usually in the range 25–40%.

Furane resins are useful in impregnation applications. Furfural alcohol resinified *in situ* with zinc chloride catalysts can be used to impregnate carbon (including graphite) products and be cured at $93\text{--}150^\circ\text{C}$ to give products of greater density and strength and which have much lower permeability to corrosive chemicals and gases.

The resins are also used for coating on to moulds to give a good finish that is to be used for polyester hand-lay up operations.

Development work by Russian workers had led to interesting products formed by reaction of furfuryl alcohol with acetone and with aniline hydrochloride. The resins formed in each case have been found to be useful in the manufacture of organic-mineral non-cement concretes with good petrol, water and gas resistance. They also have the advantage of requiring only a small amount of resin to act as a binder.

Bibliography

- GANDINI, A. 'FURAN RESINS', *Encyclopedia of Polymer Science and Technology* (2nd Edition), Vol. 7, pp. 454–73, John Wiley, New York (1987)
- MCDOWALL, R., and LEWIS, P., *Trans. Plastics Inst.*, **22**, 189 (1954)
- MORGAN, P., *Glass-reinforced Plastics*, Iliffe, London, 3rd Edn (1961)
- RADCLIFFE, A. T. (Eds. WHELAN, A., and BRYDSON, J. A.) Chapter 5 of *Developments with Thermosetting Plastics*, Applied Science, London (1975)

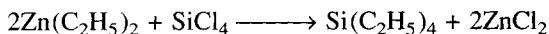
See also various articles by Itinskii, Kamenskii, Ungureau and others in *Plasticheskie Massy* from 1960 onwards. (Translations published as *Soviet Plastics* by Rubber and Technical Press Ltd, London.)

Silicones and Other Heat-resisting Polymers

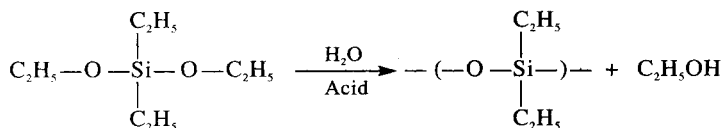
29.1 INTRODUCTION

To many polymer chemists one of the most fascinating developments of the last 80 years has been the discovery, and the attendant commercial development, of a range of semi-inorganic and wholly inorganic polymers, including the silicone polymers. Because of their general thermal stability, good electrical insulation characteristics, constancy of properties over a wide temperature range, water-repellency and anti-adhesive properties, the silicone polymers find use in a very wide diversity of applications. Uses range from high-temperature insulation materials and gaskets for jet engines to polish additives and water repellent treatments for leather. The polymers are available in a number of forms such as fluids, greases, rubbers and resins.

The possibility of the existence of organosilicone compounds was first predicted by Dumas in 1840, and in 1857 Buff and Wohler¹ found the substance now known to be trichlorosilane by passing hydrochloric acid gas over a heated mixture of silicone and carbon. In 1863 Friedel and Crafts² prepared tetraethylsilane by reacting zinc diethyl with silicon tetrachloride.



In 1872 Ladenburg³ produced the first silicone polymer, a very viscous oil, by reacting diethoxydiethylsilane with water in the presence of traces of acid.



The basis of modern silicone chemistry was, however, laid by Professor F. S. Kipping at the University College, Nottingham, between the years 1899 and 1944. During this period Kipping published a series of 51 main papers and some

supplementary studies, mainly in the *Journal of the Chemical Society*. The work was initiated with the object of preparing asymmetric tetrasubstituted silicon compounds for the study of optical rotation. Kipping and his students were concerned primarily with the preparation and study of new non-polymeric compounds and they were troubled by oily and glue-like fractions that they were unable to crystallise. It does not appear that Kipping even foresaw the commercial value of his researches, for in concluding the Bakerian Lecture delivered in 1937 he said

'We have considered all the known types of organic derivatives of silicon and we see how few is their number in comparison with the purely organic compounds. Since the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of chemistry does not seem very hopeful.'

Nevertheless Kipping made a number of contributions of value to the modern silicone industry. In 1904 he introduced the use of Grignard reagents for the preparation of chlorosilanes and later discovered the principle of the intermolecular condensation of the silane diols, the basis of current polymerisation practice. The term silicone was also given by Kipping to the hydrolysis products of the disubstituted silicon chlorides because he at one time considered them as being analogous to the ketones.

In 1931 J. F. Hyde of the Corning Glass Works was given the task of preparing polymers with properties intermediate between organic polymers and inorganic glasses. The initial objective was a heat-resistant resin to be used for impregnating glass fabric to give a flexible electrical insulating medium. As a result silicone resins were produced. In 1943 the Corning Glass Works and the Dow Chemical Company co-operated to form the Dow Corning Corporation, which was to manufacture and develop the organo-silicon compounds. In 1946 the General Electric Company of Schenectady, NY also started production of silicone polymers using the then new 'Direct Process' of Rochow. The Union Carbide Corporation started production of silicones in 1956.

There are at present about a dozen manufacturers outside the Communist bloc. Amongst major producers, in addition to those already mentioned, are Bayer, Rhone-Poulenc, Wacker-Chemie, Toshiba, Toray and Shinetsu.

During the 1970s growth rates for the silicones were higher than for many other commercial polymers, generally showing an annual rate of growth of some 10–15%. In part this is due to the continual development of new products, in part to the increasingly severe demands of modern technology and in part because of favourable ecological and toxicological aspects in the use of silicones. In the early 1980s world capacity excluding the Eastern bloc was assessed at about 270 000 tonnes per annum, being dominated by the USA (41%) with Western Europe taking about 33% and Japan 17%.

29.1.1 Nomenclature

Before discussing the chemistry and technology of silicone polymers it is necessary to consider the methods of nomenclature of the silicon compounds relevant to this chapter. The terminology used will be that adopted by the International Union of Pure and Applied Chemistry.

The structure used as the basis of the nomenclature is *silane* SiH_4 corresponding to methane CH_4 . Silicon hydrides of the type $\text{SiH}_3(\text{SiH}_2)_n \text{SiH}_3$

are referred to as disilane, trisilane, tetrasilane etc., according to the number of silicon atoms present.

Alkyl, aryl, alkoxy and halogen substituted silanes are referred to by prefixing 'silane' by the specific group present. The following are typical examples:

$(\text{CH}_3)_2\text{SiH}_2$	dimethylsilane
$\text{CH}_3 \cdot \text{Si} \cdot \text{Cl}_3$	trichloromethylsilane
$(\text{C}_6\text{H}_5)_3 \cdot \text{Si} \cdot \text{C}_2\text{H}_5$	ethyltriphenylsilane

Compounds having the formula $\text{SiH}_3 \cdot (\text{OSiH}_2)_n \cdot \text{SiH}_3$ are referred to as disiloxane, trisiloxane etc., according to the number of silicon atoms. Polymers in which the main chain consists of repeating—Si—O— groups together with predominantly organic side groups are referred to as *polyorganosiloxanes* or more loosely as *silicones*.

Hydroxy derivatives of silanes in which the hydroxyl groups are attached to a silicon atom are named by adding the suffixes -ol, -diol, -triol etc., to the name of the parent compound. Examples are:

H_3SiOH	silanol
$\text{H}_2\text{Si}(\text{OH})_2$	silanediol
$(\text{CH}_3)_3\text{SiOH}$	trimethylsilanol
$(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5\text{O})\text{SiOH}$	ethoxydiphenylsilanol

29.1.2 Nature of Chemical Bonds Containing Silicon

Silicon has an atomic number of 14 and an atomic weight of 28.06. It is a hard, brittle substance crystallising in a diamond lattice and has a specific gravity of 2.42. The elemental material is prepared commercially by the electrothermal reduction of silica.

Silicon is to be found in the fourth group and the second short period of the Periodic Table. It thus has a maximum covalency of six although it normally behaves as a tetravalent material. The silicon atom is more electropositive than the atoms of carbon or hydrogen. The electronegativity of silicon is 1.8, hydrogen 2.1, carbon 2.5 and oxygen 3.5. It has a marked tendency to oxidise, the scarcity of naturally occurring elemental silicon providing an excellent demonstration of this fact.

At one time it was felt that it would be possible to produce silicon analogues of the multiplicity of carbon compounds which form the basis of organic chemistry. Because of the valency difference and the electropositive nature of the element this has long been known not to be the case. It is not even possible to prepare silanes higher than hexasilane because of the inherent instability of the silicon-silicon bond in the higher silanes.

The view has also existed in the past that the carbon-silicon bond should be similar in behaviour to the carbon-carbon bond and would have a similar average bond energy. There is some measure of truth in the assumption about average bond energy but because silicon is more electropositive than carbon the C—Si bond will be polar and its properties will be very dependent on the nature of groups attached to the carbon and silicon groups. For example, the $\text{CH}_3\text{—Si}$ group is particularly resistant to oxidation but $\text{C}_6\text{H}_{13}\text{—Si}$ is not.

The polarity of the silicon-carbon bond will affect the manner in which the reaction with ions and molecules takes place. For example, on reaction with

alkali, or in some conditions with water, it is to be expected that the negative hydroxyl ion will attack the positive silicon atom rather than the negative carbon atom to form, initially, Si—OH bonds. Reaction with hydrogen chloride would lead similarly to silicon—chlorine and carbon—hydrogen bonds.

It is important to realise that the character of substituents on either the carbon or silicon atoms will greatly affect the reactivity of the carbon—silicon bond according to its effect on the polarity. Thus strongly negative substituents, e.g. trichloromethyl groups, attached to the carbon atom, will enhance the polarity of the bond and facilitate alkaline hydrolysis. A benzene ring attached to the carbon atom will also cause an electron shift towards the carbon atom and enhance polarity. Hydrogen chloride may then effect acid cleavage of the ring structure from the silicon by the electronegative chlorine attacking the silicon and the proton attacking the carbon.

The foregoing facts of relevance to the preparation and properties of silicone polymers may be summarised as follows

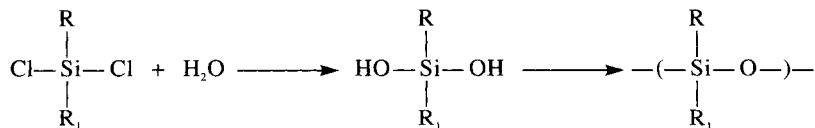
- (1) Silicon is usually tetravalent but can assume hexavalent characteristics.
- (2) Silicon is more electropositive than carbon and hence silicon—carbon bonds are polar (12% ionic).
- (3) The reactivity of the Si—C bond depends on the substituent group attracted to the Si and C atoms.
- (4) The reactivity also depends on the nature of the attacking molecule.

Two further statements may also be made at this stage.

- (5) Inclusion of silicon into a polymer does not ensure by any means a good thermal stability.
- (6) The siloxane Si—O link has a number of interesting properties which are relevant to the properties of the polyorganosiloxanes. These will be dealt with later.

29.2 PREPARATION OF INTERMEDIATES

The polyorganosiloxanes are generally prepared by reacting chlorosilanes with water to give hydroxyl compounds which then condense to give the polymer structure, e.g.

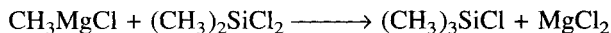
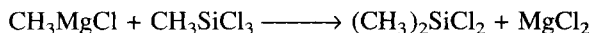
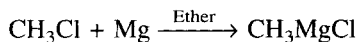


Similar reactions can also be written for the alkoxy silanes but in commercial practice the chlorosilanes are favoured. These materials may be prepared by many routes, of which four appear to be of commercial value, the Grignard process, the direct process, the olefin addition method and the sodium condensation method.

29.2.1 The Grignard Method

The use of the Grignard reagents of the type RMgX for the production of alkyl- and aryl-chlorosilanes was pioneered by Kipping in 1904 and has been for a long time the favoured laboratory method for producing these materials.

The reaction is carried out by first reacting the alkyl or aryl halide with magnesium shavings in an ether suspension and then treating with silicon tetrachloride (prepared by passing chlorine over heated silicon). With methyl chloride the following sequence of reactions occur:



The reaction proceeds in a stepwise manner but because of the differences in the reactivities of the intermediates a high yield of dichlorodimethylsilane is produced.

The products are recovered from the reaction mixture by filtration to remove the magnesium chloride, followed by distillation. It is then necessary to distil fractionally the chlorosilanes produced. The fractional distillation is a difficult stage in the process because of the closeness of the boiling points of the chlorosilanes and some by-products (*Table 29.1*) and 80–100 theoretical plates are necessary to effect satisfactory separation.

Table 29.1 Boiling point of some chlorosilanes and related compounds

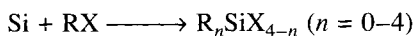
<i>Compound</i>	<i>Boiling point (°C)</i>
$(\text{CH}_3)_2\text{SiCl}_2$	70
CH_3SiCl_3	65.7
$(\text{CH}_3)_3\text{SiCl}$	57
$\text{CH}_3\text{SiHCl}_2$	41
SiCl_4	57.6
$(\text{CH}_3)_4\text{Si}$	26

The Grignard method was the first route used commercially in the production of silicone intermediates. Its great advantage is its extreme flexibility since a wide range of organic groups may be attached to the silicon in this method. Because of the need to use ether or other inflammable solvents considerable production hazards arise. On economic grounds the main drawbacks of the process are the multiplicity of steps and the dependence on silicon tetrachloride, which contains only 16% Si and is thus a rather inefficient source of this element.

29.2.2 The Direct Process

The bulk of the methylsilicones are today manufactured via the direct process. In 1945 Rochow⁴ found that a variety of alkyl and aryl halides may be made

to react with elementary silicon to produce the corresponding organosilicon halides.



The hydrocarbon can be in either the liquid or vapour phase and the silicon is finely divided. The inclusion of certain solid catalysts in the reactive mass may in some instances greatly facilitate the reaction. A mixture of powdered silicon and copper in the ratio 90:10 is used in the manufacture of alkyl chlorosilanes.

In practice vapours of the hydrocarbon halide, e.g. methyl chloride, are passed through a heated mixture of the silicon and copper in a reaction tube at a temperature favourable for obtaining the optimum yield of the dichlorosilane, usually 250–280°C. The catalyst not only improves the reactivity and yield but also makes the reaction more reproducible. Presintering of the copper and silicon or alternatively deposition of copper on to the silicon grains by reduction of copper (I) chloride is more effective than using a simple mixture of the two elements. The copper appears to function by forming unstable copper methyl, CuCH_3 , on reaction with the methyl chloride. The copper methyl then decomposes into free methyl radicals which react with the silicon.

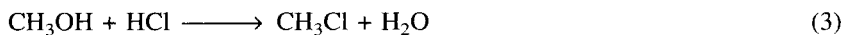
Under the most favourable reaction conditions when methyl chloride is used the crude product from the reaction tube will be composed of about 73.5% dimethyldichlorosilane, 9% trichloromethylsilane and 6% chlorotrimethylsilane together with small amounts of other silanes, silicon tetrachloride and high boiling residues.

The reaction products must then be fractionated as in the Grignard process.

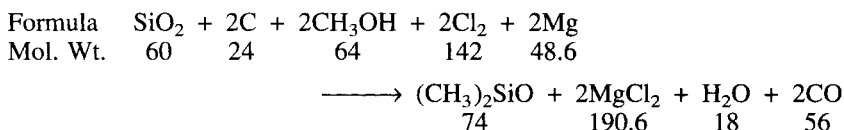
The direct process is less flexible than the Grignard process and is restricted primarily to the production of the, nevertheless all-important, methyl- and phenyl-chlorosilanes. The main reason for this is that higher alkyl halides than methyl chloride decompose at the reaction temperature and give poor yields of the desired products and also the fact that the copper catalyst is only really effective with methyl chloride.

In the case of phenylchlorosilanes some modifications are made to the process. Chlorobenzene is passed through the reaction tube, which contains a mixture of powdered silicon and silver (10% Ag), the latter as catalyst. Reaction temperatures of 375–425°C are significantly higher than for the chloromethylsilanes. An excess of chlorobenzene is used which sweeps out the high boiling chlorophenylsilanes, of which the dichlorosilanes are predominant. The unused chlorobenzene is fractionated and recycled.

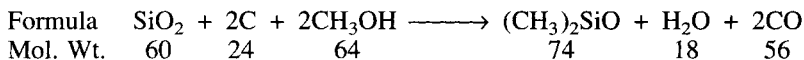
The direct process involves significantly fewer steps than the Grignard process and is more economical in the use of raw materials. This may be seen by considering the production of chlorosilanes by both processes starting from the basic raw materials. For the Grignard process the basic materials will normally be sand, coke, chlorine and methane and the following steps will be necessary before the actual Grignard reaction:



Rochow⁵ has summed the entire Grignard process from basic raw material to polymer as:

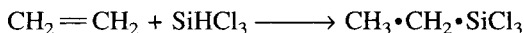


On the other hand only the additional steps (1) and (3) will be required in the direct process which gives the summarised equation:

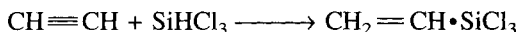


29.2.3 The Olefin Addition Method

The basis of this method is to react a compound containing Si—H groups with unsaturated organic compounds. For example, ethylene may be reacted with trichlorosilane



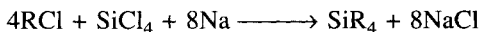
The method may also be used for the introduction of vinyl groups



The trichlorosilane may be obtained by reacting hydrogen chloride with silicon in yields of 70% and thus is obtainable at moderate cost. As the olefins are also low-cost materials this method provides a relatively cheap route to the intermediates. It is, of course, not possible to produce chloromethylsilanes by this method.

29.2.4 Sodium Condensation Method

This method depends on the reaction of an organic chloride with silicon tetrachloride in the presence of sodium, lithium or potassium.



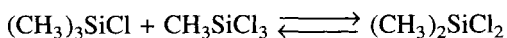
This reaction, based on the Wurtz reaction, tends to go to completion and the yield of technically useful chlorosilane is low.

The commercial value of this method is also limited by the hazards associated with the handling of sodium.

29.2.5 Rearrangement of Organochlorosilanes

Several techniques have been devised which provide convenient methods of converting by-product chlorosilanes into more useful intermediates. A typical example, valuable in technical-scale work, is the redistribution of

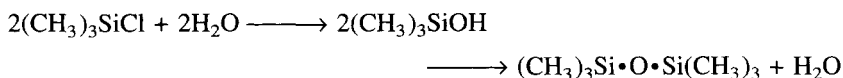
chlorotrimethylsilane and trichloromethylsilane to the dichlorosilane by reacting at 200–400°C in the presence of aluminium chloride.



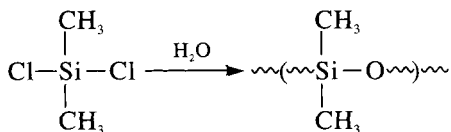
29.3 GENERAL METHODS OF PREPARATION AND PROPERTIES OF SILICONES

A variety of silicone polymers has been prepared ranging from low-viscosity fluids to rigid cross-linked resins. The bulk of such materials are based on chloromethylsilanes and the gross differences in physical states depend largely on the functionality of the intermediate.

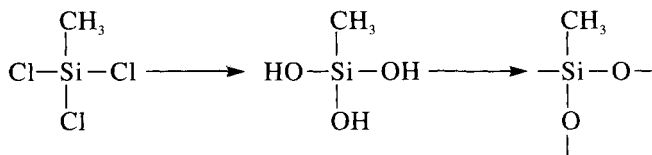
Reaction of chlorotrimethylsilane with water will produce a monohydroxy compound which condenses spontaneously to form hexamethyldisiloxane.



Hydrolysis of dimethyldichlorosilane will yield a linear polymer.



Hydrolysis of trichloromethylsilane yields a network structure.



For convenience a shorthand nomenclature is frequently used in silicone literature where

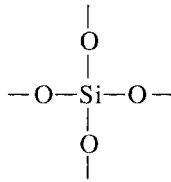
$(\text{CH}_3)_3-\text{Si}-\text{O}$ is designated M (for monofunctional)

$\begin{array}{c} \text{CH}_3 \\ | \\ -\text{Si}-\text{O}- \\ | \\ \text{CH}_3 \end{array}$ is designated D (for difunctional)

and

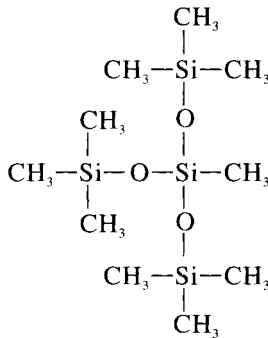
$\begin{array}{c} \text{CH}_3 \\ | \\ -\text{Si}-\text{O}- \\ | \\ \text{O} \\ | \end{array}$ is designated T (for trifunctional)

The tetrafunctional



of silica, which may be considered the derivative of silicon tetrachloride, is designated Q.

Thus hexamethylsilane may be referred to as M-M or M_2 . A linear silicone polymer with a degree of polymerisation of n would be referred to as $MD_{n-2}M$. The compound



would be referred to as TM_3 .

Difficulties arise in characterising commercial branched and network structures in this way because of their heterogeneity. In these cases the R/Si ratio (or specifically the CH_3/Si ratio in methylsilicones) is a useful parameter. On this basis the R/Si ratios of four types are given in *Figure 29.1*.

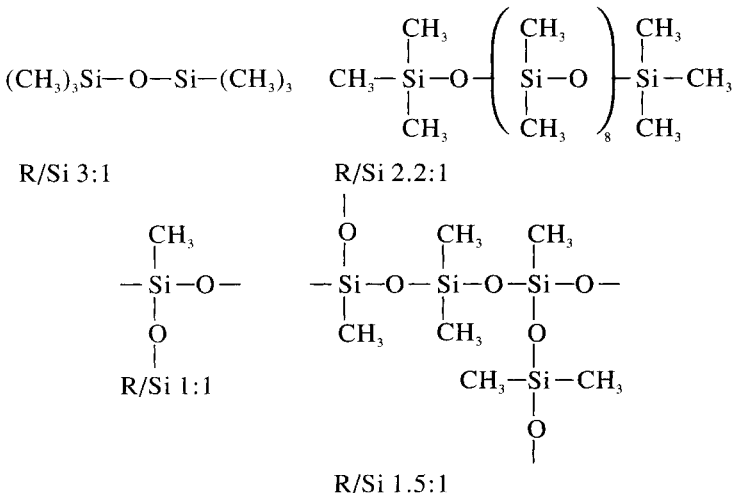


Figure 29.1

Since both Si—O and Si—CH₃ bonds are thermally stable it is predictable that the polydimethylsiloxanes (dimethylsilicones) will have good thermal stability and this is found to be the case. On the other hand since the Si—O bond is partially ionic (51%) it is relatively easily broken by concentrated acids and alkalis at room temperature.

The bond angle of the silicone–oxygen–silicon linkage is large (believed to be about 140–160°) while the siloxane link is very flexible. Roth⁶ has stated that

‘The softness of the bond angle, plus the favourable geometry reducing steric attractions of attached groups, should result in a negligible barrier to (very) free rotation about the Si—O bonds in the linear polymers. Consequently the low boiling points and low temperature coefficients of viscosity may be attributed to the rotation preventing chains from packing sufficiently closely for the short range intermolecular forces to be strongly operative.’

There is evidence to indicate that intermolecular forces between silicone chains are very low. This includes the low boiling points of organosilicon polymers, the low tensile strength of high molecular weight polymers even when lightly cross-linked to produce elastomers, the solubility data, which indicate a low cohesive energy density, and low-temperature coefficient of viscosity. The position of the polymers in the triboelectric series and the non-stick properties give similar indications. On the other hand Scott and co-workers⁷ have measured the height of the rotational barriers about the Si—O bond and believe that the peculiar properties are due to the very free rotation about the Si—O bond and not due to low intermolecular forces. By studying gas imperfection data of hexamethyldisiloxane they consider that in fact normal intermolecular forces exist.

29.4 SILICONE FLUIDS

The silicone fluids form a range of colourless liquids with viscosities from 1 to 1 000 000 centistokes. High molecular weight materials also exist but these may be more conveniently considered as gums and rubbers (see Section 29.6). It is convenient to consider the fluids in two classes:

- (1) Dimethylsilicone fluids.
- (2) Other fluids. These other fluids are used only for specialised purposes and will be considered only in the section on applications.

29.4.1 Preparation

As indicated in Section 29.3, the conversion of the chlorosilane intermediates into polymers is accomplished by hydrolysis with water followed by spontaneous condensation. In practice there are three important stages:

- (1) Hydrolysis, condensation and neutralisation by either a batchwise or continuous process.
- (2) Catalytic equilibration.
- (3) Devolatilisation.

When batch hydrolysis is being employed a weighed excess amount of water is placed in a glass-lined jacketed reactor.⁸ Dichlorodimethylsilane is run in

through a subsurface dispersion nozzle and the contents are vigorously agitated. The reaction is carried out under reflux to prevent loss of volatile components. Although the hydrolysis reaction itself is endothermic the absorption of the HCl evolved on hydrolysis generates enough heat to render the overall reaction exothermic and it is necessary to control the reaction temperature by circulating a coolant through the jacket of the reactor. When hydrolysis is complete the agitation is stopped and the oily polymer layer is allowed to separate from the dilute acid phase which is then drawn off. The oil is then neutralised in a separate operation by washing with sodium carbonate solution, decantation and filtration. The condensate at this stage consists of a mixture of cyclic and linear polymers, and careful control of reactant ratios, acid concentration, reaction temperature and oil–acid contact time should be maintained since these will affect the composition of the product, which should be as constant as possible for further processing. The batch process has the advantage that these variables are controlled without undue difficulty.

In the continuous process the chlorosilane and the water are run into the suction side of a centrifugal pump. The reacting mixture is then passed through a loop of borosilicate glass pipe where the hydrolysis is completed and from there back to the pump. The mixture then passes to a decanter to allow separation of the two ingredients. The decanting stage is critical and care must be taken in order to avoid low yields and difficulties in the neutralisation stage which is carried out as in the batch process.

The products of the hydrolysis reaction under normal conditions will consist of an approximately equal mixture of cyclic compounds, mainly the tetramer, and linear polymer. In order to achieve a more linear polymer, but with a random molecular weight distribution, and also to stabilise the viscosity it is common practice to equilibrate the fluid by heating with a catalyst such as dilute sulphuric acid. This starts a series of reactions which would lead to the formation of higher molecular weight polymer except that controlled amounts of the monofunctional chlorotrimethylsilane or more usually the dimer, hexamethyldisiloxane ($\text{Me}_3\text{Si}\cdot\text{O}\cdot\text{SiMe}_3$), are added as a 'chain stopper' to control molecular weight, the latter functioning by a trans-etherification mechanism. The more the chain stopper is added, the lower becomes the average molecular weight of the equilibrated product. When assessing the amount of chain stopper to add it is necessary to calculate the amount of trifunctional material present as an impurity in the fluid before equilibration.

In practice, for fluids of viscosities below 1000 centistokes, the equilibration reaction will take a number of hours at 100–150°C. Residual esters and siliconates which may occur during the reaction are hydrolysed by addition of water and the oil is separated from the aqueous acid layer and neutralised as before.

For some applications it is desirable that the fluids be free from the volatile low molecular products that result from the randomising equilibration reaction. This operation may be carried out either batchwise or continuously using a vacuum still. Commercial 'non-volatile' fluids have a weight loss of less than 0.5% after 24 hours at 150°C.

29.4.2 General Properties

As a class dimethylsilicone fluids are colourless, odourless, of low volatility and non-toxic. They have a high order of thermal stability and a fair constancy of physical properties over a wide range of temperature (–70°C to 200°C). Although

fluids have prolonged stability at 150°C they will oxidise at 250°C with an increase in viscosity and eventual gelling. The oxidation rate may, however, be retarded by conventional antioxidants.

The fluids have reasonably good chemical resistance but are attacked by concentrated mineral acids and alkalis. They are soluble in aliphatic, aromatic and chlorinated hydrocarbons, which is to be expected from the low solubility parameter of 14.9 MPa^{1/2}. They are insoluble in solvents of higher solubility parameter such as acetone, ethylene glycol and water. They are themselves very poor solvents. Some physical properties of the dimethylsilicone fluids are summarised in *Table 29.2*.

Table 29.2 Some physical properties of dimethylsiloxane polymers of the type $(\text{CH}_3)_3\text{SiO}[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_3$ ⁹

Value of n	1	3	6	14	90	210	350
Viscosity (centistokes)	1.04	2.06	3.88	10	100	350	1000
Specific gravity d_{25}^{25}	0.818	0.871	0.908	0.937	0.965	0.969	0.970
Refractive index n_D^{25}	1.382	1.390	1.395	1.399	1.403	1.403	1.404

Barry¹⁰ has shown that for linear dimethylsilicones the viscosity (η) in centistokes at 25°C and the number (n) of dimethylsiloxy groups are connected by the surprisingly simple relationship

$$\log \eta = 0.1 \sqrt{n} + 1.1$$

It has been shown¹¹ that branched polymers have lower melting points and viscosities than linear polymers of the same molecular weight. The viscosity of the silicone fluids is much less affected by temperature than with the corresponding paraffins (see *Figure 29.2*).

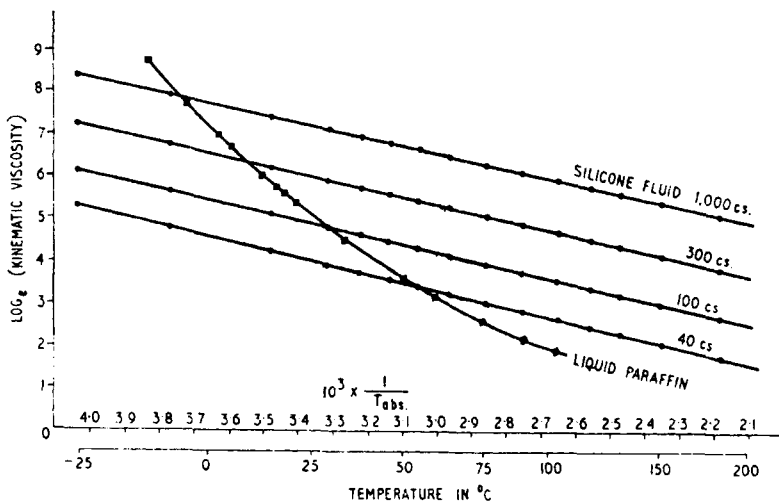


Figure 29.2. Viscosity-temperature curves for four commercial dimethylpolysiloxane fluids and for liquid paraffin. The numbers 1000, 300, 100 and 40 indicate the viscosities in centistokes at 38°C. (After Freeman¹²)

29.4.3 Applications

Silicone fluids find a very wide variety of applications mainly because of their water-repellency, anti-stick properties, low surface tension and thermal properties.

Polish additives

A well-known application of the dimethylsilicone fluids, to the general public, is as a polish additive. The polishes contain normally 2–4% of silicone together with a wax which has been formulated either into an aqueous emulsion or a solution in a volatile solvent. The value of the silicone fluid is not due to such factors as water-repellency or anti-stick properties but due to its ability to lubricate, without softening, the microcrystalline wax plates and enable them to slide past each other, this being the basis of the polishing process. The effort in polishing a car with a polish containing silicone fluid is claimed to be less than half that required with a conventional wax polish. The protective action is at least as good if not slightly superior.

Release agents

Dilute solutions or emulsions containing $\frac{1}{2}$ –1% of a silicone fluid have been extensively used as a release agent for rubber moulding, having replaced the older traditional materials such as soap. Similar fluids have also been found to be of value in the die-casting of metals. Silicones have not found extensive application in the moulding of thermosetting materials since the common use of plated moulds and of internal lubricants in the moulding power obviate the need. Their use has also been restricted with thermoplastics because of the tendency of the fluids to cause stress cracking in many polymers

Silicone greases do, however, have uses in extrusion for coating dies etc., to facilitate stripping down. Greases have also found uses in the laboratory for lubricating stop cocks and for high-vacuum work.

Water-repellent applications

The silicones have established their value as water-repellent finishes for a range of natural and synthetic textiles. A number of techniques have been devised which result in the pick-up of 1–3% of silicone resin on the cloth. The polymer may be added as a solution, an emulsion or by spraying a fine mist; alternatively, intermediates may be added which either polymerise *in situ* or attach themselves to the fibre molecules.

In one variation of the process the textile fabric is treated with either a solution or emulsion of a polymer containing active hydrogen groups, such as the polymer of dichloromethylsilane. If the impregnated fabric is heated in the presence of a catalyst such as the zinc salt of an organic acid or an organotin compound for about five minutes at 100–150°C the hydrogen atoms are replaced by hydroxyl groups which then condense so that individual molecules cross-link to form a flexible water-repellent shell round each of the fibres (*Figure 29.3*).

Leather may similarly be made water repellent by treatment with solutions or emulsions of silicone fluids. A variety of techniques is available, the method chosen depending to some extent on the type of leather to be treated. The water

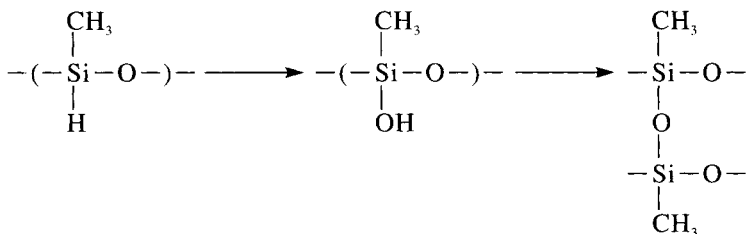


Figure 29.3

repellency may be obtained without appreciably affecting the ability of a leather to transpire.

Silicone fluids containing Si—H groups are also used for paper treatment. The paper is immersed in a solution or dilute emulsion of the polymer containing either a zinc salt or organo-tin compound. The paper is then air-dried and heated for two minutes at 80°C to cure the resin. The treated paper has a measure of water repellency and in addition some anti-adhesive properties.

Lubricants and greases

Silicone fluids and greases have proved of use as lubricants for high-temperature operation for applications depending on rolling friction. Their use as boundary lubricants, particularly between steel surfaces, is, however, somewhat limited although improvement may be obtained by incorporating halogenated phenyl groups in the polymer. Higher working temperatures are possible if phenyl-methylsilicones are used.

Greases may be made by blending the polymer with an inert filler such as a fine silica, carbon black or metallic soap. The silicone-silica greases are used primarily as electrical greases for such applications as aircraft and car ignition systems.

The fluids are also used in shock absorbers, hydraulic fluids, dashpots and other damping systems designed for high-temperature operation.

Miscellaneous

Dimethylsilicone fluids are used extensively as antifoams although the concentration used in any one system is normally only a few parts per million. They are useful in many chemical and food production operations and in sewage disposal.

The use of small amounts of the material in paints and surface coatings is claimed to help in eliminating faults such as 'silking' in dipping applications and 'orange peel' in stoved finishes.

Interesting graft polymers based on silicone polymers are finding use in the manufacture of polyurethane foams, particularly, of the polyether type (see Chapter 27), because of their value as cell structure modifiers.

Another use in conjunction with other polymers is as a flow promoter for thermoplastics such as polystyrene.

The columns in vapour phase chromatographic apparatus usually incorporate high molecular weight dimethylsilicone fluids as the stationary phase.

The fluids have also found a number of uses in medicine. Barrier creams based on silicone fluids have been found to be particularly useful against the cutting oils in metal machinery processes which are common industrial irritants. The serious and often fatal frothy bloat suffered by ruminants can be countered by the use of small quantities of silicone fluid acting as an antifoam.

29.5 SILICONE RESINS

29.5.1 Preparation

On the commercial scale silicone resins are prepared batchwise by hydrolysis of a blend of chlorosilanes. In order that the final product shall be cross-linked, a quantity of trichlorosilanes must be incorporated into the blend. A measure of the functionality of the blend is given by the R/Si ratio (see Section 29.3). Whereas a linear polymer will have an R/Si ratio of just over 2:1, the ratio when using trichlorosilane alone will be 1:1. Since these latter materials are brittle, ratios in the range 1.2 to 1.6:1 are used in commercial practice. Since chlorophenylsilanes are also often used, the $\text{CH}_3/\text{C}_6\text{H}_5$ ratio is a further convenient parameter of use in classifying the resins.

The chlorosilanes are dissolved in a suitable solvent system and then blended with the water which may contain additives to control the reaction. In the case of methylsilicone resin the overall reaction is highly exothermic and care must be taken to avoid overheating which can lead to gelation. When substantial quantities of chlorophenylsilanes are present, however, it is often necessary to raise the temperature to 70–75°C to effect a satisfactory degree of hydrolysis.

At the end of the reaction the polymer–solvent layer is separated from the aqueous acid layer and neutralised. A portion of the solvent is then distilled off until the correct solids content is reached.

The resin at this stage consists of a mixture of cyclic, linear, branched and cross-linked polymers rich in hydroxyl end-groups, but of a low average molecular weight. This is increased somewhat through ‘bodying’ the solution by heating with a catalyst such as zinc octoate at 100°C until the viscosity, a measure of molecular weight at constant solids content, reaches the desired value.

The resins are then cooled and stored in containers which do not catalyse further condensation of the resins.

The cross-linking of the resin is, of course, not carried out until it is *in situ* in the finished product. This will take place by heating the resin at elevated temperatures with a catalyst, several of which are described in the literature, e.g. triethanolamine and metal octoates. The selection of the type and amount of resin has a critical influence on the rate of cure and on the properties of the finished resin.

29.5.2 Properties

The general properties of the resins are much as to be expected. They have very good heat resistance but are mechanically much weaker than the corresponding organic cross-linked materials. This weakness may be ascribed to the tendency of the polymers to form ring structures with consequent low cross-linking efficiency and also to the low intermolecular forces.

High phenyl content resins are compatible with organic resins of the P-F, U-F, M-F, epoxy-ester and oil-modified alkyd types but are not compatible with non-modified alkyds. Silicone resins are highly water repellent.

The resins are good electrical insulators, particularly at elevated temperatures and under damp conditions. This aspect is discussed more fully in the next section.

29.5.3 Applications

Laminates

Methyl-phenylsilicone resins are used in the manufacture of heat-resistant glass-cloth laminates, particularly for electrical applications. The glass cloth is first cleaned of size either by washing with hot trichloroethylene followed by hot detergent solution or alternatively by heat cleaning. The cloth is then dipped into a solution of the resin in an aromatic solvent, the solvent is evaporated and the resin is partially cured by a short heating period so that the resin no longer remains tacky. Resin pick-up is usually in the order of 35–45% for high-pressure laminates and 25–35% for low-pressure laminates.

The pieces of cloth are then plied up and moulded at about 170°C for 30–60 minutes. Whilst flat sheets are moulded in a press at about 1000 lbf/in² (7 MPa) pressure, complex shapes may be moulded by rubber bag or similar techniques at much lower pressures (~15 lbf/in²) (0.1 MPa) if the correct choice of resin is made. A number of curing catalysts have been used, including triethanolamine, zinc octoate and dibutyl tin diacetate. The laminates are then given a further prolonged curing period in order to develop the most desirable properties.

The properties of the laminate are dependent on the resin and type of glass cloth used, the method of arranging the plies, the resin content and the curing schedule. *Figure 29.4* shows how the flexural strength may be affected by the nature of the resin and by the resin content.

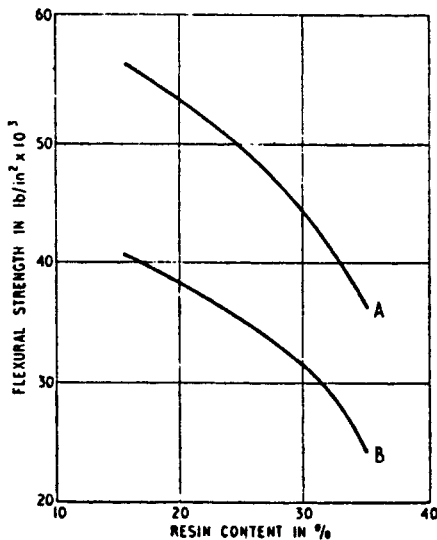


Figure 29.4. Influence of resin content on the flexural strength of glass-cloth laminates made with two silicone resins A and B. (After Gale¹⁴)

A number of different resins are available and the ultimate choice will depend on the end use and proposed method of fabrication. For example, one resin will be recommended for maximum strength and fastest cures whilst another will have the best electrical properties. Some may be suitable for low-pressure laminating whilst others will require a moulding pressure of 1000 lbf/in² (7 MPa).

Of particular importance are the electrical properties of the laminates. These are generally superior to P-F and M-F glass-cloth laminates, as may be seen from *Table 29.3*.¹³

Table 29.4 Typical properties of glass-fibre laminates¹³

Property	Unit	Test method	P-F	M-F	Silicone
Power factor (1 MHz)	—	BS1137	0.06	0.08	0.0002
Dielectric strength	V/0.001 in kV/cm	BS1137	150-200 60-80	150-200 60-80	250-300 100-120
Insulation resistance (dry)	Ω	BS1137	10 000	20 000	500 000
Insulation resistance (after water immersion)	Ω	BS1137	10	10	10 000

The dielectric constant is normally in the range 3.6-4.4 and decreases with an increase in resin content.

The dielectric properties are reasonably constant over a fair range of temperature and frequency.

The power factor of typical glass-cloth laminates decreases with aging at about 250°C, which is the main reason for post-curing (*Figure 29.5*). A power factor drift is, however, observed¹³ under wet conditions and the ratio of power factors between wet and dry conditions is about 3:1.

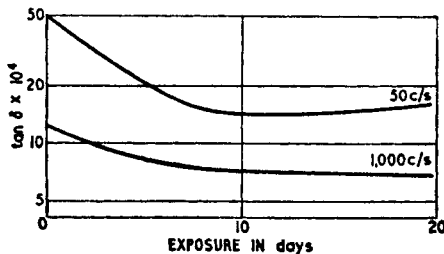


Figure 29.5. Effect of aging at 250°C on the power factor of silicone-bonded, glass-cloth laminates. (After Newland¹³)

The mechanical properties of the laminates are somewhat poorer than observed with phenolic and melamine laminates. Tensile and flexural strength figures are typically about 20% less than for the corresponding P-F and M-F materials and about 60% of values for epoxy laminates.

Silicone-asbestos laminates are inferior mechanically to the glass-reinforced laminates and have not found wide commercial use. Interesting laminates have,

however, been introduced based on mica paper and it is expected that their use will increase.

Silicone laminates are used principally in electrical applications such as slot wedges in electric motors, particularly class H motors, terminal boards, printed circuit boards and transformer formers. There is also some application in aircraft, including use in firewalls and ducts.

Moulding compositions

Compression moulding powders based on silicone resins have been available on a small scale from manufacturers for a number of years. They consist of mixtures of a heat-resistant fibrous filler (e.g. glass fibre or asbestos) with a resin and catalyst. Non-fibrous inorganic fillers may also be included. They may be moulded, typically, at temperatures of about 160°C for 5–20 minutes using pressures of $\frac{1}{2}$ –2 ton/in² (7–30 MPa). Post-curing is necessary for several hours in order to develop the best properties. Materials currently available suffer from a short shelf life of the order of 3–6 months but have been used in the moulding of brush rings holders, switch parts and other electrical applications that need to withstand high temperatures. They are extremely expensive and are of even greater volume cost than PTFE.

Some typical properties of a cured silicone moulding composition are given in Table 29.4.

Table 29.4 Some typical properties of a silicone moulding compound

<i>Property</i>	<i>ASTM test</i>	
Specific gravity (25°C)	—	1.65
Flexural strength	D.790	
23°C		14 000 lbf/in ² (97 MPa)
200°C		5000 lbf/in ² (35 MPa)
Flexural modulus	D.790	
23°C		1.8 × 10 ⁶ lbf/in ² 12 400 MPa
200°C		0.9 × 10 ⁶ lbf/in ² 6200 MPa
Tensile strength		
23°C	D.651	4400 lbf/in ² (30 MPa)
200°C	D.652	1300 lbf/in ² (9 MPa)
Dielectric constant		
10 ³ –10 ⁶ Hz	D.150	3.6
Power factor		
10 ³ –10 ⁶ Hz	D.150	~0.005

Miscellaneous applications

Like the fluids, the silicone resins form useful release agents and although more expensive initially are more durable. The resin is applied in solution form and the coated surface is then dried and the resin cured by heating for about two hours at 200–230°C. The bakery industry has found a particular use for these materials in aiding the release of bread from baking pans.

Resins, usually in a partially condensed form, are used to provide a water-repellent treatment for brickwork and masonry. Methyl-phenylsilicone resins are used as coatings for electrical equipment and in the impregnation of class H electrical equipment. Dimethylsilicone fluids are also used as water-repellent coatings for class A or class B insulation.

The heat resistance and water resistance of the resins are attractive properties for surface coatings but the poor scratch resistance of the materials has limited applications of straight silicone resins.

Blends with alkyd or other organic resins have, however, been prepared and these show heat resistance intermediate between those of the organic resins and the silicones. Of particular interest is the use of silicone-organic resin blends filled with aluminium powder for the coating of metal chimneys and furnace doors. At the operating temperatures the resins are destroyed, leaving a layer of aluminium film.

29.6 SILICONE RUBBERS

In spite of their high cost, silicone rubbers have over the last 40 years established themselves in a variety of applications where heat resistance and retention of properties over a wide range of temperatures are required.

29.6.1 Dimethylsilicone Rubbers

The elastomers consist of very high molecular weight ($\sim 0.5 \times 10^6$) linear gums cross-linked after fabrication. In order to achieve such polymers it is necessary that very pure difunctional monomers be employed since the presence of monofunctional material will limit the molecular weight while trifunctional material will lead to cross-linking. Where dimethylsilicone rubbers are being prepared, the cyclic tetramer, octamethylcyclotetrasiloxane, which may be obtained free from mono- and trifunctional impurities, is often used. This tetramer occurs to the extent of about 25% during the hydrolysis of dichlorosilanes into polymers.

To obtain high molecular weight polymers the tetramer is equilibrated with a trace of alkaline catalyst for several hours at 150–200°C. The product is a viscous gum with no elastic properties. The molecular weight is controlled by careful addition of monofunctional material.

In recent years there has been some interest in the ring-opening polymerisation of cyclic trimers using a weak base such as lithium silanolate which gives high molecular weight products of narrow molecular weight distribution free of cyclic materials other than the unreacted trimer.

For reasons that will be explained in the next section the simple polydimethylsiloxane rubbers are seldom used today.

29.6.2 Modified polydimethylsiloxane Rubbers

Dimethylsilicone rubbers show a high compression set which can be reduced to some extent by additives such as mercurous oxide and cadmium oxide. These materials are undesirable, however, because of their toxicity. Substantially reduced compression set values may be obtained by using a polymer containing

small amounts of methylvinylsiloxane (~0.1%). These materials may be vulcanised with less reactive peroxides than usual and may also be reinforced with carbon black if desired. Most commercial silicone rubbers today contain such vinyl modification.

Rubbery polymers in which some of the methyl groups had been replaced by groups containing fluorine or nitrile components became available in the 1950s (Figure 29.6). Although the nitrile-containing polymers failed to become commercially significant, the fluorine-containing polymers with their excellent resistance to oils, fuels and solvents have found quite extensive application in spite of their high price.

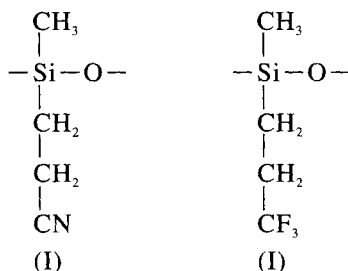


Figure 29.6

Although the nitrile-containing polymers failed to become significant, the fluorine-containing polymers have found commercial application. Commonly referred to as *fluorosilicones* and with the ASTM designation FVMQ, they were first introduced by Dow Corning in 1953 as LS-53 and are now also supplied by General Electric and Shinetsu. The commercial materials usually contain a small amount (about 0.2%) of methyl vinyl siloxane as a cure site monomer, whilst the fluorosilicone component can range from 40% to 90%, the latter figure being more common.

Whilst exhibiting the excellent low-temperature flexibility (with a T_g of about -80°C) and very good heat resistance (up to 200°C) typical of a silicone rubber, the fluorosilicones also exhibit good aliphatic oil resistance and excellent aging resistance. However, for some applications they have recently encountered a challenge from the polyphosphazenes (see Section 13.10).

Whilst the T_g of poly(dimethylsiloxane) rubbers is reported to be as low as -123°C they do become stiff at about -60 to -80°C due to some crystallisation. Copolymerisation of the dimethyl intermediate with a small amount of a dichlorodiphenylsilane or, preferably, phenylmethylchlorosilane, leads to an irregular structure and hence amorphous polymer which thus remains a rubber down to its T_g . Although this is higher than the T_g of the dimethylsiloxane it is lower than the T_m so that the polymer remains rubbery down to a lower temperature (in some cases down to -100°C). The T_g does, however, increase steadily with the fraction of phenylsiloxane and eventually rises above that of the T_m of the dimethylsilicone rubber. In practice the use of about 10% of phenyldichlorosilane is sufficient to inhibit crystallisation without causing an excess rise in the glass transition temperature. As with the polydimethylsiloxanes, most methylphenyl silicone rubbers also contain a small amount of vinyl groups.

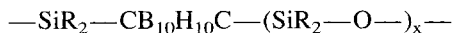
The ISO and ASTM D1418 use the following classification for silicone rubbers:

- MQ Silicone rubbers having only methyl substituent groups on the polymer chain (polydimethyl siloxanes).
- VMQ Silicone rubbers having both methyl and vinyl substituent groups on the polymer chain.
- PMQ Silicone rubbers having both methyl and phenyl groups on the polymer chain.
- PVMQ Silicone rubbers having methyl, phenyl and vinyl substituent groups on the polymer chain.
- FVMQ Silicone rubbers having fluoro and methyl substituent groups on the polymer chain (the fluorosilicones)

Interesting products may also be produced by introducing boron atoms into the chain. The amount of boron used is usually small (B:Si 1:500 to 1:200) but its presence increases the self-adhesive tack of the rubber, which is desirable where hand-building operations are involved. The products may be obtained by condensing dialkylpolysiloxanes end-blocked with silanol groups with boric acid, or by reacting ethoxyl end-blocked polymers with boron triacetate.

The material known as *bouncing putty* is also a silicone polymer with the occasional Si—O—B group in the chain, in this case with 1 boron atom to about every 3–100 silicon atoms. The material flows on storage, and on slow extension shows viscous flow. However, small pieces dropped onto a hard surface show a high elastic rebound, whilst on sudden striking they may shatter. The material had some use in electrical equipment, as a children's novelty and as a useful teaching aid, but is now difficult to obtain.

Substantial improvements in the heat-resisting capability of silicone rubbers were achieved with the appearance of the *poly(carborane siloxanes)*. First described in 1966, they were introduced commercially by the Olin Corporation in 1971 as Dexsil. The polymers have the essential structure



where $\text{CB}_{10}\text{H}_{10}\text{C}$ represents a *m*-carborane group of structure shown in *Figure 29.7*.

Introduction of some vinyl groups in a side chain enables vulcanisation to take place. It is claimed that when stabilised with ferric oxide the materials may be used operationally to 250°C and the possibility of short-term use up to 400°C has

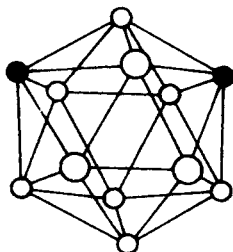


Figure 29.7. *m*-Carborane structure: ● = C; ○ = BH

been suggested. One such rubber loaded with 30 parts of silica per hundred of rubber and vulcanised with dicumyl peroxide has a tensile strength of 10 MPa and an elongation at break of 260%. One disadvantage of the materials is that the polymers are partially cross-linked during the initial polymerisation and this makes them somewhat difficult to fabricate. A modified method of polymerisation developed at Union Carbide gives more linear products but with somewhat lower tensile strength and breaking elongation. One such material had a limiting oxygen index as high as 62.

Room temperature vulcanising silicone rubbers (r. t. v. rubbers) have proved of considerable value where elaborate processing equipment is not available. These rubbers are low molecular weight silicones with reactive end-groups and loaded with reinforcing fillers. The RTV silicone rubbers may be classified into two types:

- (1) Two-pack systems (sometimes known as RTV-2 rubbers). These are widely used for making flexible moulds, particularly for craft work.
- (2) One-pack systems (RTV-1 rubbers). These are very widely used for sealing and caulking applications.

The two-pack systems may be subdivided further into:

- (1) Condensation cross-linked materials.
- (2) Addition cross-linked polymers.

A typical condensation system involves the reaction of a silanol-terminated polydimethylsiloxane with a multi-functional organosilicon cross-linking agent such as $\text{Si}(\text{RO})_4$ (Figure 29.8). Pot life will vary from a few minutes to several hours, depending on the catalysts used and the ambient conditions. Typical catalysts include tin octoate and dibutyl tin dilaurate.

Addition-cured materials are particularly suitable for casting polyurethane materials, but require scrupulous cleanliness when processing since cure may be affected by such diverse materials as unsaturated hydrocarbon solvents, sulphur, organo-metallic compounds, plasticine and some epoxide resins. Addition cross-linking commonly involves a process variously known as hydrosilation or hydrosilylation. In such a process a polymer containing vinyl groups is reacted with a reagent containing a number of hydrosilane ($\text{Si}-\text{H}$) groups, Pt(II) compounds being frequently used as catalysts for the reaction. In practice such a system requires a two-pack operation, which for convenience is often in a 1:1 ratio, and when mixed the shelf life will be limited to a few days at room temperature.

The RTV-1 rubbers are produced by first producing a polydialkylsiloxane with terminal hydroxyl groups. This is then reacted with a multi-functional organosilicon cross-linking agent of the type RSiX_3 , where X may be

- NH—R (amine)
- O—(CO)— CH_3 (acetate)
- O—N=C(R_2) (oxime)

The $\text{Si}-\text{X}$ linkages react with water to form a $\text{Si}-\text{O}-\text{Si}$ linkage with the liberation of HX . Typical catalysts include diaryl alkyl tin acylates. Such a curing reaction may be brought about by atmospheric humidity and such rubbers are

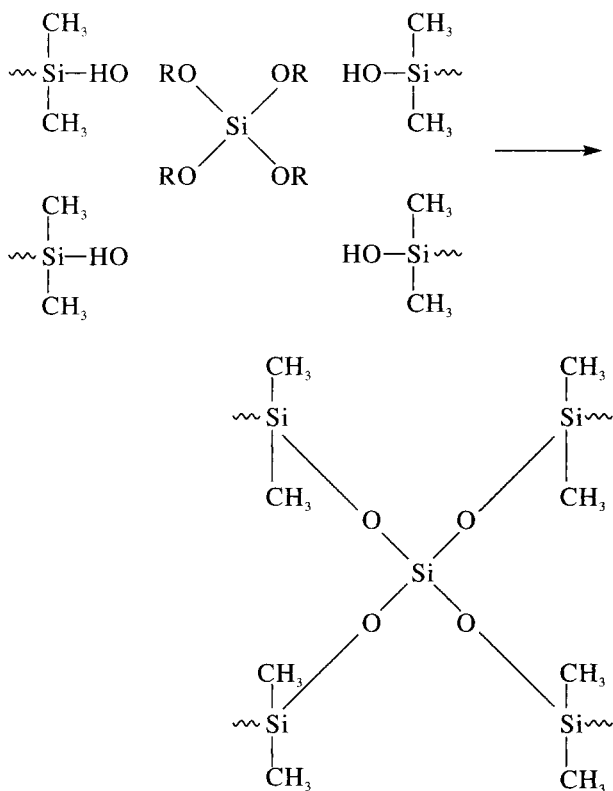


Figure 29.8

also known as moisture-curing silicones. Because of the need for diffusion of the water into the polymer, the rubber layer should not exceed 10mm if the ingress is from one side only. For this thickness a typical cure at 23°C at 50% RH would take about five days, whereas a sample 2 mm thick would cure in about 1 day.

In 1975 Wacker-Chemie introduced silicones under the name of *m*-polymers. These are also room temperature curing liquid polymers which give rubbery materials on cross-linking and are available both as one- and two-component systems. Their particular feature is that they contain dispersions of copolymers such as those of styrene and *n*-butyl acrylate in the shape of rods or rice grains in the fluid silicone polymer. A small amount of the organic copolymer is also grafted onto the silicone backbone.

The RTV rubbers find use in the building industry for caulking and in the electrical industry for encapsulation. It also provides a useful casting material for craft work. Perhaps most important of all it provides a method for producing rubbery products with the simplest of equipment and can frequently solve a problem where only a small number of articles are required.

29.6.3 Compounding

Before fabrication it is necessary to compound the gum with fillers, vulcanising agent and other special additives on a two-roll mill or in an internal mixer.

Incorporation of fine fillers is necessary if the vulcanisates are to have any strength. Unfilled polymers have negligible strength whereas reinforced silicone rubbers may have strengths up to 2000 lbf/in² (14 MPa). Since carbon blacks do not give outstanding reinforcement, adversely affect electrical insulation properties and may interfere with the curing action, fine silica fillers are generally used. These materials have particle sizes in the range 30–300 Å and are prepared by combustion of silicon tetrachloride (fume silicas), by precipitation or as an aerogel. Dilution of the rubber by filler will also reduce cost, shrinkage on cure, and thermal expansions and may aid processing. It is to be noted that different silica fillers may lead to large differences in processing behaviour, cure rates and the properties of the finished product.

Silicone rubbers are normally cured with peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide and t-butyl perbenzoate being used for the dimethyl-silicones in quantities of 0.5–3%. These materials are stable in the compounds for several months at room temperature but will start to cure at about 70°C.

Polymers containing vinyl side groups may be cured with less reactive peroxides such as dicumyl peroxide and t-butyl peracetate.

Heat aging characteristics may be improved by the addition of a few per cent of ferric oxide and barium zirconate to name but two materials mentioned in the literature.

29.6.4 Fabrication and Cross-Linking

Compounded rubbers may be fabricated by the normal techniques employed in rubber technology, e.g. extrusion, calendaring and compression moulding. In order to develop rubbery properties it is necessary to cross-link (vulcanise) the compound after shaping. With moulded articles this may be accomplished by heating in a press for 5–25 minutes at a range of temperatures from 115 to 175°C, according to the composition of the compound. Calendered and extruded materials are generally cured in a hot air or steam pan. Prolonged post-curing at temperatures up to 250°C may be necessary in order to achieve the best mechanical and electrical properties.

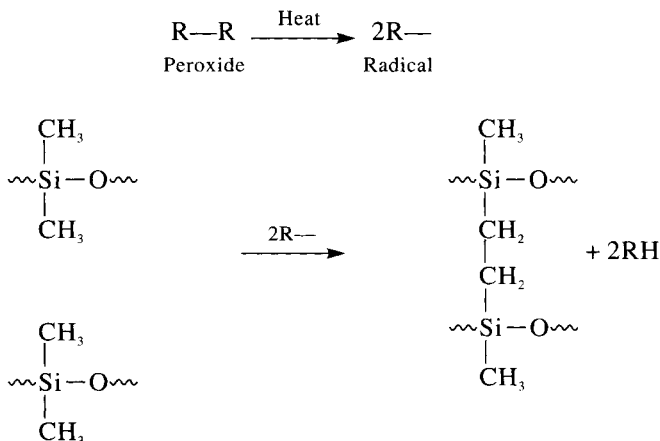


Figure 29.9

Indications are that cross-linking of dimethylsilicone rubbers occurs by the sequence of reactions shown in *Figure 29.9*.

The peroxide decomposes at elevated temperatures to give free radicals, which then abstract a hydrogen atom from the methyl group. The radicals formed then combine to form a hydrocarbon linkage. Results obtained by reacting model systems with benzoyl peroxide and analysing the reaction products are consistent with this type of mechanism.¹⁵

Rubbers containing traces of vinyl groups can be cross-linked by weaker peroxide catalysts, the reaction involving a vinyl group. It is, however, unlikely that vinyl-to-vinyl linking occurs. Where there is a high vinyl content (4–5% molar) it is possible to vulcanise with sulphur.

29.6.5 Properties and Applications

The important properties of the rubbers are their temperature stability, retention of elasticity at low temperatures and good electrical properties. They are much more expensive than the conventional rubbers (e.g. natural rubber and SBR) and have inferior mechanical properties at room temperature.

The temperature range of general purpose material is approximately –50 to +250°C but both ends of the range may be extended by the use of special purpose materials. Whereas the general purpose silicone compounds have a tensile strength of about 1000 lbf/in² (7 MPa) it is possible using fumed silicas to achieve values of up to 2000 lbf/in² (14 MPa). Similarly, whereas the normal cured compounds have a compression set of 20–50% after 24 hours at 150°C, values of as low as 6% may be obtained with the special rubbers.

Compared with organic rubbers the silicones have a very high air permeability, being 10–20 times as permeable as the organic rubbers. The thermal conductivity is also high, about twice that of the natural rubber. Some typical figures for the physical properties of a general purpose rubber are given in *Table 29.5*.

Table 29.5 Physical properties of general purpose silicone rubbers
(Values determined at 20°C after curing for 24 hours at 250°C)¹⁰

Tensile strength (lbf/in ²)	500–1000 (3.5–7 MPa)
Elongation at break (%)	100–400
Hardness (BS°)	40–50
Compression set (% after 24 h at 150°C)	20–50
Minimum useful temperature (°C)	–55
Maximum useful temperature (°C)	250
Linear shrinkage (%)	2–6
Thermal conductivity (c.g.s. units)	7×10^{-4}
Volume resistivity (Ω cm)	10^{16}
Dielectric strength (V/0.001 in at 50% RH)	500 (200 kV/cm)
Power factor (60 Hz)	0.002
Dielectric constant (60 Hz)	3–6

Silicone rubbers find use because of their excellent thermal and electrical properties, their physiological inertness and their low compression set. Use is, however, restricted because of their poor hydrocarbon oil and solvent resistance (excepting the fluorosilicones), the low vulcanisate strength and the somewhat high cost.

It also has to be mentioned that the silicone rubbers also possess two peculiar undesirable characteristics. On mixing the rubber with many fine silicas a reaction occurs during storage which gives the rubber the outward appearance of being vulcanised and it becomes very difficult to mould and extrude successfully. It is therefore common practice to ensure that shaping operations are carried out within 1–3 weeks of mixing to minimise these ‘bin aging’ problems as they are called. An alternative approach is to add *structure control additives* such as diphenylsilanediol or pinacoydimethylsilane or even to treat the filler with a chlorosilane and subsequently wash out the liberated hydrochloric acid.

The second unusual feature is that it has frequently been observed that the rubbers soften or *reverse* when subjected to high temperatures in a confined space. This is believed to be due to the presence of trapped moisture which, when not able to escape, causes hydrolysis of the polymer.

Auto uses are said to account for about one-third of the 30 000 tonnes of silicone rubber consumed annually around the world (in turn about 10% of total silicone consumption). Specific uses include shaft sealing rings, spark plug caps, O-rings (the major market for the fluorosilicones), gaskets, coolant and heater hoses for buses and trucks, and ignition cables.

It is stated¹⁰ that modern passenger and military aircraft each use about 1000 lb of silicone rubber. This is to be found in gaskets and sealing rings for jet engines, ducting, sealing strips, vibration dampers and insulation equipment.

Silicone cable insulation is also used extensively in naval craft since the insulation is not destroyed in the event of a fire but forms a protective and insulating layer of silica.

The rubbers are also used for such diverse applications as blood transfusion tubing capable of sterilisation, antibiotic container closures, electric iron gaskets, domestic refrigerators and non-adhesive rubber-covered rollers for handling such materials as confectionery and adhesive tape. The cold-curing rubbers are of value in potting and encapsulation.

Silicone rubbers have been widely used for medical applications, particularly for body implants in structural cosmetic surgery. One high-profile application has been that of breast implants, but the award in early 1994 of enormous damages by a US court in respect of faulty implants may discourage development of this application.

29.6.6 Liquid Silicone Rubbers

The early 1980s saw considerable interest in a new form of silicone materials, namely the liquid silicone rubbers. These may be considered as a development from the addition-cured RTV silicone rubbers but with a better pot life and improved physical properties, including heat stability similar to that of conventional peroxide-cured elastomers. The ability to process such liquid raw materials leads to a number of economic benefits such as lower production costs, increased output and reduced capital investment compared with more conventional rubbers. Liquid silicone rubbers are low-viscosity materials which range from a flow consistency to a paste consistency. They are usually supplied as a two-pack system which requires simple blending before use. The materials cure rapidly above 110°C and when injection moulded at high temperatures (200–250°C) cure times as low as a few seconds are possible for small parts. Because of the rapid mould filling, scorch is rarely a problem and, furthermore, post-curing is usually unnecessary.

Most injection moulding machines can be modified to handle liquid silicone rubbers and in addition a number of injection moulding machines are available which are already adapted for liquid silicone rubber operation. In spite of the fact that the raw materials are somewhat expensive, the low capital costs, rapid cures, virtual elimination of finishing and deflashing operations and the absence of post-curing can reduce the process overheads to such an extent that such materials can sometimes compete with some of the organic elastomers. One such example is in baby bottle teats which, although more expensive than those from natural rubber, have a much longer working life and have been claimed to be less expensive in the long term.

Liquid silicone rubbers have also been used in some extruded applications, although these generally require the support of tapes and wire. With such materials a conventional screw extruder is not required, the liquid silicone rubber being pumped directly to a cross-head from the meter mix unit or pressure pot. Vulcanisation may be carried out using infrared heaters or circulated hot air. This technology has been applied successfully to wire coating, optical fibres, ignition cables, various tapes and braided glass-fibre sleeving. One particular advantage when extruding these materials is that delicate products may be covered without the need for a solvent-based material. This avoids the various problems encountered when using solvents, such as blistering in the cured article, the need for solvent recovery and various solvent hazards. In addition, thicker coats can also be applied in one pass through the extruder.

29.6.7 Polysiloxane–polyetherimide Copolymers

These materials are developed from the polyetherimides introduced by General Electric (see also Section 18.14.2). At the time of writing one grade, Ultem Siltem STM 1500, is being offered. It is of particular interest as a material for wire and cable insulation, as it not only has excellent flame resistance coupled with low smoke generation but also avoids possible toxic and corrosion hazards of halogenated polymers. This can be of importance where there are possible escape problems in the event of a fire, such as in tunnels, aircraft and marine (particularly submarine) vessels.

This polymer has a good strength for a flexible silicone polymer coupled with the good heat resistance which may be expected from its components, together with an outstanding value for the limiting oxygen index of 48.

Some typical properties are given in *Table 29.6*.

Table 29.6 Some typical properties of a polysiloxane–polyetherimide copolymer (Ultem Siltem STM 1500)

Specific gravity		1.18
Tensile strength (at yield)	ISO178	20 MPa
(at break)		25 MPa
Elongation at break		110%
Hardness (Shore)	ISO868	D60
Izod notched impact at 23°C	ISO180	25 kJ/m ²
	at -30°C	15 kJ/m ²
Limiting oxygen index	ISO4589	48
IEC Glow Wire Test	IEC695-2-1	960°C at 3.2 mm thickness
Surface resistivity	ASTM D257	>10 ¹⁵ Ω
Volume resistivity		>10 ¹⁴ Ω cm
Dissipation factor at 50 Hz	IEC 250	0.010

29.7 POLYMERS FOR USE AT HIGH TEMPERATURES

The bulk of plastics materials are required to operate within the range of -30 to $+100^{\circ}\text{C}$. There has, however, been a steadily increasing demand for materials to operate outside of these ranges, particularly in certain aerospace, military and telecommunications applications. A considerable amount of research work has been carried out in response to this demand and many thousands of polymers, both organic and inorganic, have been prepared. Many of those which have achieved commercial use have been considered in earlier chapters but in the final part of this chapter it is intended to review the overall situation.

Polymers for use at high temperatures fall into two groups:

- (1) High-temperature low- T_g polymers (rubbers).
- (2) High-temperature high- T_g Polymers (rigid plastics).

The range of high-temperature rubbers is very small and limited to the silicones, already considered in this chapter, and certain fluororubbers. With both classes it is possible to produce polymers with lower interchain attraction and high backbone flexibility and at the same time produce polymers in which all the bonds have high dissociation energies and good resistance to oxidation.

In the case of the high-temperature high- T_g plastics the two main requirements are that:

- (1) The polymer should have a high softening point.
- (2) It should be stable to heat even in an atmosphere of oxygen up to the softening point and possibly beyond.

In certain cases resistance to hydrolysis and solvents (particularly oils) may also be required.

Over the years various lines of attack have been used in the search for heat-resistant polymers, which may be considered under the following headings:

- (1) Fluorine-containing polymers.
- (2) Inorganic polymers.
- (3) Cross-linked organic polymers.
- (4) Polymers containing *p*-phenylene groups and other ring structures.
- (5) Ladder polymers.
- (6) Spiro polymers.
- (7) Co-ordination polymers.

29.7.1 Fluorine-containing polymers

The fluorine chemistry approach was stimulated by the considerable success of polytetrafluoroethylene (Chapter 13). In part this had been fortuitous since although the C—C and C—F bonds gave an inherent stability against thermal degradation the high softening point arose because of the tight packing of the fluorine atoms around the C—C backbone. Such a feature would not in general be expected to be repeated in other fluorine-containing polymers. Nevertheless, as has already been seen, a number of useful fluorine-containing plastics have been produced but none have the excellent heat deformation characteristic of PTFE. Fluorine-containing rubbers have also found use for high-temperature

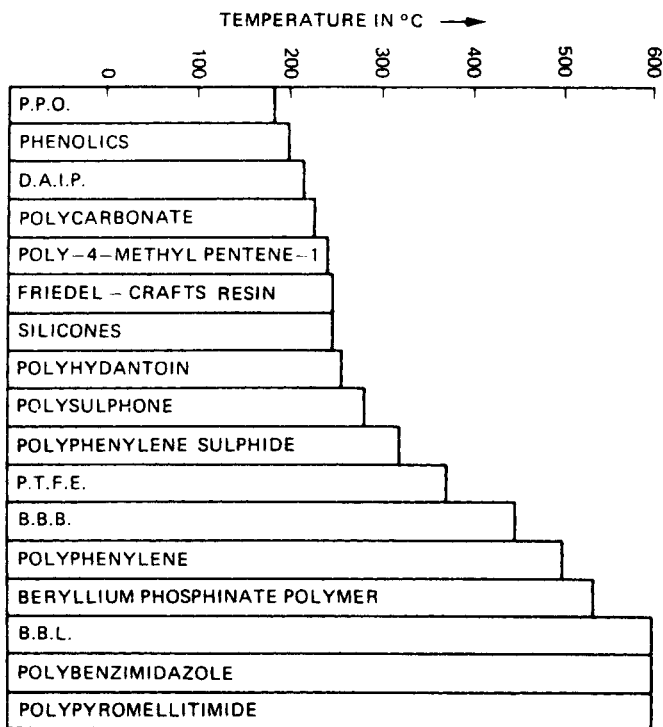


Figure 29.10. Estimates of softening or decomposition temperature (whichever is lower) of most heat-resistant varieties of different polymer species

applications with the additional feature of oil resistance and good low-temperature properties. Figure 29.10 indicates the maximum service temperature of fluorine-containing polymers in comparison with other polymers. Commercially available fluorine-containing polymers were discussed more fully in Chapter 13.

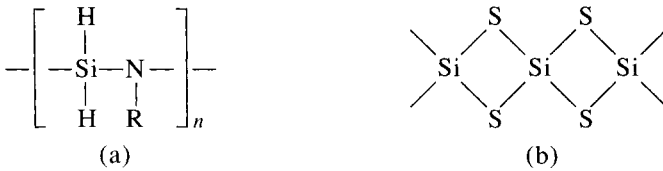
29.7.2 Inorganic polymers

The well-known thermal stability of most minerals and glasses, many of which are themselves polymeric, has led to intensive research into synthetic inorganic and semi-inorganic polymers. These materials can be classified into the following groups:

- (1) Polymers containing main chain silicon atoms.
- (2) Polymetallosiloxanes.
- (3) Polymetalloxanes.
- (4) Phosphorus-containing polymers.
- (5) Boron-containing polymers.
- (6) Sulphur-containing polymers.
- (7) Miscellaneous polymers.

In addition to the silicates and silicones, several polymers which contain silicon atoms in the main chain have been studied in recent years. These include the

silicon–nitrogen structure (a) and silicon sulphides (b). Unfortunately neither of these materials shows hydrolytic stability.



Of greater interest were the polymetallosiloxanes which were investigated by Andrianov and co-workers in the Soviet Union. These polymers may be classed as polyorganosiloxymetalloxanes, of which those shown in *Figure 29.11* form typical types.

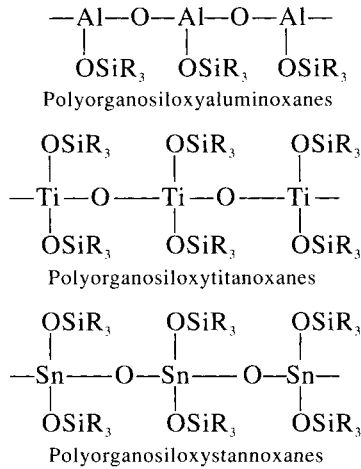


Figure 29.11

Such polymers have a potential utility because experience indicates that thermal stability is often increased by increasing the polarity of the bond. Therefore where the metal is more electropositive than silicon the metal–oxygen bond will be more polar than the silicon–oxygen bond and greater thermal stability may be expected. By surrounding the inorganic skeleton of the molecules, Andrianov produced thermally stable materials which are soluble in organic solvents and may therefore be cast on films, on lacquers or used in laminating resins.

American workers produced a different class of polymetallosiloxanes in which the metal atom and the silicon atom are both incorporated into the main chain (e.g. *Figure 29.12*).

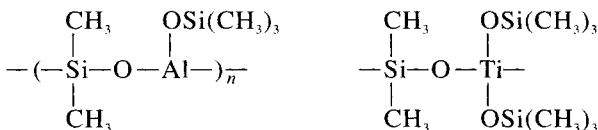
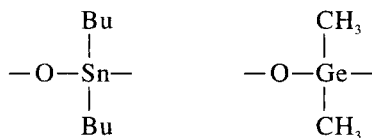


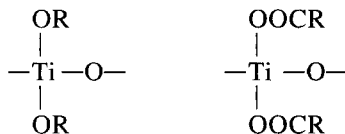
Figure 29.12

The metallosiloxanes are liable to hydrolysis but the rate of hydrolysis is very dependent on the metal used in the polymer. Examination of three low molecular weight metallosiloxanes indicates the relative rates of hydrolysis to be 2220:27.2:1 for the tin, aluminium and titanium derivatives respectively. Russian workers state that polyorganometallosiloxanes are being used industrially but little detailed information is available.

The polymetallosiloxanes above may in fact be considered as variants of a series of polymetalloxanes which are akin to the silicones but which contain, for example, tin, germanium and titanium instead of silicon. Of the polyorganostannoxanes, dibutyl tin oxide finds use as a stabiliser for PVC and as a silicone cross-linking agent. Polyorganogermanoxanes have also been prepared (*Figure 29.13*).

*Figure 29.13*

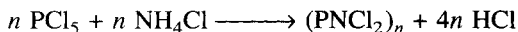
Although titanium does not form a stable bond with carbon, organotitanium polymers have been formed such as polyalkoxytitanoxanes and polymeric titanate esters (*Figure 29.14*).

*Figure 29.14*

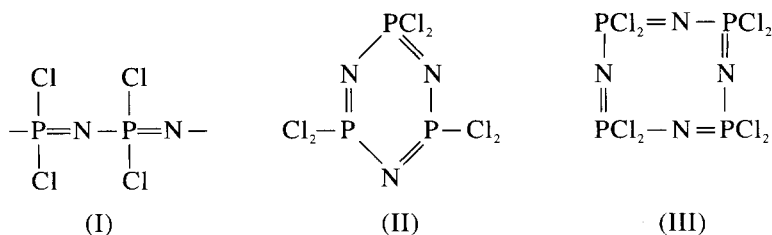
Butyl titanate polymers find use in surface coatings¹⁶ but as a class, titanium polymers lack hydrolytic stability.

Of the phosphorus-containing polymers the polyphosphates have been known for many years. Aluminium phosphate had been used in the manufacture of heat-resistant silica-fibre-reinforced laminates.

If phosphorus pentachloride is reacted with ammonium chloride in an inert solvent such as sym-tetrachloroethane, polymers will be formed by the following reaction



If an excess of pentachloride is employed, linear polymers of the type (I) will be produced but if the pentachloride is added slowly to a suspension of ammonium chloride then cyclic polymers such as the trimer (II) and tetramer (III) will be produced.



Heating of the cyclic polymer at 250°C will also lead to the production of the linear polymer, which is rubbery and stable to 350°C. On standing, however, the material hydrolyses and after a few days loses its elastic properties and becomes hard and covered with drops of hydrochloric acid solution.

In attempts to improve the hydrolytic stability of these materials the active chlorine atom has been replaced by other groups such as F, CF₃, NH₂, CH₃ and phenyl to give a range of polymers of general form PNX₂. One heat-resistant resin based on phosphonitrilic polymers has been marketed (Inorganic Resin 251—Albright and Wilson). The uncured resin is somewhat soluble in water and aqueous solutions may be used for impregnating asbestos fabric for subsequent lamination. Glass fibre, silica fibre and mineral wool are unsuitable as they are degraded during cure. Lamination is carried out at 300°C for 30 minutes under pressure of about 2 ton/in² (30 MPa). The cured laminates have flexural strength of 13 000–15 000 lbf/in² (90–105 MPa) and retain 45% of their strength after 500 hours at 300°C.

In the mid-1970s Firestone announced the availability of PNF Rubber. This rubber has been discussed in Section 13.10 and whilst referred to as a poly(fluoroalkoxyphosphazene) may be considered to be a direct descendant of the inorganic rubber first prepared by Stokes in 1895.

Other phosphorus-based polymers have been investigated and have proved to be of some interest. An example is phosphorus oxynitride, which forms a glass above 1000°C.

Many polymers containing boron in the main chain have been prepared but most of them have either been of low molecular weight or intractable cross-linked structures. Some interest has been shown in the tri-β-aminoborazoles, which polymerise on heating (*Figure 29.15*)¹⁷.

These materials are intractable and easily hydrolysed in hot water but are stable to heating to 600°C.

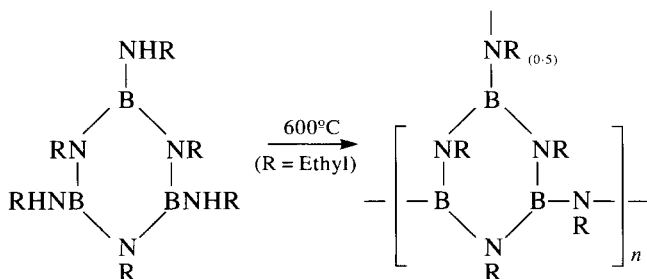


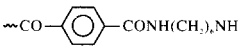
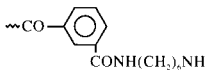
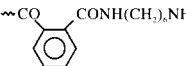
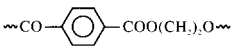
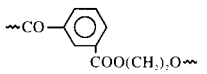
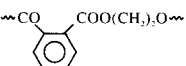
Figure 29.15

by introducing occasional flexible groups into the polymer but at some detriment to the heat resistance. Apart from the phenolics the other resins mentioned above are usually used in conjunction with glass, asbestos or carbon fibres in the form of laminates.

29.7.4 Linear Polymers with *p*-Phenylene Groups and Other Ring Structures

Another approach has been the development of thermoplastics with *p*-phenylene groups in the main chain. Considered in Chapters 20, 21 and 25, some of these materials have very good heat resistance. Generally speaking the greater the content of *p*-phenylene groups the higher the T_g . Furthermore, unsubstituted polymers generally have the higher softening points. It is also interesting to note (Table 29.7) that *p*-phenylene groups lead to much higher T_g as than the *ortho* or *meta* analogues.

Table 29.7 Effect of isomerism of ring structure in linear polymers on melting point

<i>Para</i>	<i>Meta</i>	<i>Ortho</i>
 350°C	 150°C	 50°C
 256°C	 103°C	 63°C

A considerable number of non-cross-linked aromatic and heterocyclic polymers has been produced. These include polyaromatic ketones, aromatic and heterocyclic polyanhydrides, polythiazoles, polypyrazoles, polytriazoles, polyquinoxalines, polyketoquinolines, polybenzimidazoles, polyhydantoin, and polyimides. Of these the last two have achieved some technical significance, and have already been considered in Chapters 21 and 18 respectively. The most important polyimides are obtained by reacting pyromellitic dianhydride with an aromatic diamine to give a product of general structure (Figure 29.17).

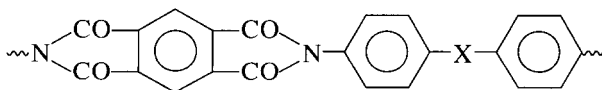


Figure 29.17

It will be noted here that such polymers have few single bonds in the repeating unit and contain a substantial proportion of linked ring structures. This has been taken further by the reaction of tetramines with tetra-acids, as indicated in Figure 29.18.

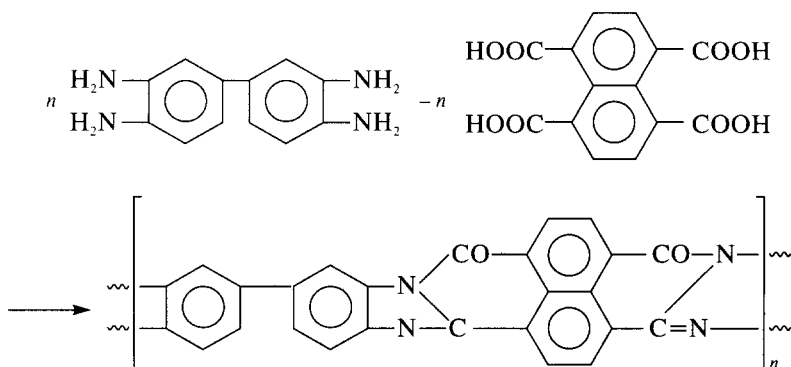


Figure 29.18

The chemical name for such materials is poly(bisbenzimid-azobenzophenanthrolines) but they are better known as BBB materials. Such polymers have a T_g in excess of 450°C and show only a low weight loss after aging in air for several hundred hours at 370°C . Measurements using thermal gravimetric analysis indicate a good stability to over 600°C . The main interest in these materials is in the field of heat-resistant films and fibres.

29.7.5 Ladder Polymers and Spiro Polymers

It is not a large step to go from polymers like BBB to polymers in which there are no single bonds holding the chain together. Such polymers, which consist of a series of ring structures linked to each neighbouring ring by at least two bonds, are known as *ladder polymers* and three general methods of preparation are known.

- (1) Equilibrium condensation.
- (2) Polyfunctional condensation.
- (3) Modification of preformed polymers.

The first ladder polymer with a high degree of structural perfection was reported in 1960 and was prepared by the equilibrium condensation of phenyltrichlorosilane (Figure 29.19).

The resulting poly(*cis*-syndiotactic-phenylsilsesquioxanes) are claimed to have equal thermal stability to conventional silicones but with markedly improved hydrolytic stability.

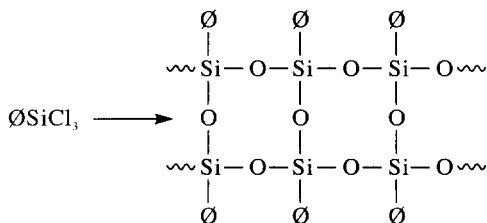


Figure 29.19

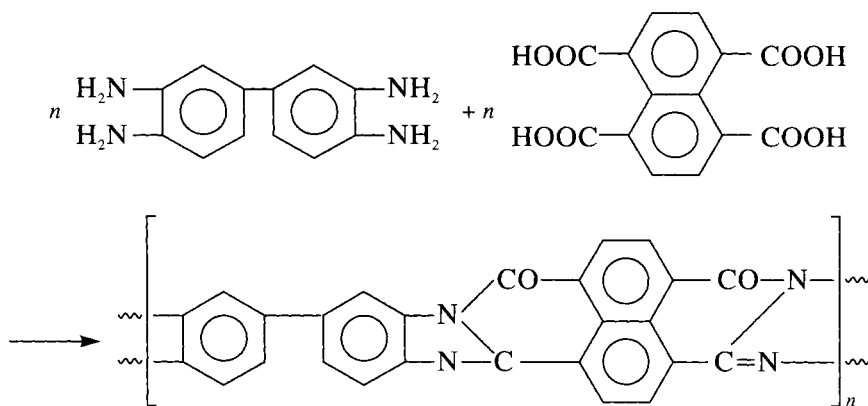


Figure 29.20

Using a mononuclear tetramine a polycondensation very similar to that used with BBB can occur which leads to a ladder polymer of high structural perfection (BBL) (Figure 29.20).

It is reported that the BBL polymers have a thermal stability as assessed by TGA tests in excess of 600°C whilst they also show negligible heat loss after several hundred hours in air at 370°C .

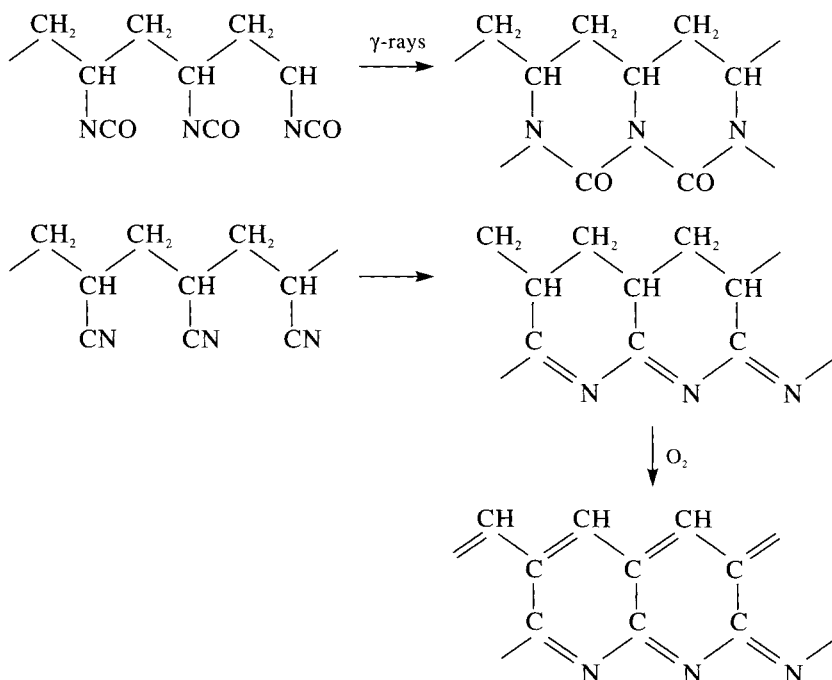


Figure 29.21

Polyfunctional condensation has also been used to prepare ladder polymers from, for example, the following other intermediates:

- (1) Tetraketopyrene and tetra-aminobenzene.
- (2) Pyromellitic dianhydride and tetra-aminobenzene.
- (3) Dimethyldiacrylmethane.

Perhaps the most thoroughly investigated approach is the modification of preformed polymers in particular poly(vinyl isocyanate) and polyacrylonitrile (*Figure 29.21*).

The product from acrylonitrile will withstand a bunsen flame in the open air and is the basis of one type of carbon fibre. None of the polymers produced by this route have a high degree of perfection in their ladder structure.

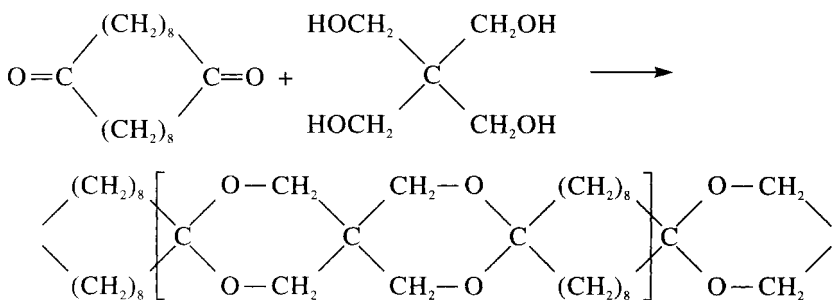


Figure 29.22

Related to the ladder polymers are the *spiro polymers* as typified by the reaction product of cyclo-octadecane-1, 10-dione with pentaerythritol (*Figure 29.22*).

Such polymers are not known to have any commercial application.

29.7.6 Co-ordination Polymers

A large number of polymers have been prepared in the laboratory in which co-ordinate bonds play a significant role. Probably the most investigated are the bis-diketone polymers, of which one type is shown in *Figure 29.23*.

Amongst the metals (M) investigated the copper derivatives are said to melt with decomposition at 380°C.

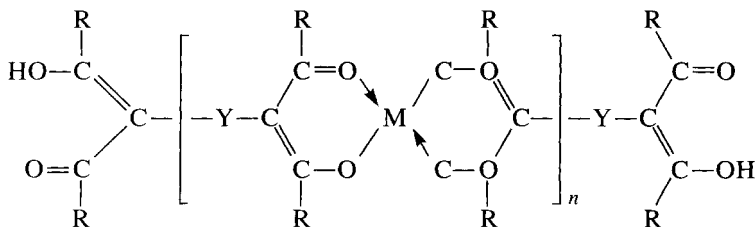


Figure 29.23

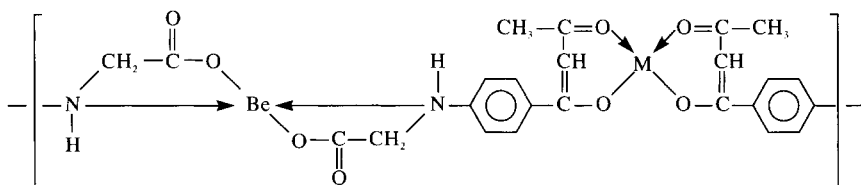


Figure 29.24

The co-ordinate polymer (Figure 29.24) is said to decompose in the range 430–450°C. Perhaps the most stable co-ordination polymer reported so far is poly(di- μ -diphenyl phosphinate-beryllium) (Figure 29.25), which is stable up to 530°C.

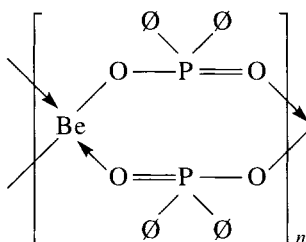


Figure 29.25

This is also a further example of a spiro-polymer as well as being of the inorganic backbone type.

29.7.7 Summary

It has been seen that there are a number of approaches possible in order to achieve rigid polymers of greater heat resistance than could have been contemplated 40 years ago. In the highest temperature range the greatest success to date has been achieved with the aromatic polyimides, but several azole-type polymers have also shown promise whilst inorganic and co-ordination polymers have generally been disappointing.

Beside their excellent heat resistance, very good electrical insulation characteristics, good hydrolytic stability and generally good physical properties, the polyimides have the added attraction that soluble, fusible intermediates are available, which makes fabrication flexible although in some cases far from simple. This is an important factor because it should be remembered that one of the important characteristics of plastics is their ability to be formed at low temperature. Where ease of shaping is absent it may well be that metals, ceramics or glasses would be preferred to polymers. There is in fact a developing technology involving the production of putty-like materials based on some inorganic particle material such as glass beads, silicone nitride and so on, blended with small quantities of some low T_g and often-plasticised polymer. After shaping of the product the plasticised polymer is removed by thermal decomposition and volatilisation and the residue particles subjected to high-temperature sintering.

References

1. BUFF, H., and WOHLER, F., *Liebigs Ann.*, **104**, 94 (1857)
2. FRIEDEL, C., and CRAFTS, J. M., *Compt Rend.*, **56**, 592 (1863)
3. LADENBURG, A., *Liebigs Ann.*, **164**, 300 (1872)
4. ROCHOW, E. G., *J. Am. Chem. Soc.*, **67**, 963 (1945)
5. ROCHOW, E. G., *An Introduction to the Chemistry of the Silicones*, Chapman and Hall, London, 2nd Edn (1951)
6. ROTH, J., *J. Am. Chem. Soc.*, **69**, 474 (1947)
7. SCOTT, D. W., *et al. J. Phys. Chem.*, **65**, 1320 (1961)
8. GUTOFF, R., *Ind. Eng. Chem.*, **49**, 1807 (1957)
9. HARDY, D. V. N., and MEGSON, N. J. L., *Quart. Rev. (London)*, **2**, 25 (1948)
10. BARRY, A. J., *J. Appl. Phys.*, **17**, 1020 (1946)
11. WILCOCK, D. J., *J. Am. Chem. Soc.*, **68**, 691 (1946)
12. FREEMAN, G. G., *Silicones*, Iiffe, London (1962)
13. NEWLAND, J. J., *Trans. Plastics Inst.*, **25**, 311 (1957)
14. GALE, P. A. J., *Trans. Plastics Inst.*, **28**, 194 (1960)
15. NITZSCHE, S., and WICK, M., *Kunststoffe Plastics*, **47**, 431 (1957)
16. BRADLEY, D. C., *Metal-Organic Compounds, Advances in Chemistry Series* Vol. 23, p. 10, American Chemical Society, Washington (1959)
17. AUBREY, D. W., and LAPPERT, M. F., *J. Chem. Soc.*, 2927 (1959)

Bibliography

- CASSIDY, P. E., *Thermally Stable Polymers*, Marcel Dekker, New York (1982)
- CRITCHLEY, J. P., KNIGHT, G. J. and WRIGHT, W. W., *Heat-resistant Polymers*, Plenum, New York-London (1983)
- FORDHAM, G. (Ed.), *Silicones*, Newnes, London (1961)
- FRAZER, A. H., *High Temperature Resistant Polymers*, Interscience, New York (1968)
- FREEMAN, G. G., *Silicones*, Iiffe, London (1962)
- GIBBS, W. E., and HELMINIAK, T. E., 'Polymers for Use at High and Low Temperatures', *Polymer Science* Vol. 2 (Ed. JENKINS, A. D.), North-Holland, Amsterdam (1972)
- GIMBLETT, F. G. R., *Inorganic Polymer Chemistry*, Butterworth, London (1963)
- HUNTER, D. N., *Inorganic Polymers*, Blackwell, Oxford (1963)
- Inorganic Polymers*, Special Publication No. 15, Chemical Society, London (1961)
- LAPPERT, M. F., and LEIGH, G. J. (Eds.), *Developments in Inorganic Polymer Chemistry*, Elsevier, Amsterdam (1962)
- MCGREGOR, R. R., *Silicones and their Uses*, McGraw-Hill, London (1954)
- NOLL, W., *Chemistry and Technology of Silicones*, Academic Press, London (1968)
- RAY, N. H., *Inorganic Polymers*, Academic Press, London (1978)
- ROCHOW, F. G., *An Introduction to the Chemistry of Silicones*, Chapman and Hall, London, 2nd Edn (1951)
- STONE, F. G. A., and GRAHAM, W. A. G. (Eds.), *Inorganic Polymers*, Academic Press, London, New York (1962)
- WRIGHT, W. W., and LEE, W. A., 'The Search for Thermally Stable Polymers', *Progress in High Polymers* Vol. II (Eds. ROBB, J. C., and PEAKER, F. W.), Heywood, London (1968)

Review

- TREGO, B. R. and WINNAN, H. W., *RAPRA Review Report—Silicone Rubbers*, RAPRA Technology Ltd, Shawbury (1990)

30

Miscellaneous Plastics Materials

30.1 INTRODUCTION

The materials dealt with in this chapter may be classed chemically into two groups:

- (1) Plastics derived from natural polymers.
- (2) Non-polymeric plastics whose resinous behaviour stems from the colloidal complexity of a mixture of heterogeneous molecules.

With the exception of some of the natural rubber derivatives these materials were available during the first decade of this century and, together with celluloid, actually completed the range of plastics materials then in commercial use. In spite of being ousted from important markets they have continued to find use in specialised applications, details of which will be given in subsequent sections of this chapter. The historical significance of these materials was dealt with in the first chapter of this book.

30.2 CASEIN

Casein is a protein found in a number of animal and vegetable materials but only one source is of commercial interest, cow's skimmed milk. The amount of casein in milk will vary but a typical analysis of cow's milk is:

Water	87%
Fat	3.5–4%
Lactose	5%
Casein	3%
Globulin + albumin	0.5–1%
Other ingredients	0.5–1%

The butter fat is a coarse dispersion readily removable on standing or by a centrifuging operation. The casein will be present in the skimmed milk as colloiddally dispersed micelles of diameter of the order of 10^{-5} cm, and is associated with calcium and phosphate ions.

Plastics materials may be produced from casein by plasticising with water, extrusion and then cross-linking with formaldehyde (formolisation). The resultant products have a pleasant horn-like texture and are useful for decorative purposes. The amount of casein produced has decreased since World War II but was still one of the preferred materials for use in the decorative button industry until quite recently.

30.2.1 Chemical Nature

Casein is one member of the important group of natural polymers, the proteins. These materials bear a formal resemblance to the polyamides in that they contain repeating —CONH— groups and could be formally considered as polymers of amino acids. However, unlike, polymers such as nylon 6 and nylon 11 a number of different α -amino acids are found in each molecule whereas the nylons 6 and 11 have only one ω -amino acid molecule (*Figure 30.1*).

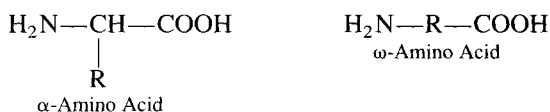


Figure 30.1

Over 30 amino acids have been identified in the hydrolysis product of casein of which glutamic acid, hydroxyglutamic acid, proline, valine, leucine and lysine comprise about 60%. The residues of the aminoacid arginine also appear to be of importance in the cross-linking of casein with formaldehyde.

The protein polymers are highly stereospecific, the aminoacid residues always adopting the L-configuration, i.e. the same configuration as the reference substance L-malic acid.

It is interesting to note that the amino acid side chains may be either neutral as in valine, acidic as in glutamic acid or basic as in lysine. The presence of both acidic and basic side chains leads to proteins such as casein acting as amphoteric electrolytes and their physical behaviour will depend on the pH of the environment in which the molecules exist. This is indicated by *Figure 30.2*, showing a simplified protein molecule with just one acidic and one basic side group.

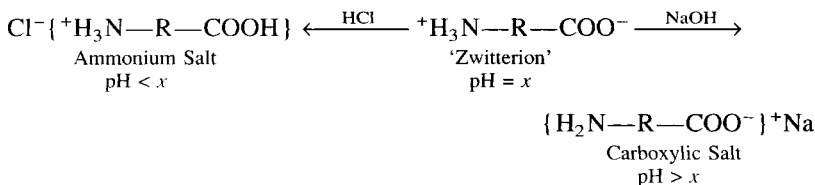


Figure 30.2

At the $\text{pH} = x$ there is a balance of charge and there is no migration in an electric field. This is referred to as the isoelectric point and is determined by the relative dissociation constants of the acidic and basic side groups and does not necessarily correspond to neutrality on the pH scale. The isoelectric point for casein is about $\text{pH} = 4.6$ and at this point colloidal stability is at a minimum. This fact is utilised in the acid coagulation techniques for separating casein from skimmed milk.

Casein may be considered to be a conjugated protein, that is the protein is associated in nature with certain non-protein matter known as prosthetic groups. In the case of casein the prosthetic group is phosphoric acid. The protein molecule is also associated in some way with calcium. The presence of these inorganic materials has an important bearing on the processability and subsequent use of casein polymers.

30.2.2 Isolation of Casein from Milk

Destruction of the casein micelles in the milk with subsequent precipitation of the casein can be accomplished in a number of ways. The action of heat or the action of alcohols, acids, salts and the enzyme rennet all bring about precipitation. In commercial practise the two techniques used employ either acid coagulation or rennet coagulation mechanisms.

Addition of acetic or mineral acid to skimmed milk to reduce the pH value to 4.6, the isoelectric point, will cause the casein to precipitate. As calcium salts have a buffer action on the pH, somewhat more than the theoretical amount of acid must be used. Lactic acid produced in the process of milk 'souring' by fermentation of the lactoses present by the bacterium *Streptococcus lactis* will lead to a similar precipitation.

Although acid caseins are employed for a number of purposes, rennet caseins in which the protein remains associated with calcium and phosphate are preferred for plastics applications. Rennet is the dried extract of rennin, obtained from the inner lining of the fourth stomach of calves, and is a very powerful coagulant. As little as 0.2 parts per million are said to be sufficient to coagulate slightly acidic milk. Its coagulating power is destroyed at 100°C .

In the rennet coagulation process fresh skimmed milk is adjusted to a pH of six and about 40 ounces of a 10% solution of rennet are added per 100 gallons of milk. The initial reaction temperature is about 35°C and this is subsequently raised to about 60°C . The coagulation appears to take place in two stages. Firstly the calcium caseinate is converted to the insoluble calcium paracaseinate and this then coagulates.

Great care is essential in controlling the temperature and the coagulation process as otherwise impurities, particularly other proteins, will be brought down with the casein. Such impurities will adversely affect the transparency of the product.

The condition of the curd on precipitation is important. As the milk starts to gel, agitators in the coagulation tanks are started as the temperature is raised to about 65°C . Under these conditions the protein is thrown out in fine particles. Too slow an agitation will produce large clots difficult to wash whilst too fine a curd also presents washing problems. In order to obtain the requisite consistency of the precipitate it may be necessary to add inorganic material to the skimmed milk. For example, the addition of phosphate ions will prevent undesirable flaky polymer. Similarly, calcium-deficient casein will not coagulate satisfactorily and the addition of calcium ions may be necessary.

The coagulated particles are given four to five preliminary washings after precipitation and the washed curd is then passed through a curd press to extract the maximum amount of water.

The casein must be dried with considerable care. If dried too rapidly an impervious layer is formed on the outside of the particles which prevents the inside of the particles from drying out. Too slow a drying operation will lead to souring.

The drying of the curd is completed by passing through a rotary drier such as the Pillet-Bordeaux. In this machine the curd passes down a chute with hot air running counter to the direction of flow of material. Strict temperature control is essential, the maximum discharge temperature being below 65°C. If such control is not made then the resin will be dark in colour.

Table 30.1 Properties of rennet casein. Determined according BS1416:1961

<i>Grade</i>	<i>Premium</i>	<i>First</i>	<i>Standard</i>
Moisture content%	11-13	11-13	11-13
Ash content%	7-8	7-8	7-8
Fat content%	0.5-0.7	0.7-1.0	1.0-1.5
pH	7.0-7.2	6.9-7.2	6.8-7.2
Gross contamination	0-50	50-100	>100
Fine contamination	0-50	50-100	>100
Colour	A	B	C
Wet heat resistance	A	B	C

Dried casein is normally imported into Great Britain largely from New Zealand and to some extent France and Scandinavia. Some typical properties of the proteins as imported are shown in Table 30.1.

30.2.3 Production of Casein Plastics

Casein plastics are today produced by the 'dry process'. Although a wet process was used originally in Great Britain it has been obsolete for over 50 years and need not be discussed here.

In the dry process the casein is ground so that it will pass through a 30 mesh sieve but be retained by one of a 100 mesh. The powder is then loaded into a dough mixer, usually of the Artofex type. Water is fed slowly into the mixer until the moisture present forms about 20% of the total. The water has a plasticising effect on the casein and heat is generated during the mixing operation. Any large lumps formed must be broken down individually and returned to the mixer. Mixing times for a 60kg batch are usually about 30 minutes.

In addition to the casein and water, other ingredients are added at this stage. They may include dyes or pigments, titanium dioxide as a white pigment or colour base and 'clearing agents' to enhance the transparency. Typical clearing (or 'clarifying') agents are ethylbenzylamine, tritoyl phosphate, trixylyl phosphate and chlorinated diphenyls. The incorporation of 1% trixylyl phosphate may increase the percentage light transmission from 40 to 80 through a 2 mm thick sample.

The resultant compound, in spite of the high water content, is a free-flowing powder. It should be processed soon after mixing since it will tend to putrefy.

In commercial operations the next stage of the process involves passing the compound through a small extruder so that under heat and pressure the granular powder is converted to a rubbery material. Extruders, somewhat simpler in construction than those generally employed in the plastics industry but very similar to rubber extruders, are used. A typical machine would have a 2:1 compression ratio and 8:1 length diameter ratio screw. The barrel is heated by steam or water, temperatures at the feed end being at about 30°C with temperatures at the die end at about 75°C. The die itself may be heated with a simple gas burner. Breaker plates and screens have the function not only of building up back pressure but of helping to develop the pattern in a coloured extrudate.

The extrudate is cut up into appropriate lengths and cooled by plunging into cold water. Subsequent operations depend on the end-product required.

When rods are required they are placed in wooden trays in a formolising bath. If the requirement is for a disc or 'blank' such as used by the button trade the extrudate is cut up by an automatic guillotine and the blanks are immersed in the formalin solution. For manufacture of sheets the rods are placed in moulds and pressed into sheets before formolising. Many attractive patterns may be made by pressing different coloured rods into grooves set on the bias to the rods, thus forming new multi-coloured rods. This operation may be repeated a number of times in order to produce complex patterns.

The rod, blank or sheet must then be cured by a formolising process. They are immersed into a 4–5% solution of formaldehyde in water (formalin) for anything from two days to several months according to the thickness of the section. The formolising temperature is kept at about 16°C and the pH between four and seven.

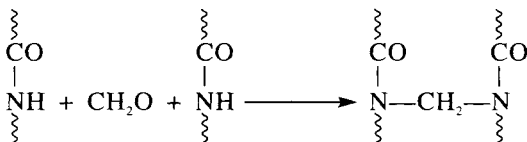
Too high a concentration of formaldehyde will cause rapid curing of the surface of the section, thus reducing its permeability to formaldehyde, and as a result it is extremely difficult to cure adequately the centre of the casein. Too low a concentration will unnecessarily prolong the time of cure.

By the time that the desired degree of formolisation has been reached the casein will contain a large quantity of water and free formaldehyde which has to be removed. This must be done slowly to prevent cracking and warping of the material. Warm drying cabinets of rotating perforated cylinders are used with slightly humid circulating air. The drying operation is also a very lengthy process and may take anything from three days to as long as three weeks.

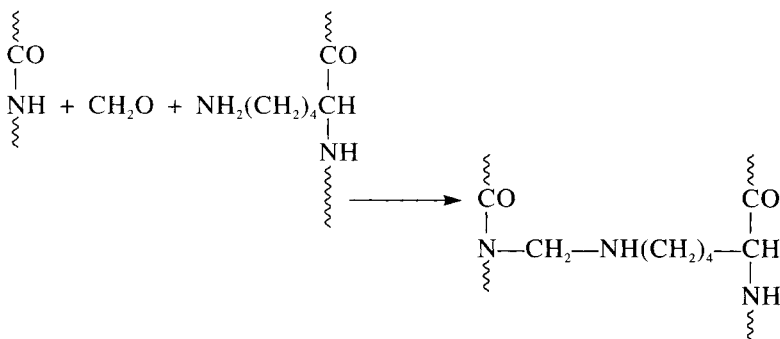
The finished articles may be obtained by machining and polishing the dried formolised sections.

The precise mode of interaction between the casein and the formaldehyde has not been fully elucidated but the following reactions are believed to occur:

(1) Reaction across the peptide (—CONH—) groups



(2) Reaction between a peptide group and a lysine side chain



(3) Similar reactions between amino groups on both side chains.

These three reactions fail to account for all the observed phenomena that occur in curing casein and therefore a number of alternative mechanisms no doubt also occur.

The very long times required for the formolising stages have promoted research to discover methods of speeding the process and also of finding alternative cross-linking techniques. The most effective modification to date is to incorporate small quantities (~1%) of a water-soluble cellulose material such as sodium carboxymethyl cellulose into the casein mix. During the formolisation process a fibrous cellulose compound appears to be formed, acting as a multiple wick along which the formalin may pass much more rapidly. By this technique formolisation times may be cut by as much as 25%. The use of the cellulose compound will slightly impair the clarity of the finished product.

Attempts have also been made to avoid the formolising process by incorporating formaldehyde donors, i.e. materials that will evolve formaldehyde at elevated temperatures after shaping has been completed. Amongst materials for which patents have been taken out are paraformaldehyde and hydroxydimethylurea. Since premature evolution of only small quantities of formaldehyde will seriously affect the flow properties of the mix this technique causes further problems. The use of formaldehyde evolution inhibitors such as carbamide compounds and amides has been suggested in the patent literature. Although processable moulding powders may be made in this way the products are both dark and brittle and offer no attractive advantage over either normal casein products or conventional thermosetting moulding powders. They have therefore failed to achieve any commercial significance.

A number of alternative curing agents to formaldehyde are known but once again have achieved no commercial significance. They include isocyanates, benzoquinone and chromium salts.

30.2.4 Properties of Casein

Formolised casein is a rigid horn-like material which may be made available in a wide variety of colours and patterns. By common consent it is recognised as having a pleasant feel and appearance and its properties which are relevant to current commercial application.

Mechanical properties are typical of a rigid plastics material and numerical values (*Table 30.2*) are similar to those for poly(methyl methacrylate). Although thermosetting, it has a low heat distortion temperature ($\sim 80^{\circ}\text{C}$) and is not particularly useful at elevated temperatures.

Table 30.2 Some physical properties of casein plastics

Specific gravity	1.35
Tensile strength	8000–10 000 lbf/in ² (55–69 MPa)
Elongation at break	2.5–4%
Modulus of elasticity (in tension)	6×10^5 lbf/in ² (4000 MPa)
Izod impact strength	1.0–1.5 ft lbf in ⁻¹
Brinell hardness	18–24
Rockwell hardness	M75
Breakdown voltage (50Hz)	200 V/0.001 in
Powder factor (10 ⁶ Hz)	0.06
Water absorption (4 mm thickness)	
24 h	5–7%
28 days	30%
Heat distortion temperature (ASTM) (66 lbf/in ²)	80–85°C

When dry, casein is a good electrical insulator but is seriously affected by humid conditions. For this reason it can no longer compete with the many alternative plastics materials now available for electrical applications.

Both acids and alkalis will adversely affect the material. Strong alkalis and acids will cause decomposition. The water absorption is high and consequently casein is easily stained. As a corollary to this it may be dyed without difficulty. Acidic and basic water-soluble dyes are normally used. Typical properties of casein plastics are given in *Table 30.2*.

30.2.5 Applications

The use of casein plastics was severely curtailed with the development of synthetic polymers, particularly after the Second World War. In addition stricter regulations concerning health and safety at work will have caused attention to be drawn to the formolising process. In the experience of the author the environment surrounding the formolising baths is most unpleasant and this will have accelerated the demise of the casein manufacturing industry.

In the past casein plastics were widely used for decorative applications where a pleasant appearance was of value. The button industry was by far the largest user with further use for buckles, slides, hair pins, knitting pins, pens and pencils.

Casein is used for a number of miscellaneous purposes in which formolisation is not required. These include adhesives, stabilisers for rubber latex, paper finishing agents and miscellaneous uses in the textile industry. Mention may also be made of casein fibres, available in Italy between the two world wars under the name of Lanital.

30.3 MISCELLANEOUS PROTEIN PLASTICS

Casein is the only protein that has achieved commercial significance as a plastics raw material. Many other proteins are readily available in many vegetable material residues which arise from such processes as the extraction of oils and starches from seeds. It would be advantageous to countries possessing such residues if plastics could be successfully exploited commercially. Although plastics materials have been produced they have failed to be of value since they are invariably dark in colour and still have the water susceptibility and long curing times, both of which are severe limitations of casein.

Of these materials zein, the maize protein, has been used for plastics on a small scale. It can be cross-linked by formaldehyde but curing times are very long. Complicated bleaching processes have led to the production of almost colourless samples in the laboratory but the process cannot readily be extended to large-scale operation. The cured product has a greater water resistance than casein. Proteins from soya bean, castor bean and blood have also been converted into plastic masses but each have the attendant dark colour.

In addition to the natural protein fibres wool and silk, fibres have been produced commercially from other proteins. These materials were introduced as wool substitutes but today have little or no significance. Mention may, however, be made of 'Ardil' products from the groundnut protein and marketed for some years after World War II by ICI. Compared with wool it had inferior wet and dry strength and abrasion resistance. The inclusion of up to 20% 'Ardil' into wool, however, yielded a product with negligible loss in wearing properties.

30.4 DERIVATIVES OF NATURAL RUBBER

The chemistry and technology of natural rubber were considered briefly in Chapter 11. In this chapter some non-elastomeric derivatives will be reviewed.

The most important of these is *ebonite*, which may be considered as the world's earlier thermosetting plastics material. It is obtained by vulcanising (natural) rubber with large quantities of sulphur. Whereas ordinary vulcanised rubber as used in tyres contains normally only 2–3% of sulphur a typical rubber/sulphur ratio for ebonite is 68:32. Compared with ordinary vulcanisates, ebonite is more rigid, shows less swelling in hydrocarbon solvents and has a higher density. These factors indicate a fairly high degree of cross-linking. As the vulcanisation reaction proceeds it is observed that the non-extractable sulphur content steadily increases to reach a maximum of 32% and at this point the unsaturation of the composition falls to zero. The sulphur content is in accord with the empirical formula C_5H_8S so that in effect for each atom of sulphur combined there is a loss of one double bond.

The detailed structure of ebonite is not known but it is believed that the same structures occur in the rigid material as have been suggested for vulcanised rubber. There will, however, be far more S-containing structures per unit volume and the ratios of the various structures may differ. The curing reaction is highly exothermic.

Ebonite compositions may be prepared without difficulty either in an internal mixer or on a two-roll mill. In addition to the rubber and sulphur, fillers are invariably present in commercial mixes. These materials have the important function of diluting the rubber phase. Because of this the exotherm will be

diluted and there will be less shrinkage on cure. Ebonite dust is very useful for such diluent purposes as its use has the minimum adverse effect on the properties of the finished product. For many purposes mineral fillers may be incorporated to reduce cost. The vulcanisation time may be reduced by addition of 2–3 parts phr of an accelerator such as diphenylguanidine or butyraldehyde–aniline and this is common practice. Softeners and processing aids may also be added.

The ebonite compound before cure is a rather soft plastic mass which may be extruded, calendered and moulded on the simple equipment of the type that has been in use in the rubber industry for the last century. In the case of extruded and calendered products vulcanisation is carried out in an air or steam pan. There has been a progressive reduction in the cure times for ebonite mixes over the years from 4–5 hours down to 7–8 minutes. This has been brought about by considerable dilution of the reactive rubber and sulphur by inert fillers, by use of accelerators and an increase in cure temperatures up to 170–180°C. The valuable effect of ebonite dust in reducing the exotherm is shown graphically in *Figure 30.3*.

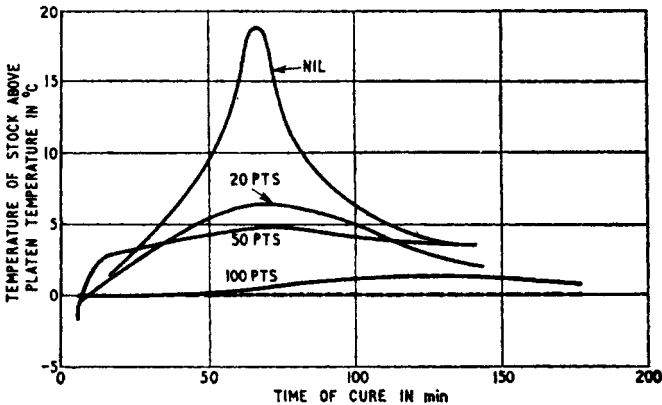


Figure 30.3. Variation of internal temperature during cure of ebonite stocks containing 0, 20, 50 and 100 parts of ebonite dust per 100 parts (rubber and sulphur). (After Scott, see bibliography)

Ebonite, or hard rubber as it is often known, is black in colour and has a specific gravity, in the absence of mineral fillers, of about 1.18.

The best physical properties may be realised only with unfilled compounds. As with other thermosetting compounds different properties will be at their best after different amounts of cure. Care should also be taken in the selection of the rubber/sulphur ratio. High sulphur contents, up to 40%, may be used for greatest resistance to swelling and for minimum dielectric loss. The best mechanical properties and the greatest heat resistance are generally obtained with about 35% sulphur whereas the best impact strength is obtained with somewhat less combined sulphur. Hot air and steam cures usually result in poorer ebonites than with press cures since volatilisation of sulphur from the surface layers of the product leads to surface undercure.

Typical properties of a high-quality ebonite are given in *Table 30.3*.

On exposure of ebonite to light there is a rapid deterioration in surface resistivity. It is believed that this is due to the formation of sulphuric acid through

Table 30.3 Properties of unfilled ebonite vulcanisates (as BS903 where applicable)

Specific gravity	1.18
Tensile strength	9000 lbf/in ² (62 MPa)
Elongation at break	3%
Cross-breaking strength	12 000–16 000 lbf/in ² (90–110 MPa)
Impact strength	0.5 ft lb in ⁻¹ notch
Yield temperature	85°C
Dielectric constant	2.7–3.0 (10 ³ –10 ⁶ Hz, 25–75°C)
Power factor (10 ⁶ Hz)	~0.01
Dielectric strength	1.0–1.5 × 10 ⁵ kV/mm ⁻¹
Volume resistivity	~10 ¹⁹ Ωm
Surface resistivity (of unexposed samples)	10 ¹⁸ Ω
Equilibrium water absorption	~0.25%

oxidation of the rubber–sulphur complex. The sulphuric acid sweats out into droplets on the surface of the polymer and eventually a stage is reached where the droplets link up into a continuous film, forming a conductive path along the surface. The influence of this phenomenon on the surface resistivity is shown in *Figure 30.4*.

Ebonite has a good resistance to a range of inorganic liquids, including most non-oxidising acids. It is severely swollen by aromatic and chlorinated hydrocarbons.

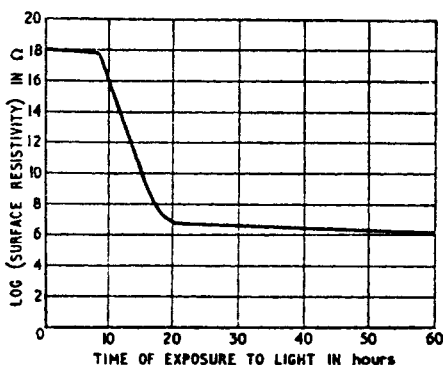


Figure 30.4. Influence of exposure to light on the surface resistivity of ebonite. (After Scott)

The continuing use of ebonite is due to the good insulating characteristics, good chemical resistance and ease of machining. Its use is limited by the long curing times, the limited temperature range, its colour limitations and its poor resistance to air, light and oxidising chemicals. Its principal applications are in chemical plant and car batteries which are largely based on very low cost reclaimed rubber. Miscellaneous uses include the manufacture of water meters and pipe stems. It is, however, under continual challenge in all of these applications from synthetic plastics materials.

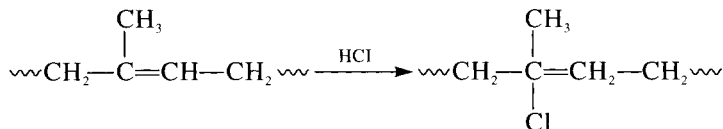
The terms ebonite and hard rubber are now extended to cover hard products made from synthetic rubbers. SBR is now replacing the natural materials in many ebonite applications whilst nitrile rubber ebonites are of interest where oil resistance is required.

Hard products may also be made by vulcanising rubber (natural or synthetic) using only about two parts of sulphur per 100 parts of rubber. In these cases either the so-called 'high-styrene resins' or phenolic rubber compounding resins are incorporated into the formulation. These compounds are processed using the methods of rubber technology but, like those of ebonite, the products are more akin to plastics than to rubbers. Examples of the usage of these materials are to be found in battery boxes, shoe heels and car washer brushes.

A number of other natural rubber derivatives may be prepared by addition reaction at the double bond.

Hydrogenation may be accomplished by heating a dispersion of rubber and Ni-Kieselguhr catalyst in cyclohexane with hydrogen under pressure at 170–250°C in the complete absence of oxygen. The hydrogenation is accompanied by degradation and cyclisation and the product has not been commercially exploited. It is to be noted, however, that hydrogenated polybutadiene, of the same fundamental structure as polyethylene, is used for some specialised rubber-to-metal bonding operations.

Reaction of the natural rubber hydrocarbon with hydrochloric acid yields *rubber hydrochloride*. The hydrogen chloride adds on according to Markownikoff's rule (that the halogen atom attaches itself to the carbon atom with the least number of hydrogen atoms).



The hydrohalide is usually prepared by passing hydrogen chloride into a solution of masticated high-grade raw rubber in benzene at 10°C for about six hours. Excess acid is then neutralised and plasticisers and stabilisers are added. The benzene is removed by steam distillation and the product washed and dried. Alternatively the solution is cast on to a polychloroprene rubber belt, leaving a tough film after evaporation of the solvent.

The hydrohalide is liable to dehydrochlorination, particularly when moist acid is used in its preparation, so that hydrochloric acid acceptors such as lead carbonate are useful stabilisers. Dibutyl phthalate and tritoyl phosphate are effective plasticisers. Rubber hydrochloride is used as a packaging film (Pilofilm) and as a rubber-to-metal bonding agent (e.g. Typly).

If natural rubber is treated with proton donors a product is formed which has the same empirical formula, (C₅H₈), and is soluble in hydrocarbon solvents but which has a higher density, is inelastic and whose unsaturation is only 57% that of natural rubber. It is believed that intramolecular ring formation occurs to give products containing the segments shown in *Figure 30.5*. Known as *cyclised rubber* it may be prepared by treating rubber, on a mill, in solvent or in a latex with materials such as sulphuric acid or stannic chloride.

Attempts have been made to popularise cyclised rubber as an additive for use in shoe soling compounds but they have not been able to compete with

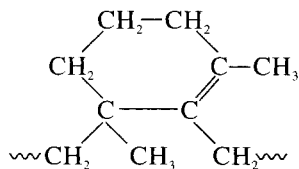


Figure 30.5

the 'high-styrene resins' used extensively for this purpose. They have found a small use for rubber-to-metal bonding and as an ingredient in surface coatings.

Treatment of natural rubber with chlorine gives a product, *chlorinated rubber*, with a maximum chlorine content of 65% corresponding to the empirical formula $C_{10}H_{11}Cl_7$. Such a compound corresponds neither to a hypothetical simple addition to the double bond (Figure 30.6 (I)) nor to a product with α -methylene substitution in addition (II).

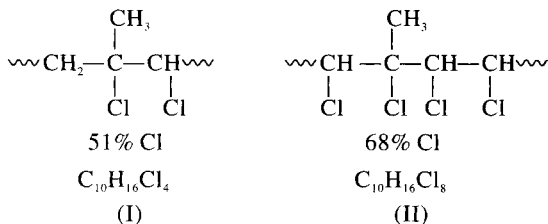
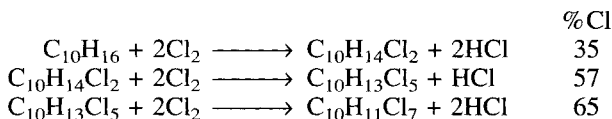


Figure 30.6

It has been shown that the reaction occurs in three stages, illustrated by the following empirical equation:



The first and third stages involve substitution only whilst the second stage involves simultaneous addition and substitution.

The structure of the completely chlorinated product has not been fully elucidated but one suggested structure for the repeating unit is shown in Figure 30.7.

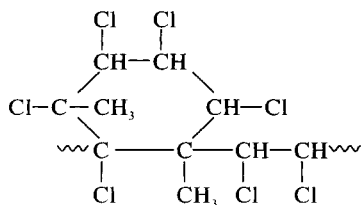


Figure 30.7

Of these the most interesting, from the point of view of the plastics technologist, is gutta percha. This material may be obtained from trees of the genera *Palaquium* and *Payena* of which *Pal. oblongifolium* is the most important. This plant is found in Malaysia and Indonesia and is cultivated mainly in Sumatra. The latex is more viscous than natural rubber latex and is now most commonly extracted from the leaves rather than by making incisions in the bark. The coagulated latex would give a typical analysis of hydrocarbon 70%, resin 11%, dirt 3% and moisture 16%. The *trans*-1,4-polyisoprene is reported to have molecular weight of 30 000, which is somewhat lower than obtained with the natural rubber hydrocarbon. X-ray evidence indicates that gutta percha may exist in one of two crystalline states. As produced from the tree the gutta percha crystallites are in the α -form, which melts at 65°C. On slow cooling the α -form is reproduced but rapid cooling will produce the β -form, which melts at 56°C. The latter form slowly reverts to the α -form. About 60% of gutta percha is crystalline at room temperature, when it has the character of a hard inelastic solid.

As with *cis*-polyisoprene, the gutta molecule may be hydrogenated, hydrochlorinated and vulcanised with sulphur. Ozone will cause rapid degradation. It is also seriously affected by both air (oxygen) and light and is therefore stored under water. Antioxidants such as those used in natural rubber retard oxidative deterioration. If the material is subjected to heat and mechanical working when dry, there is additional deterioration so that it is important to maintain a minimum moisture content of 1%. (It is not usual to vulcanise the polymer.)

Gutta percha has a lower water absorption than natural rubber and is a good dielectric. It is dissolved by carbon disulphide, chloroform and benzene but alkaline solutions and dilute acids do not affect it. It is destroyed by nitric acid and charred by warm concentrated sulphuric acid but resists hydrofluoric acid.

At one time gutta percha had an important outlet in undersea cable insulation and a lesser use in chemical plant, in particular for storage of hydrofluoric acid. It is now virtually obsolete.

An alternative source of the *trans*-1,4-polyisoprene is *balata*, obtained from *Mimosops balata*, occurring in Venezuela, Barbados and Guyana. The latex is thin and may be tapped in the same way as natural rubber.

The coagulated material consists of about 50% polyisoprene and the remainder is primarily composed of resins. Deresinated balata has been used as an alternative to gutta percha, which it resembles in properties and also in belting applications. It is still used for making high-quality golf ball covers but for the cheaper balls it has now been replaced almost entirely by the ionomers (see Chapter 11).

The latex of the *Sapota achras* yields a thermoplastic material, *chicle*, consisting of about 17.4% hydrocarbon, 40% acetone soluble resin and 35% occluded water. The hydrocarbon appears to contain both *trans*- and *cis*-polyisoprene. Although originally introduced as gutta percha and natural rubber substitutes, deresinated chicle has become important as the base for chewing gum. Like other polyisoprenes, it is meeting competition from synthetic polymers.

An alternative chewing gum base is obtained from *jelutong*, a mixture of polyisoprene and resin obtained from latex of the *Dyera costulata*. This tree is found in many countries but Borneo is the principal commercial source. At one time jelutong was an important rubber substitute and 40 000 tons were produced in 1910. Production in recent years has been of the order of 5000 tons per annum, mainly for chewing gum.

30.6 SHELLAC

The importance of shellac to the plastics industry has declined rapidly since 1950. Before that time it was the principal resin employed in 78 rev/min gramophone records. The advent of the long playing microgroove record meant that mineral fillers could no longer be tolerated because any imperfections in the microgroove led to a high background noise on the record. The record industry therefore turned towards alternative materials which required no mineral filler, and vinyl chloride–vinyl acetate copolymers eventually became pre-eminent. It is, however, still used for a number of purposes outside the normal realm of plastics.

30.6.1 Occurrence and Preparation

Shellac is the refined form of lac, the secretion of the lac insect parasitic on certain trees in India, Burma, Thailand and to a minor extent in other Asian countries.

The larvae of the lac insect, *Laccifer lacca* (Kerr), swarm around the branches and twigs of the host trees for 2–3 days before inserting their probosces into the phloem tissues to reach the sap juices. There may be as many as 100–150 larvae on each inch of twig. This is followed by secretion of the lac surrounding the cells. Whereas the male insects subsequently move out of their cells the female insects become entombed for life. After about eight weeks of life the male insects fertilise the females and die within a few days. The fertilised females subsequently exude large quantities of lac and shed eyes and limbs. The female gives birth to 200–500 further insects and finally dies.

In commercial practice the crop is taken from the tree shortly before emergence of the new brood. Some of these twigs are then tied to new trees to provide future sources of lac but the rest, *sticklac*, is subjected to further processing. The average yield per tree is about 20 lb per annum, usually one crop being allowed per tree per year.

Subsequent treatment of the sticklac carried out by hand or by mechanical methods first involves removal of woody matter and washing to remove the associated lac dye to produce seedlac, containing 3–8% of impurities. This may be further refined by various methods to produce the shellac flakes of commerce.

The hand process for producing shellac has been used since ancient times and is carried on largely as a cottage industry. It has been estimated that 3–4 million people were dependent for their livelihood on this process. The lac encrustation is first separated from woody matter by pounding with a smooth stone, the latter being removed by a winnowing process. The lac dye is then removed by placing the lac in a pot together with a quantity of water. A villager, known as a ghasander, then stands in the pot and with bare feet treats out the dye from the resin. At one time lac dye was of commercial value but is today a worthless by-product. The product, *seedlac*, is then dried in the sun.

The next stage may best be described as a primitive hot-filtration process. Two members of the village sit across the front of a simple fire resembling a Dutch oven, holding between them a bag about 30 feet long and about two inches in diameter. The lac inside the bag melts and, through one of the operators twisting the end of the bag, the lac is squeezed out. The lac is then removed from the outside of the bag and collected into a molten lump which is then stretched out

by another operator using both hands and feet until a brittle sheet is produced. This is then broken up to produce the shellac of commerce.

In the factory processes the sticklac is first passed through crushing rollers and sieved. The lac passes through the sieve but retains the bulk of the woody matter. The sieved lac is then washed by a stream of water and dried by a current of hot air. A second mechanical cleaning process removes small sticks which have not been removed in the earlier roller process. The product, seedlac, now contains 3–8% of impurities.

The seedlac may then be converted to shellac by either a heat process or by solvent processes. In the heat process the resin is heated to a melt which is then forced through a filter cloth which retains woody and insoluble matter. In the solvent process the lac is dissolved in a solvent, usually ethyl alcohol. The solution is filtered through a fine cloth and the solvent recovered by distillation.

Variation in the details of the solvent processes will produce different grades of shellac. For example, when cold alcohol is used, lac wax which is associated with the resin remains insoluble and a shellac is obtained free from wax. Thermally processed shellacs were greatly favoured for gramophone records as they were free from residual solvent and also contained a small quantity of lac wax which proved a useful plasticiser.

30.6.2 Chemical Composition

The lac resin is associated with two lac dyes, lac wax and an odiferous substance, and these materials may be present to a variable extent in shellac. The resin itself appears to be a polycondensate of aldehydic and hydroxy acids either as lactides or inter-esters. The resin constituents can be placed into two groups, an ether-soluble fraction (25% of the total) with an acid value of 100 and molecular weight of about 550, and an insoluble fraction with an acid value of 55 and a molecular weight of about 2000.

Hydrolysis of the resins will produce aldehydic acids at mild concentration of alkali ($\sim\frac{1}{2}$ N); using more concentrated alkalis (5N) hydroxy acids are produced, probably via the aldehydic acids. Unfortunately most of the work done in order to analyse the lac resin was carried out before the significance of the hydrolysis conditions was fully appreciated. It does, however, appear to be agreed that one of the major constituents is aleuritic acid (*Figure 30.9*).

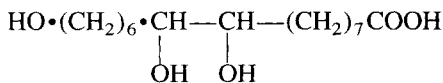


Figure 30.9

This is present to the extent of about 30–40% and is found in both the ether-soluble and ether-insoluble fractions. Both free hydroxyl and free carboxyl groups are to be found in the resin.

30.6.3 Properties

The presence of free hydroxy and carboxyl groups in lac resin makes it very reactive, in particular to esterification involving either type of group. Of particular interest is the inter-esterification that occurs at elevated temperatures ($>70^\circ\text{C}$) and

leads to an insoluble 'polymerised' product. Whereas ordinary shellac melts at about 75°C, prolonged heating at 125–150°C will cause the material to change from a viscous liquid, via a rubbery state, to a hard horny solid. One of the indications that the reaction involved is esterification is that water is evolved. The reaction is reversible and if heated in the presence of water the polymerised resin will revert to the soluble form. Thus shellac cannot be polymerised under pressure in a mould since it is not possible for the water to escape. 'Polymerisation' may be retarded by basic materials, some of which are useful when the shellac is subjected to repeated heating operations. These include sodium hydroxide, sodium acetate and diphenyl urea. 'Polymerisation' may be completely inhibited by esterifying the resin with monobasic saturated acids. A number of accelerators are also known, such as oxalic acid and urea nitrate. Unmodified lac polymerises in about 45 minutes at 150°C and 15 minutes at 175°C.

Shellac is soluble in a very wide range of solvents, of which ethyl alcohol is most commonly employed. Aqueous solutions may be prepared by warming shellac in a dilute caustic solution.

The resin is too brittle to give a true meaning to mechanical properties. The thermal properties are interesting in that there appears to be a transition point at 46°C. Above this temperature, specific heat and temperature coefficient of expansion are much greater than below it. The specific heat of hardened shellac at 50°C is lower than that of unhardened material, this no doubt reflecting the disappearance, or at least the elevation, of the transition temperature.

Table 30.4 Some properties of shellac

<i>Property</i>	<i>Condition</i>	<i>Units</i>	<i>Value</i>
Specific gravity	15.5°C	—	1.20
Refractive index	—	—	1.51–1.53
Colour	—	—	pale yellow–dark red
Specific heat	10–40°C	c.g.s.	0.36–0.38
	45–50°C	c.g.s.	0.56
	(heat hardened)		
Volume resistivity	20°C	Ωm	1.8×10^{18}
Surface resistivity	20%RH	Ω	2.2×10^{14}
	40%RH	Ω	1.1×10^{14}
Dielectric constant	30°C	—	3.91
	80°C	—	7.85
Dielectric loss	30°C	—	0.02
	80°C	—	0.435

From the point of view of the plastics technologist the most important properties of shellac are the electrical ones. The material is an excellent room temperature, low-frequency insulator and particular mention should be made of the resistance to tracking.

Some typical physical properties of shellac are given in *Table 30.4*.

30.6.4 Applications

Until 1950 the principal application of shellac was in gramophone records. The resin acted as a binder for about three times its weight of mineral filler, e.g. slate

dust. The compound had a very low moulding shrinkage and was hard-wearing but not suitable for the microgroove records because of the effect of the filler on the background noise.

Today the most important applications are in surface coatings, including some use as French polish, as adhesives and cements, including valve capping and optical cements, for playing card finishes and for floor polishes. The material also continues to be used for hat stiffening and in the manufacture of sealing wax.

Although development work on shellac in blends with other synthetic resins has been carried out over a period of time, the only current use in the plastics industry is in the manufacture of electrical insulators. At one time electrical insulators and like equipment were fabricated from mica but with increase in both the size and quantity of such equipment shellac was introduced as a binder for mica flake. For commutator work the amount of shellac used is only 3–5% of the mica but in hot moulding Micanite for V-rings, transformer rings etc., more than 10% may be used. The structures after assembly are pressed and cured, typically for two hours at 150–160°C under pressure.

In recent years the dominance of shellac in mica-based laminates has met an increasing challenge from the silicone resins.

30.7 AMBER

In addition to shellac a number of other natural resins find use in modern industry. They include rosins, copals, kauri gum and pontianak. Such materials are either gums or very brittle solids and, although suitable as ingredients in surface coating formulations and a miscellany of other uses, are of no value in the massive form, i.e. as plastics in the most common sense of the word.

One resin, however, can be considered as an exception to this. Although rarely recognised as a plastics material it can be fabricated into pipe mouthpieces, cigarette holders and various forms of jewellery. It may also be compression moulded and extruded. It is the fossil resin amber.

Amber is of both historical and etymological interest as its property of attracting dust was known over 2000 years ago. From the Greek word for amber, *elektron*, has come the word electricity. Pliny in his works makes an interesting and informative dissertation on the occurrence and properties of amber.

Amber is a fossil resin produced in the Oligocene age by exudation from a now extinct species of pine. It occurs principally in the region known before World War II as East Prussia. It may be obtained by mining and also by collecting along the seashore. Small amounts of amber may also be found off the coasts of England, Sweden, Holland and Denmark. Similar resins are found in Burma, Rumania and Sicily but only the Baltic variety, known also as succinite, is considered a true amber. At one time a Royal Amber Works existed in Königsberg (now Kaliningrad) and in 1900 annual production was approximately 500 tons.

30.7.1 Composition and Properties

The chemical nature of amber is complex and not fully elucidated. It is believed not to be a high polymer, the resinous state being accounted for by the complexity of materials present. The empirical formula is $C_{10}H_{16}O$ and true amber yields on distillation 3–8% of succinic acid.

The resin is fairly soluble in alcohol, ether and chloroform and is decomposed by nitric acid. It becomes thermoplastic at temperatures above 150°C and decomposes at a temperature rather below 300°C, yielding an oil of amber and leaving a residue known as amber colophony or amber pitch.

X-ray evidence shows the material to be completely amorphous as might be expected from such a complex mixture. The specific gravity ranges from 1.05 to 1.10. It is slightly harder than gypsum and therefore just not possible to scratch with a fingernail. Yellow in colour, it is less brittle than other hard natural resins and may therefore be carved or machined with little difficulty. The refractive index is 1.54.

Amber has been a much prized gem material for many millennia and has been found at Stonehenge, in Mycenaean tombs and in ancient European lake dwellings. In modern times it is used for beads and other ornaments, cigarette holders and pipe mouthpieces.

At one time the small fragments of amber produced during the fabrication and machining operations were used to produce varnishes. In 1880 they were first used in the production of Ambroid. This is made by pressing the fragments in a hydraulic press at temperatures somewhat above 160°C. The moulded product has a close resemblance to amber. A form of extrusion has also been used to produce amber rods for subsequent conversion into pipe and cigarette-holder mouthpieces.

30.8 BITUMINOUS PLASTICS

Although generally ignored in plastics literature the bituminous plastics are still of interest for specific applications. The moulding compositions consist of fibrous and mineral fillers held together by a bituminous binder together with a number of minor ingredients.

A number of types of bituminous material exist and terminology is still somewhat confusing. The term *bitumens* in its widest sense includes liquid and solid hydrocarbons but its popular meaning is restricted to the solid and semisolid materials. The bitumens occur widely in nature and may be considered to be derived from petroleum either by evaporation of the lighter fraction under atmospheric conditions or by a deeper seated metamorphism. The purer native bitumens are generally known as *asphaltites* and include Gilsonite, extensively used for moulding, which occurs in Utah.

Where the bitumens are associated with mineral matter the mixture is referred to as *native asphalt*. These are widely distributed in nature, the best known deposit being the asphalt lake in Trinidad which covers an area of about 100 acres (40 hectares). The terms *asphalt* or *asphaltic bitumen* are applied to petroleum distillation residues and these today form the bulk of commercial bituminous matter. Related chemically and in application but not in origin are the *pitches*. These are the industrial distillation residues. They include wood tar, stearin pitch, palm oil pitch and coal tar pitch. The last varies from soft semisolid to hard brittle products. Of these materials those most useful in moulding compositions are coal tar pitches with a softening range of 115–130°C and natural bitumens such as Gilsonite and Rafaelite with softening points in the range 130–160°C.

The bitumens are complex mixtures of paraffinic, aromatic and naphthenic hydrocarbons. A small amount of unsaturation is usually present which accounts

for the slow oxidation which occurs on exposure to ultra violet light and the ability to bring about a form of vulcanisation on heating with sulphur.

The bulk of bituminous materials are used for road making and building applications which are outside the scope of this book. Only a very small percentage is used in moulding compositions and few data have been made publicly available concerning the properties of these compositions.

The bitumens have a good order of chemical corrosion resistance, have reasonably good electrical insulation properties and are very cheap. Their main disadvantages are their black colour and their somewhat brittle nature.

Moulding compositions contain a number of ingredients. These may include:

- (1) Bituminous binder.
- (2) Fibrous filler.
- (3) Inert filler.
- (4) Softener.
- (5) Drying oil and drier.

Of the fibrous fillers which greatly reduce the brittleness, blue asbestos fibre is normally used for battery boxes, the principal outlet. Other materials that may be used include cotton fibres, ground wood, slag wool and ground cork.

Mineral fibres are incorporated to reduce cost and to raise the softening point. China clay, natural silicas, talc and slate dust are frequently used.

To facilitate moulding a softener is incorporated. These may include soft industrial pitches or heavy tars, coumarone-indene resins or waxes.

In the United States softer stocks have been employed using a drying oil which is incorporated with a drier such as cobalt naphthenate to harden the oil.

The compositions are mixed in heated trough mixers, the mixing temperature being in the range of 150–200°C. Skill is required in order to achieve good dispersion of the fibrous filler without charring the bituminous matter. Moulding is carried in compression moulds using prewarmed doughs. For battery boxes the mould temperature on charging the composition is about 100°C, which is reduced to at least 50°C before extraction of the moulding. Some simple mouldings can be carried out using prewarmed mixes but cold moulds.

The largest outlet for the bituminous plastics has been for automobile battery boxes. Bituminous battery boxes do, however, have a susceptibility to electrical breakdown between the cells and in Europe their use has been mainly confined to the cheaper batteries installed initially in new cars. Bituminous compositions have also been used for toilet cisterns and to some extent for cheap containers. They are no longer important.

Bibliography

Casein

COLLINS, J. H., *Casein Plastics*, Plastics Institute Monograph No. C5, 2nd Edn, London (1952)

PINNER, S. H., *Brit. Plastics*, **18**, 313 (1946)

SUTERMEISTER, F., and BROWNE, F. L., *Casein and its industrial Applications*, American Chemical Society, Monograph No 30, New York (1939)

Rubber, Derivatives of Rubber and Similar Polymers

BLOW, C. M., and HEPBURN, C. (Eds.), *Rubber Technology and Manufacture* (2nd Edition), Butterworths, London (1982)

- BRYDSON, J. A., *Rubber Chemistry*, Applied Science, London (1978)
BRYDSON, J. A., *Rubbery Materials and their Compounds*, Applied Science, London (1988)
DAVIES, B. L., and GLAZER, J., *Plastics derived from Natural Rubber*, Plastics Institute Monograph No. C8, London (1955)
NAUNTON, W. J. S. (Ed.), *The Applied Science of Rubber*, Arnold, London (1961)
SCOTT, J. R., *Ebonite*, MacLaren, London (1958)

Shellac

- GIDVANI, B. S. *Shellac and Other Natural Resins*, Plastics Institute Monograph No. S1, 2nd Edn. London (1954)
Shellac, Angelo Brothers Ltd., Calcutta (1956)

Amber

- HERBERT SMITH, G. F., *Gemstones*, Methuen, London (1952)
LEY, WILLY, *Dragons in Amber*, Sidgwick and Jackson, London (1951)
Pliny, Book 37, Chapter 3

31

Selected Functional Polymers

31.1 INTRODUCTION

Chapters 10 to 29 consisted of reviews of plastics materials available according to a chemical classification, whilst Chapter 30 rather more loosely looked at plastics derived from natural sources. It will have been obvious to the reader that for a given application plastics materials from quite different chemical classes may be in competition and attempts have been made to show this in the text. There have, however, been developments in three, quite unrelated, areas where the author has considered it more useful to review the different polymers together, namely thermoplastic elastomers, biodegradable plastics and electrically conductive polymers.

All three types of material have now been available for some years and it is probably also true that none have yet realised their early promise. In the case of the thermoplastic elastomers most of the commercial materials have received brief mention in earlier chapters, and when preparing earlier editions of this book the author was of the opinion that such materials were more correctly the subject of a book on rubbery materials. However, not only are these materials processed on more or less standard thermoplastics processing equipment, but they have also become established in applications more in competition with conventional thermoplastics rather than with rubbers.

The concept of degradable polymers arose largely from concern about the large quantities of plastics materials used for packaging and which, having fulfilled their function, were then discarded and unwanted. Interest has, however, now moved on to include medical and related applications.

Electrically conductive polymers are just one of a number of esoteric possible uses for synthetic polymers. These materials are now being considered for a variety of applications.

31.2 THERMOPLASTIC ELASTOMERS

It was pointed out in Chapter 3 that conventional vulcanised rubbers were composed of highly flexible long chain molecules with light cross-linking

(covalently) which enabled the chains to coil and uncoil but prevented them slipping past each other. This gives a highly extensible network structure. Once cross-linking has taken place, such materials cannot be reprocessed (at least without severe degradation). In addition, the 'setting' operation involves a chemical reaction rather than the, apparently, simpler setting brought about by cooling as used with thermoplastics materials.

For this reason, many attempts have been made over the years to produce a rubbery material which has a network structure over a useful temperature range but which, if heated further, loses this structure. In many cases this involves a form of cross-linking that is said to be *heat fugitive*. In Section 3.4 four types of heat-fugitive cross-link were identified, namely:

- (1) Ionic cross-links.
- (2) Hydrogen bonding.
- (3) Triblock copolymers.
- (4) Multiblock copolymers.

A further important class of thermoplastic elastomer has been obtained by blending a rubbery material (usually an ethylene-propylene rubber) with a polyolefin (usually polypropylene, sometimes in conjunction with polyethylene). In this case the thermoplastic material tends to be the continuous phase and the rubbery material (which is often subjected to a cross-linking operation during the mixing stage (dynamic vulcanisation) the discrete phase. It is conceptually difficult to see why a system consisting of tiny vulcanised rubbery spheres embedded in a rigid thermoplastics material should be capable of showing rubbery behaviour. The explanation lies in the fact that the morphology is more complex, and it is better to consider the hard phase as a reticulated structure which allows large-scale deformations to occur (rather like that in a human skeleton), with the rubbery phase facilitating the recovery from deformation.

The main commercial types of thermoplastic elastomers are:

- (1) Styrene-butadiene-styrene triblocks and the related S-I-S and SEBS materials (Section 11.8).
- (2) Polyester-based thermoplastic polyurethane elastomers (Section 27.4).
- (3) Polyether-based thermoplastic polyurethane elastomers (Section 27.4).
- (4) Thermoplastic polyester elastomers (Section 25.10).
- (5) Thermoplastic polyamide elastomers (Section 18.15).
- (6) Thermoplastic polyolefin rubbers (Section 11.9).

It may also be argued that plasticised PVC may be considered as a thermoplastic elastomer, with the polymer being fugitively cross-linked by hydrogen bonding via the plasticiser molecules. These materials were, however, dealt with extensively in Chapter 12 and will not be considered further here. The *ionomers* are also sometimes considered as thermoplastic elastomers but the commercial materials are considered in this book as thermoplastics. It should, however, be kept in mind that ionic cross-linking can, and has, been used to fugitively cross-link elastomeric materials.

This section is intended to summarise some basic principles of the chemistry of such materials and to compare the various types.

Although there will be specific requirements for specific applications, the principal properties of importance with the thermoplastic elastomers are:

- (1) The minimum temperature at which the material will be a serviceable rubber.
- (2) The maximum service temperature.
- (3) Oil resistance and chemical resistance.
- (4) The range of hardness possible.
- (5) Recovery from deformation and general high-elasticity properties.
- (6) Density.
- (7) Cost, not simply raw material cost, but the cost of making, installing and servicing the product.

The minimum service temperature is determined primarily by the T_g of the soft phase component. Thus the SBS materials can be used down towards the T_g of the polybutadiene phase, approaching -100°C . Where polyethers have been used as the soft phase in polyurethane, polyamide or polyester, the soft phase T_g is about -60°C , whilst the polyester polyurethanes will typically be limited to a minimum temperature of about -40°C . The thermoplastic polyolefin rubbers, using ethylene-propylene materials for the soft phase, have similar minimum temperatures to the polyether-based polymers. Such minimum temperatures can also be affected by the presence of plasticisers, including mineral oils, and by resins if these become incorporated into the 'soft' phase. It should, perhaps, be added that if the polymer component of the soft phase was crystallisable, then the higher T_m would also affect the minimum service temperature, this depending on the level of crystallinity.

It should also be pointed out that the T_g of the soft blocks, which consist of fairly short polymer chains, will be somewhat lower than for a corresponding homopolymer of high molecular weight, for the reasons given in Section 4.2. This effect may, however, be more than compensated by the loss of molecular freedom due to the presence of and interaction with the hard phase polymer present.

Providing the polymer is thermally stable in the range under consideration, the maximum service temperature is largely determined by the T_g of the hard phase (or the T_m if the hard phase is crystallisable). As a general rule, thermoplastic elastomers with a crystallisable hard phase will be usable to higher temperatures, although some amorphous thermoplastic polyamide elastomers with a high hard phase T_g can have good maximum service temperatures. As pointed out in the previous paragraph, the effective T_g (and for that matter T_m) of the short polymer blocks may differ somewhat from the transition points of a high molecular weight homopolymer.

Oil resistance demands polar (non-hydrocarbon) polymers, particularly in the hard phase. If the soft phase is non-polar but the hard phase polar, then swelling but not dissolution will occur (rather akin to that occurring with vulcanised natural rubber or SBR). If, however, the hard phase is not resistant to a particular solvent or oil, then the useful physical properties of a thermoplastic elastomer will be lost. As with all plastics and rubbers, the chemical resistant will depend on the chemical groups present, as discussed in Section 5.4.

Most of the thermoplastic elastomers can be produced in a wide hardness range without resort to additives. If it is practical to use soft and hard phases in any proportions, then the hardness range will be from that of the soft phase

polymer to that of the hard phase polymer. This may not always be possible, since, for example, a minimum level of hard phase component may be necessary for the elastomer to have acceptable recoverable elasticity. Unfortunately, there is no word in the English language describing a condition between 'hard' and 'soft' and one can only talk about 'degrees or levels of hardness (or softness)'. The polymer technologist (and more specifically this writer) has a problem in classifying a number of the harder grades of the so-called thermoplastic elastomers which are more like leather than traditional rubber or thermoplastic.

Properties such as low permanent set, low creep and low hysteresis are really measures of the efficiency of the 'heat fugitive' network system. This is a complex function of the morphology. As a very general statement, the problem would seem to be less important with the harder grades of thermoplastic elastomer.

The density of the polymer will clearly depend on the density of the soft phase (usually low), and the density of the hard phase (generally higher with crystallisable polar blocks) and the ratio of the soft and hard phases present. It will also clearly depend on the additives present and to some extent on the processing conditions, which may affect the crystalline morphology.

Table 31.1 Comparative properties of commercial thermoplastic elastomers

Type	Soft phase T_g ($^{\circ}\text{C}$)	Hard phase T_g or T_m ($^{\circ}\text{C}$)	Oil resistance	Hardness range	Specific gravity
S-B-S or (S-B) _n x	-90	95 (T_g)	Poor	60-90A	0.94
S-I-S	-60	95 (T_g)	Poor	30-40A	0.92
S-EB-S	-60	95 (T_g)	Poor	65-75A	0.91
Polyester-urethane	-20 to -40	190 (T_m)	Good	70A-70D	1.18-1.24
Polyether-urethane	-60 to -80	190 (T_m)	Good	40-90A	1.1
Polyester	-40 to -65	190 (T_m)	Good	35-75D	1.15-1.45
Polyamide	-40 to -65	120-275 (T_m)	Good	75A-65D	1.0-1.15
PP/EPDM blends	-60	140-165 (T_m)	Poor	60A-75D	0.9-1.1

Type	Approximate/cost Relative to SBS	Special features
S-B-S or (S-B) _m x	100	Low density and cost. Good chemical resistance
S-I-S	110	Adhesive applications
S-EB-S	200	Improved aging and weathering
Polyester-urethane	200	Abrasion and oil resistance
Polyether-urethane	200	Better hydrolytic stability and resistance to fungal growth than above but less good abrasion resistance
Polyester	250	Similar to PU but can be harder Better at low temperatures Low compression set and creep and less variation of modulus with temperature
Polyamide	250-450	Similar to PU but can be softer Very good at low temperatures Wide range of products and wide range of properties possible

Notes:

- (1) Data are given for unfilled polymers.
- (2) Transition data are very dependent on the method of measurement.
- (3) Hardness values are for Shore A and Shore D.
- (4) The relative cost values can only be considered as very general approximations.

The basic cost of thermoplastic elastomers is often higher than that of more conventional and comparable rubbers and plastics. However, there can be considerable savings in their use. It is clearly a positive feature that the materials will not need complex vulcanising processes taking time and energy and also that they may be processed on conventional thermoplastics material, with scrap being capable of being recycled. There have also been examples of industrial and auto uses where a part had previously been made by impregnating cloth with rubber (frictioning), assembling layers of the impregnated cloth and then compression moulding the assembly. The cloth had been used to give a level of stiffness of which the rubber compound was on its own incapable. Replacement of the traditional rubber with a hard grade of a thermoplastic elastomer can enable the reinforcing fabric to be dispensed with and production to become a comparatively simple one-stage operation. (It should be stressed that the use of cloth or other laminating material may still be required if the product is required to have different levels of stiffness in different directions.)

31.2.1 Applications of Thermoplastic Elastomers

In general, the thermoplastic elastomers have yet to achieve the aim of replacing general purpose vulcanised rubbers. They have replaced rubbers in some specialised oil-resistant applications but their greatest growth has been in developing materials of consistency somewhat between conventional rubbers and hard thermoplastics. A number of uses have also been developed outside the field of conventional rubber and plastics technology.

A manufacturer considering using a thermoplastic elastomer would probably first consider one of the *thermoplastic polyolefin rubbers* or *TPOs*, since these tend to have the lowest raw polymer price. These are mainly based on blends of polypropylene and an ethylene–propylene rubber (either EPM or EPDM) although some of the polypropylene may be replaced by polyethylene. A wide range of blends are possible which may also contain some filler, oil and flame retardant in addition to the polymers. The blends are usually subject to dynamic vulcanisation as described in Section 11.9.1.

TPOs have found a number of mechanical rubber goods applications, particularly in the automotive industry. Examples are convoluted bellows, flexible diaphragms, protective sleeving, steering gear boots, extruded profiles, torque couplings and tubing. There has also been a considerable market for these materials for car bumpers, rather more in Europe than America. Other major applications include wire insulation and weather stripping. TPOs are of interest where low manufacturing cost and good weathering properties are of more importance than a high level of oil resistance and heat (deformation) resistance. TPOs are one of the two most widely used thermoplastic elastomers.

The other ‘most widely used’ thermoplastic elastomers are the S–B–S and related materials. These are usually blended with large amounts of a stiffening resin (polystyrene), mineral oils, fillers and even other polymers so that the amount of S–B–S in the finished compound is usually less than 50%. In the area of replacements for commercial vulcanised rubber, the S–B–S compounds are largely used for shoe soles, tubing, sound deadening and flexible automotive parts. The related hydrogenated polymers (S–EB–S) are of particular interest for wire insulation and other applications where enhanced aging and weathering properties are required.

S-B-S, S-I-S and S-EB-S polymers are widely used in adhesive, sealing and coating formulations as well as being important additives to many asphalt formulations.

Thermoplastic polyurethane elastomers have now been available for many years (and were described in the first edition of this book). The adipate polyester-based materials have outstanding abrasion and tear resistance as well as very good resistance to oils and oxidative degradation. The polyether-based materials are more noted for their resistance to hydrolysis and fungal attack. Rather specialised polymers based on polycaprolactone (Section 25.11) may be considered as premium grade materials with good all round properties.

Whilst approximately twice the raw material cost of TPO- and S-B-S-type polymers, thermoplastic polyurethane elastomers find applications where abrasion resistance and toughness are particular requirements. Uses include gears, timing and drive belts, footwear (including ski boots) and tyre chains. Polyether-based materials have also achieved a number of significant medical applications. There is also some minor use as hot melt adhesives, particularly for the footwear industry.

Thermoplastic polyester elastomers such as the Du Pont product Hytrel were developed later than the polyurethane materials, being first introduced in 1972. They have similar characteristics to the polyurethanes but there is an upward shift in the hardness range (i.e. the softest grades are not so soft, but the hardest grades are harder than the corresponding extreme grades in the polyurethanes).

In spite of their cost the thermoplastic polyester rubbers have found use as replacement for oil-resisting rubbers such as the polychloroprenes, not simply because of their improved processability but also because of such superior physical properties as tear and tensile strength up to 150°C. They tend to be somewhat easier to process than the thermoplastic polyurethane elastomers. Applications include flexible couplings and diaphragms, convoluted bellows, ski boots, quiet-running gear wheels, high-pressure hose lines, outer coverings for wire and optical fibre cables, seals and segmented tracks for snow vehicles.

Thermoplastic polyamide elastomers first became available in 1978 and have many features similar to those of the polyurethane and polyester thermoplastic elastomers. They are block copolymers with an oil-resistant hard phase polymer. There is, however, a considerable flexibility in formulation. Either polyesters or polyethers may be used for the soft phase and a wide range of polyamides for the hard block. These can include crystallisable polymers such as nylons 6, 66, 610, 11 and 12, or amorphous aromatic materials which rely on a high T_g to give polymers of good heat resistance. Block copolymers with polyester soft blocks have excellent resistance to thermal and oxidative degradation whilst those with polyether soft segments are more resistant to hydrolysis and remain rubbery down to lower temperatures. Whilst moisture resistance is usually quite good, special hydrophilic products are available which can absorb up to 120% of their weight in water.

The thermoplastic polyamide elastomers may be considered as premium grade materials available in a wide range of hardness values with, in some instances, very good heat resistance. Particular properties of interest are the flexibility and impact resistance at low temperatures and the good dynamic properties and related resilience, hysteresis and alternating flexural properties.

In addition to the above well-known groups of thermoplastic elastomer, other materials continue to be introduced. One such material is Alcryn, introduced by Du Pont in 1985 but of undisclosed composition. This material exhibits the good

weathering, ozone and heat resistance of TPOs but with enhanced oil resistance. Other potentially important blends have been made by mixing nitrile rubber and polypropylene (and then subjecting the rubber to dynamic vulcanisation) and by reacting PVC and ionically cross-linked butadiene–acrylonitrile rubber. It is perhaps worth restating at this point that the all-important plasticised PVC materials could reasonably be classified as thermoplastic elastomers.

There remains considerable scope for producing novel block copolymers but these tend to involve sophisticated polymer science and any commercial products are likely to be more expensive than the easier-to-make blends. They would thus need to possess some quite outstanding properties for them to be a commercial proposition.

31.2.2 The Future for Thermoplastic Elastomers

Thermoplastic elastomers have now been available for over 30 years and the writer recalls organising a conference on these materials in 1969. In spite of considerable publicity since that time these materials still only comprise about 5–10% of the rubber market (equivalent to about 1–2% of total plastics consumption). It is important to appreciate that simply being a thermoplastic material (and hence being processed and reprocessed like a thermoplastic plastics material) is not enough to ensure widespread application. Crucially the material must have acceptable properties for a potential end-use and at a finished product price advantageous over other materials.

The styrenic and the TPO type elastomers share, very roughly equally, about 85% of the total market but in the case of the former over half the output goes into what might be considered ‘non-rubber’ applications such as bitumen and thermoplastic modifiers and for adhesives and coatings, with the bulk of the remainder being used in footwear. On the other hand TPOs have achieved broader penetration particularly into the automotive market. It is to be expected that growth in this area will exceed general economic growth for a number of reasons. These include ‘recyclability regulations’ now existing in many countries, high polymer stiffness allowing thinner section products sometimes eliminating the need for fabric reinforcement (with the number of additional operations that this involves) and the ability to use processes such as blow moulding that are not appropriate to conventional rubbers. The more expensive polyester, polyamide, polyurethane and other materials will continue to find niche markets where their properties justify their cost.

31.3 DEGRADABLE PLASTICS

In recent years there has rightly been a marked increase in concern for the environment. The continual global population explosion together with the increase in purchasing power has led to a vast increase in the amount of pollution and rubbish. Because of their visibility and inability to degrade at a reasonable rate, plastics materials have been particularly criticised.

For more than 20 years, polymer scientists and plastics technologists have been working to develop plastics materials that would be more acceptable *environmentally*, and in the third edition of this book, published in 1975, the author devoted a section to photo- and biodegradation of polymers. In spite of such effort, an article in 1992 stated that ‘Degradable plastics are still in the early

stages of their technological and usage evolution', and more recently in 1998 a spokesman for a leading polymer supplier could state that 'the market for biodegradables is still in its infancy'. It has been subsequently forecast that the biodegradable polymer market should reach 70 000 t.p.a. by 2001.

Whereas cellulose films are biodegradable, that is they are readily attacked by bacteria, films and packaging from synthetic polymers are normally attacked at a very low rate. This has led to methods of degrading polymers to a sufficiently low molecular mass (typically about 10 000) which are then accessible to biodegradation.

Several approaches are used, either individually or collectively, to degrade polymers in this way. Of these the most important are:

- (1) Photodegradation.
- (2) Oxidation.
- (3) Hydrolysis.

Photodegradation may involve use of inherently photo-unstable polymers or the use of photodegradant additives. An example of the former are ethylene-carbon monoxide polymers in which absorption of light by the ketone group leads to chain scission. The polymer becomes brittle and forms a powder. Such materials are marketed by Dow and by Du Pont. Other examples are the copolymers of divinyl ketone with ethylene, propylene or styrene marketed by Eco Atlantic.

The alternative approach is to add a photodegradant which is an ultraviolet light absorber. However, instead of dissipating the absorbed energy as heat (as with conventional ultraviolet absorbers) the aim is to generate highly reactive chemical intermediates which degrade the polymer. One such material is iron dithiocarbamate.

It is important that any photodegradation should be controlled. It is essential that plastics should not degrade prematurely. Possible approaches are to use photodegradants that are only activated by light waves shorter than those transmitted by ordinary window glass. This will help to ensure that samples kept indoors will not deteriorate on storage. Dyestuffs which change colour shortly before the onset of degradation could also be used to warn of impending breakdown.

One example of the use of photodegradable polyethylene is for beverage can ring holders in North America.

The author is unaware of any commercial polymers that are specifically designed to degrade oxidatively, although oxidation may be involved in association with hydrolytic and biological degradation. It may be of interest to note that before World War II products known as *rubbones* were produced by degrading natural rubber with cobalt linoleate in the presence of cellulosic materials to produce low molecular weight, fluid oxidised natural rubber (Section 30.4).

An example of the hydrolysis approach is that used by Du Pont with their Biomax polymer. This is a copolyester based on poly(ethylene terephthalate) technology, can therefore be produced on conventional PET polymerisation plant and is therefore only marginally more expensive than PET. Film from this copolymer is claimed to have general physical properties similar to PET (see Chapter 25) other than a lower melting point of about 200°C and may be processed on standard equipment designed for use with PET. Up to three different comonomers may be used according to the end-use and these are designed to provide weak points in the polymer chain making them susceptible

to degradation via hydrolysis. In practice the larger molecules are split by moisture present during composting into smaller molecules that are in turn further degraded into carbon dioxide and water by naturally occurring microbes. However, during composting hydrolysis takes place reducing the molecular weight to a level at which biodegradation may then proceed. The BASF Ecoflex materials appear to be somewhat similar in their behaviour.

A further approach is used by Bayer with their polyesteramide BAK resins. A film grade, with mechanical and thermal properties similar to those of polyethylene is marketed as BAK1095. Based on caprolactam, adipic acid and butane diol it may be considered as a nylon 6-co-polyester. An injection moulding grade, BAK 2195, with a higher melting point and faster crystallisation is referred to as a nylon 66-co-polyester and thus presumably based on hexamethylene diamine, adipic acid and butane diol.

Some typical properties of these two materials are given in *Table 31.2*.

Table 31.2 Properties of biodegradable polyesteramides

<i>Type</i>	<i>PA6Copolyester (BAK1095)</i>	<i>PA66Copolyester (BAK2195)</i>
Application	Film grade	Injection moulding grade
Melting point (°C)	125	177
Tensile modulus (MPa)	220	550
Elongation @ break (%)	>400	120

Although very good rates of biodegradation have been claimed in composting tests it is stated that biodegradation will only occur where there is sufficient moisture and concentration of soil bacteria and fungi and somewhat elevated temperatures.

Mention should also be made here of the extensive use of poly(vinyl alcohol) in potentially biodegradable applications. At appropriate hydroxyl contents these polymers will dissolve in water (see Chapter 14) and can apparently be conveniently washed away after use as a water-soluble packaging. Biodegradation does, however, appear to be slow and first requires an oxidative step involving enzymatic attack to a ketone such as polyenolketone, which then biodegrades more rapidly.

There has been considerable use of polyethylene film containing about 5–15% of cornstarch for making dustbin bags. The starch biodegrades rapidly, when for example it is composted under aerobic conditions. In the late 1980s production of over 50 000 t.p.a. has been reported. More recently plastics with starch contents of 60–70% have been introduced using a synthetic polymer binder which is itself degradable.

In 1991 Rhone-Poulenc offered biodegradable cellulose acetate compounds in which an additive acts both as plasticiser and biodegrading agent (see Section 22.2.2.1).

There has been recent interest in lactic acid polymers and copolymers. These materials are environmentally attractive in that renewal and cheap source materials such as potato waste and cheese whey may be used. Such materials have been used for some time in degradable and resorbable surgical sutures but recent efforts have been directed at food packaging applications. There is

particular interest in the use of the materials as a biodegradable plastic coating for paper and board.

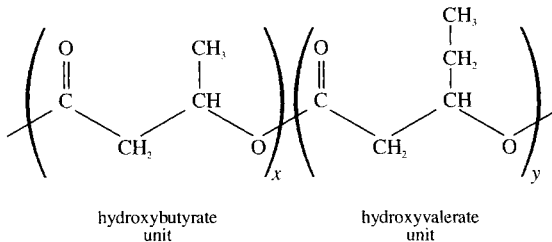
Polycaprolactones (see also Section 25.11), although available since 1969, have only recently been marketed for biodegradable purposes. Applications include degradable film, tree planting containers and slow-release matrices for pharmaceuticals, pesticides, herbicides and fertilisers. Its rate of biodegradability is said to be less than that of the polyactides.

After many years of research initiated in the 1970s, ICI introduced polyhydroxybutyrate–valerate copolymers in 1990. Because of their particularly interesting manufacturing technology, these materials are dealt with in depth separately in the next section.

31.3.1 Polyhydroxybutyrate–valerate Copolymers (PHBV)

These copolymers are very unusual for a commercial plastics material in that they are produced by biochemical methods. A fermentation process is used in which a bacterium or micro-organism *Alcaligenes eutrophus* is fed with a carbohydrate (usually glucose). This causes the bacteria to produce and accumulate ‘bacterial fat’ or energy-storing polyesters in their bodies. At the end of fermentation 80% of the weight of the bacteria is composed of the polyester, which is then ‘harvested’ by breaking open the cells and extracting and purifying the polymer.

This is a copolymer consisting of hydroxybutyrate and hydroxyvalerate units incorporated randomly along the chain. The hydroxyvalerate content may be varied by adding controlled amounts of a simple organic acid.



While stable under normal conditions of storage and use, the polymer degrades when deposited in microbially active environments.

At the present time there are two causes of variation between grades:

- (1) The level of hydroxyvalerate units.
- (2) The presence or otherwise of a plasticiser.

The hydroxybutyrate homopolymer has a T_m in the range 173–180°C and a T_g of about 5°C.

The hydroxyvalerate (HV) content is usually in the range of about 5% to 12%. As might be expected from considerations of the relation of structure to properties given in Chapter 4 and 5, the ethyl side chain of the valerate unit will reduce chain packing and lower crystalline melting point, modulus and tensile strength and at the same time increase flexibility, impact strength and ductility. This is shown in *Figures 31.1, 31.2 and 31.3*.

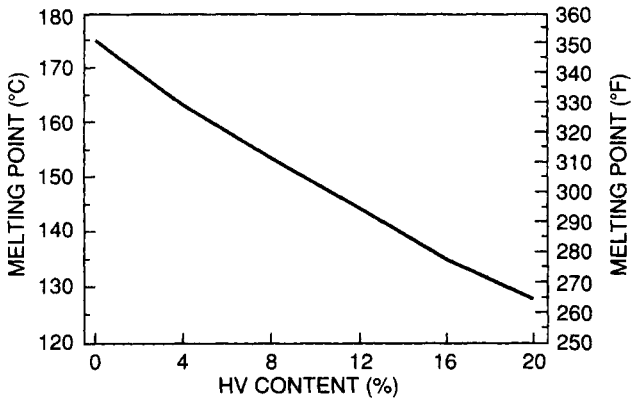


Figure 31.1. Effect of HV content on melting point

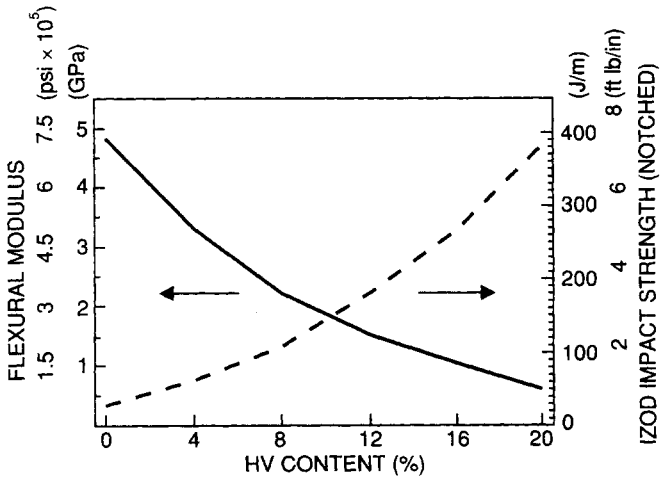


Figure 31.2. Effect of HV content on flexibility and toughness

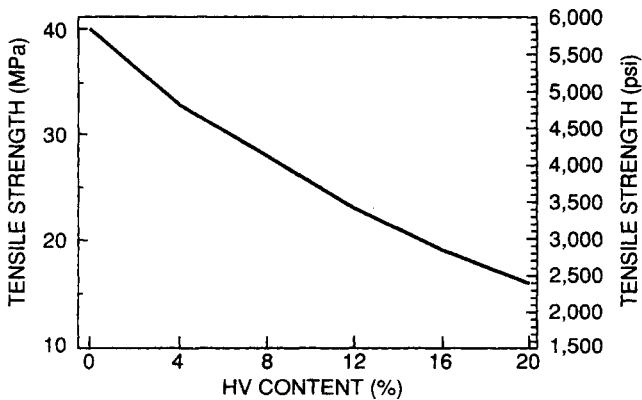


Figure 31.3. Effect of HV content on tensile strength

It would seem that the two units are reasonably isomorphous in that the copolymers are crystalline although the higher hydroxyvalerate materials exhibit lower crystallisation rates. All commercial grades contained a nucleating agent to facilitate crystallisation and shorten processing cycles during moulding operations.

Also, as might be expected, the use of plasticiser has a similar effect to that of increasing the hydroxyvalerate content. It also has a more marked effect on depressing the glass transition temperature and therefore improves properties such as impact strength and ductility at lower temperatures.

As with most polyesters, the polymers have quite good resistance to oils, particularly hydrocarbons, but are hydrolysed by acids and bases.

Some typical properties are shown in *Table 31.3*.

Table 31.3 Some selected properties of polyhydroxybutyrate–valerate copolymers (Biopol—Zeneca)

Grade	Low HV	High HV	Plasticised high HV
T_m (°C)	162	144	136
MFI (ASTM 1238–906) 190°C (2.16 kg load)	8	12	
Tensile Strength (MPa)	31	23	20
E_B (%)	8	35	42
Flexural modulus (GPa)	2.7	1.4	0.8
Izod impact strength (ft lb/in) notch	1.12	3.75	6.74
Specific gravity	1.25	1.25	1.25

The Biopol copolymers are fully degradable in a range of microbially active environments. Because of the enhanced crystallinity due to the presence of nucleating agents, biodegradation commences at the surface of the polymer. Enzymes degrade the resin into molecular fragments of hydroxybutyrate and hydroxyvalerate. Under aerobic conditions these fragments break down into carbon dioxide and water, and under anaerobic conditions into carbon dioxide and methane. Where polymer is immersed in an activated sewage sludge, according to the procedures of ASTM D5209 it is found that carbon dioxide evolution reaches 85% of its theoretical limit after 40 days. In a composting test 90% biodegradation (as measured by carbon dioxide evolution) was achieved in 7–8 months. Experiments have also been carried out with moulded bottles to study the effect of composting in industrial composting plant at 70°C. Up to 80% weight losses were observed after just 15 weeks. Bottles have also been tested under simulated managed landfill conditions. A weight loss of about 50% after 40 weeks has been reported.

There are two main points to bear in mind when processing PHBV plastics:

- (1) The limited thermal stability of the polymer, the polymer degrading rapidly above 195°C.
- (2) The need to optimise conditions to allow a maximum rate of crystallisation and thus reduce cycle times. The maximum rate of crystallisation is reported to be at about 55–60°C, which, interestingly, is significantly closer to the T_g than the T_m (see Section 3.3).

Processing temperatures should not exceed 180°C, and the duration of time that the material is in the melt state should be kept to a minimum. At the end of a run the processing equipment should be purged with polyethylene. When blow moulding, the blow pin and mould should be at about 60°C to optimise crystallisation rates. Similarly, injection moulds are recommended to be held at 60±5°C.

The low-HV unplasticised grades are the most critical to process, requiring the higher processing temperatures. Conditions are slightly less critical with the higher HV and plasticised grades.

The first applications for PHBV materials were for shampoo bottles in 1990 and since then they have been increasingly used for packaging of cosmetics and toiletries. There is also interest as a packaging material for pharmaceuticals and for 'medical disposables' such as urine bags and surgical trays. Of greater potential is the use of the material as a laminating coating for paper products such as paper cups and packages for household detergents, so that the whole material will be biodegradable. Other potential applications include disposable razors, plant pots and fishing nets. In some of these applications it may be expected that PHBV will be in competition with other biodegradable materials such as the biodegradable cellulose acetate discussed in Section 22.2.2.1 and the polylactides and polycaprolactones referred to above.

One noteworthy application announced in the Autumn of 1998 was the use of PHBV for biodegradable credit cards issued by at least one bank and one major conservation organisation.

Although first marketed by Zeneca, a company split off from ICI in 1993, under the trade name of Biopol, marketing was transferred to Monsanto in May 1996. In 1993 production capacity was 600 t.p.a. but prior to the Monsanto takeover had been expected to rise to 5000–10 000 t.p.a. by the late 1990s. However, in November 1998 Monsanto announced that it was discontinuing the Biopol programme.

31.3.2 The Future for Degradable Plastics

In the past development and widespread acceptance of degradable plastics has been very restricted because of the rather poor all-round performance of the materials and the high premium cost inevitable with small-quantity production. Furthermore, to an extent contrary and contradictory demands are made on these materials. To be acceptable as a degradable material it should fit in with normal composting cycles, completely degrade within three months and be compostable. At the same time the material must be stable during storage, processing and the service life of the product. To date these materials have penetrated little more than niche markets but there is now some evidence that the more recent polylactic acid polymers, the Du Pont Biomax copolymers and related copolymers and the polyesteramides will find uses because of their general properties and not simply on their degradability. If this happens then the degradable plastics could become of significance.

31.4 INTRINSICALLY ELECTRICALLY CONDUCTING POLYMERS (ICPs)

For many years it has been common practice to improve the electrical conductivity of plastics and rubbers by incorporating certain additives, such as special grades of carbon black. Such compounds have been important, for

example, in hospital operating theatres, where it was essential that static charges did not build up, leading to explosions involving anaesthetics.

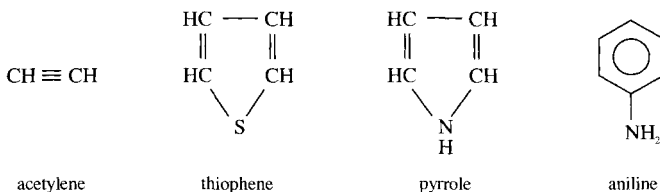
During the past 30 years considerable research has been undertaken that has led to electrically conducting polymers that do not rely on the use of fillers, the so-called *intrinsically conductive polymers*. Such polymers depend on the presence of particles which can transport or carry an electric charge. Two types may be distinguished:

- (1) Ionically conductive polymers.
- (2) Intrinsically electronically conductive polymers.

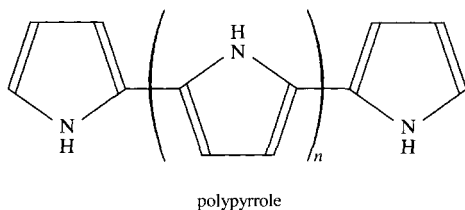
An example of an ionically conductive polymer is polyethylene oxide containing LiClO_4 , which is used as a solid phase electrolyte in batteries.

The intrinsically electronically conductive polymers are a result of the presence of an extensive system of conjugated double bonds with π -electrons, to which electrons may be either added or removed so that they exhibit an electric charge. The conjugated backbones have low ionisation potentials and high electron affinities and they can be oxidised and reduced more easily than conventional polymers. They may in fact conceptually be considered as polymeric salts. The process of creating an excess charge involves treatment of the polymer with oxidising or reducing agents and, by analogy with semiconductor technology, is referred to as *doping*. The excess charge is in the range of one per two to ten monomer units.

The polymers which have stimulated the greatest interest are the polymers of acetylene, thiophene, pyrrole and aniline, poly-*p*-phenylene, polyphenylvinylene and poly-1,6-heptadiyne. Of these materials polypyrrole has been available from BASF under the trade name Lutamer P160 since 1988.



A variety of methods have been used to produce these polymers but the use of chemical or electrochemical oxidative polymerisation has been particularly important. Whilst the doping operation may follow the polymerisation stage, in the case of polypyrrole an excess charge may be formed during the oxidative polymerisation stage. Where doping is carried out subsequent to polymerisation, oxidising agents such as AsF_5 , SbF_5 , NOPF_6 and FeCl_3 have been used successfully.



The properties and applications of intrinsically conductive polymers have been reviewed (Frommer and Chance, 1986; Sauerer, 1991). The important pyrrolles have been separately reviewed (Jasne, 1988).

Whilst the conductivity of these polymers is generally somewhat inferior to that of metals (for example, the electrical conductivity of polyacetylenes has reached more than 400 000 S/cm compared to values for copper of about 600 000 S/cm), when comparisons are made on the basis of equal mass the situation may be reversed. Unfortunately, most of the polymers also display other disadvantages such as improcessability, poor mechanical strength, poor stability under exposure to common environmental conditions, particularly at elevated temperatures, poor storage stability leading to a loss in conductivity and poor stability in the presence of electrolytes. In spite of the involvement of a number of important companies (e.g. Allied, BASF, IBM and Rohm and Haas) commercial development has been slow; however, some uses have begun to emerge. It is therefore instructive to review briefly the potential for these materials.

Clearly, ICPs will not find application solely on their conductivity. They do, however, offer an interesting range of properties in addition to conductivity, such as:

- (1) Ability to store a charge.
- (2) Ability to ion exchange.
- (3) Absorption of visible light to give coloured products.
- (4) Transparency to X-rays.

Sauerer (1991) has listed possible applications for these polymers (*Table 31.4*).

Successful application will, however, depend on achieving the following features:

- (1) Advantages in processing.
- (2) Better product properties.

Table 31.4 Possible applications for ICPs

<i>Application or useful effects</i>	<i>Examples</i>
Electronic conductivity	Flexible conductor of electricity heating elements (resistance heating), shielding of electromagnetic radiation field flattening (high-voltage cables), materials with antistatic capability
Electrodes	Rechargeable batteries (accumulators) fuel cells, photoelectrochemical cells, analytical sensors (pH, O ₂ , NO _x , SO ₂ , NH ₃ , glucose), electrocardiography (ECG)
Boundary layer effects	Membranes (selective permeability for ions, gases etc.), ion exchangers, controlled release of pharmaceuticals.
Electronics	Production of circuit boards (producing contacts in boreholes), modified electrolytic condensers, modified field effect transistors, molecular electronics (unidirectional conductors), photostructural lacquers based on ICPs (electron beam lithography), novel photoluminescent diodes (LED), data storage (e.g. spatially resolved electrochromics)
Optics	Electrochromic displays, optical filters (windows with adjustable transparency), materials with non-linear optical properties

- (3) Lower price.
- (4) Greater product stability.
- (5) Demonstration of ecological advantages.
- (6) More efficient recycling.

At the present time, doped ICPs are not normally capable of being processed like normal thermoplastics. Processes usually involve high-pressure moulding of finely powdered polymers under vacuum or an inert gas. However, modification of some ICPs with, for example, alkyl or alkoxy side groups may produce soluble, and thus more tractable, polymers.

The poor stability on exposure to air and water, particularly at elevated temperatures, which results in a reduction in conductivity, also poses problems. In the case of polypyrrole it has been found that conductivity can, however, be maintained either by the drastic measure of storing under the protective layer of the inert gas argon or embedding polypyrrole film in a matrix of an epoxide resin-glass-fibre composite.

Somewhat more practical is the use of an ICP as a conductive filler instead of carbon black. The addition of as little as 10% of carbon black will severely reduce the tensile strength, elongation at break and impact strength of polypropylene mouldings. In contrast, up to 40% of polypyrrole will have little effect on tensile strength and also give a much higher impact strength than obtained with a carbon black-filled compound at only 10% black loading. Such compounds are of interest in electromagnetic shielding, as are also laminated structures in which a polypyrrole film is sandwiched between protective non-conductive polymers.

The ecological advantages of ICPs have made them of particular interest in the field of rechargeable batteries, since they do not involve heavy metals and do not appear to have any serious toxicological problems.

As indicated in *Table 31.4*, the potential of ICPs is in somewhat esoteric applications. In some instances the potential has reached commercial realisation. For example, coating the walls of boreholes in circuit boards before electroplating with copper involves fewer stages than with older established processes and is claimed to be cost effective, faster and simpler. ICPs are also now being marketed in Japan for use in solid electrolyte conductors.

Reviews

Thermoplastic elastomers

BRYDSON, J. A., *Thermoplastic Elastomers – Properties and Applications*, RAPRA Review Report 81 (Vol. 7, no. 9) 1995

LEGGE, N. R., HOLDEN, G. and SCHROEDER, H. E., *Thermoplastic Elastomers*, Hanser, Munich, Vienna, New York (1987)

MOORE, G. F. and SAUNDERS, S. M., *Advances in Biodegradable Polymers*, RAPRA Review Report 98 (Vol. 9, no. 2) 1997

Biodegradable plastics

MOORE, J. W., *Modern Plastics*, December, p. 58 (1992)

Intrinsically conducting polymers

FROMMER, J. E. and CHANCE, R. R., *Encyclopedia of Polymer Science and Technology*, Vol. 5, p. 462, Wiley, New York, (1986)

JASNE, S., *Encyclopedia of Polymer Science and Technology*, Vol. 13, p. 42, Wiley, New York (1988)

SAUERER, W., *Kunststoffe*, **81**, 8 (1991)

Material Selection

32.1 INTRODUCTION

The previous chapters of this book have covered many hundreds of polymers. Each of these finds use in the field of plastics materials although only about 100 may be considered to be used in mainstream applications. In many cases the polymers may be greatly modified by the use of additives, as can be illustrated by the wide range of plastics materials made from PVC. It is convenient to consider materials based on a general chemical structure as a *generic group*, e.g. polycarbonates. It is also useful to consider distinctive variants of such a generic group as sub-generic groups. In the case of polycarbonates one well-known software package identifies nine sub-generic groups for polycarbonates, including standard grades, structural foam, high flow, glass or carbon reinforced, PTFE lubricated, ultraviolet stabilised and fire retardant. Even this is a considerable simplification, since in 1993 one manufacturer alone was offering 88 grades of polycarbonate (not including the important polycarbonate alloys with ABS).

Indeed in recent years there has been increased use of blends of polymers as a less expensive way of extending the spectrum of properties available rather than that of developing highly specialised polymers. Clearly the selection of material for a particular application is not a simple exercise. Before discussing material selection it is important to appreciate the extent to which processing conditions can affect polymer properties. *Table 32.1*¹ illustrates the range of values of selected properties that can be obtained with a specific grade of material in a given injection mould simply by varying processing parameters such as melt temperature, injection time and injection pressure. Such a variation may well be greater than the difference in properties shown between materials under consideration. Intelligent use of the moulding process may well be more effective and more economical than the use of a more expensive material.

Table 32.1 Range of values of physical properties of injection mouldings obtained by alteration of moulding conditions (after Allen and Van Putte, 1974)²

<i>Property</i>	<i>Polystyrene</i>	<i>Polypropylene</i>
Tensile load at failure (N)	698–1120	578–898
Flexural strength (MPa)	35–57	16–28
Izod impact strength (ft lb/in notch)*	1.4–4.0	0.9–8.3
Ball-drop impact strength (J)	0.113–6.666	5.197–13.558
Shrinkage across flow (mm/mm)	0–0.005	0.007–0.016
Shrinkage with flow (mm/mm)	0–0.006	0.010–0.014
Stiffness modulus (MPa)	1517–2137	620–1241

*Izod figures cannot realistically be converted from the f.p.s. units of the original data.

32.2 ESTABLISHING OPERATIONAL REQUIREMENTS

The first requirement must be to specify carefully the operational requirements of the item to be produced and of the material(s) to be used in its construction. This is seldom easy and is usually the most difficult part of the selection process. The most common factors to be considered are:

- (1) Regulations and specifications. There may be international (e.g. EU), national or local regulations concerning the use of materials. These may be with respect to factors such as flammability, contact with foodstuffs, environmental considerations and medical criteria.
- (2) Mechanical properties. Properties commonly of importance here are rigidity, creep resistance, strength and toughness. For some applications resistance to repeated flexing or abrasion may be critical.
- (3) Environmental operating conditions. This will include such factors as operating temperatures, including duration of use at elevated temperatures, presence of water, solvents, oils and chemicals which may be reactive with the plastics materials (not just the polymer but also with the additives) and expected humidity levels.
- (4) Other requirements. These could include electrical insulation properties, including resistance to tracking and arcing, transparency, frictional properties, surface finish, scuff resistance and specific gravity.
- (5) Particular fabrication requirements, including the need to assemble or plate parts.

Once such criteria have been established and a shortlist of possible materials drawn up, it will be important to consider:

- (1) Processing problems associated with the shortlist materials.
- (2) Economics.

32.3 ECONOMIC FACTORS AFFECTING MATERIAL CHOICE

In most instances there will be more than one material that will meet a technical specification, and choice will then be largely a matter of economics. Since parts

are usually made by volume rather than by weight, a simple comparison of the price per unit weight, e.g. £/kg or \$/tonne, is quite misleading. Figures for comparative volume cost are an important first requirement.

It may also be the case that, of two materials, that with a higher volume cost may prove to be more economical. One reason for this may be that the more expensive material may be stiffer and can thus be used in thinner section mouldings, so allowing material savings. Simpler processing operations and conditions, including shorter downtimes and more economical purging requirements, may also tilt the economic balance. In the previous chapter mention was made of the replacement of fabric-reinforced vulcanised rubbers with easily moulded intrinsically stiff thermoplastic rubbers for diaphragms and other automotive parts. Implications of possible differences in scrap rates should also be considered.

32.4 MATERIAL DATA SOURCES

Sources for material data may be classified into three groups:

- (1) Journals and textbooks (such as *Plastics Materials!*).
- (2) Trade literature issued by raw material suppliers.
- (3) Computer-based information sources.

The writer would suggest that the use of all three in combination would be synergistic.

No textbook can provide data on all the materials available, nor can it ever be completely up to date. It can, however, provide a useful background, helping the user to understand material behaviour. It can guide the reader between different classes of materials and it can point out deficiencies in materials.

Trade literature can provide a wealth of information. Users should, however, bear in mind that suppliers will naturally wish to emphasise data in the best possible light. For example, if the Izod impact strength increases sharply with decrease in sample thickness, then results may be quoted for thinner section test pieces. Whilst the facts may be stated, the underlying significance may not be fully appreciated by the casual reader.

Much trade literature is of a high standard, particularly that of suppliers of the so-called 'engineering polymers'. In many cases these manufacturers supply a range of such polymer types and they provide much useful comparative material. This may be in the form of descriptive material and tables of numerical data. Suitable choice of graphs and other diagrams can often give the reader a more immediately absorbed visual comparison.

One such graphical device about which this writer is equivocal is the polar diagram. In this case a number of properties, e.g. 6, are selected and the value of the property is indicated on a radial line. The points are then joined up. In some cases, as in *Figure 32.1*, maximum and minimum values of the properties (which vary between grades) is given. Diagrams for three such materials are given in *Figure 32.1*.

Whilst the data presented in such diagrams is useful, particularly where many such diagrams may be inspected simultaneously, I do have certain reservations. The purpose of a graph or diagram is to provide an instant visual impact. My personal experience when I look at these diagrams is that the instant impact is of

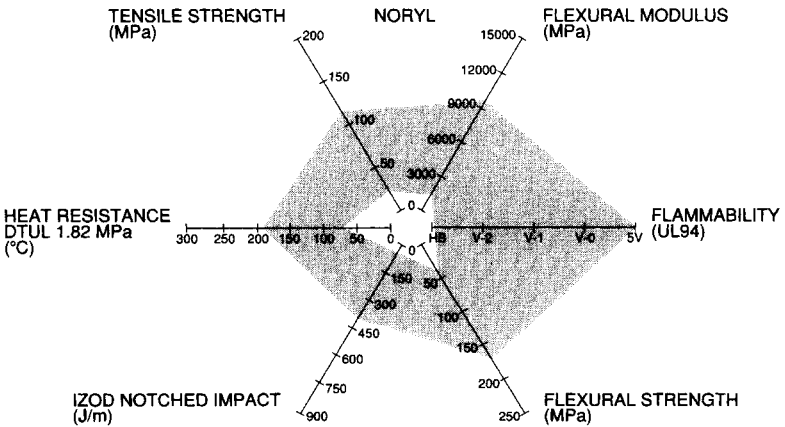
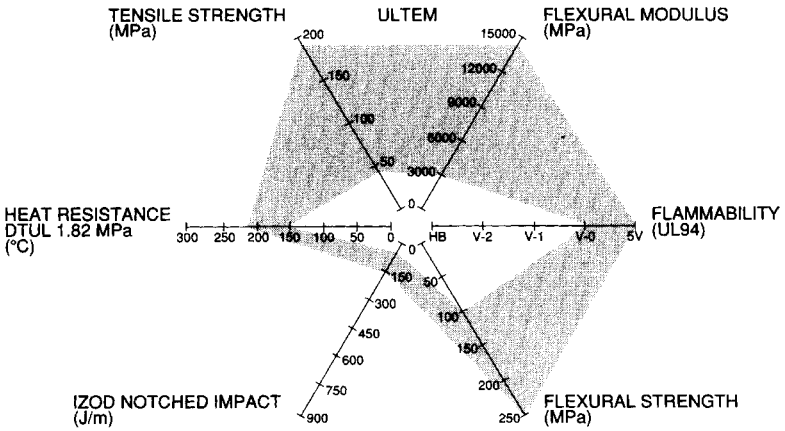
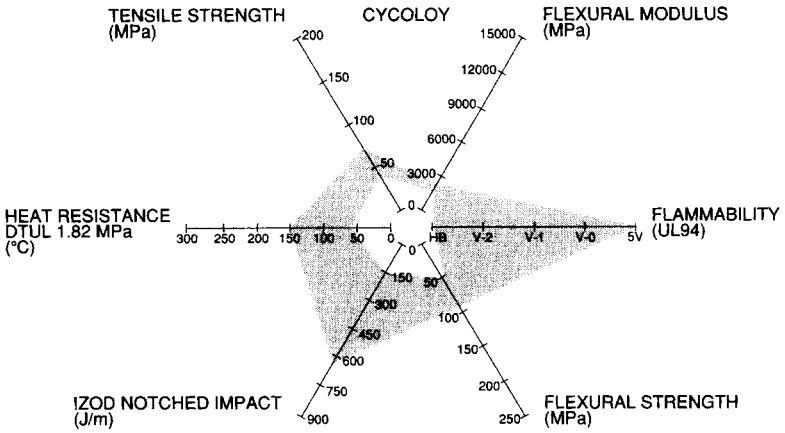


Figure 32.1. Polar diagrams for three thermoplastic materials, CYCOLOY (a PC/ABS blend), ULTEM (polyetherimide) and NORLYL (a styrenic PPO). The shaded area indicates the range available with different grades

the shape of the polygon, which is quite irrelevant, and to a large extent determined by the order in which the properties are arranged radially. The magnitude of the individual properties recorded by the peaks and troughs on the radii, which are all-important, requires more scrutiny and gives less immediate impact. However, if at the same time histograms or bar charts comparing various materials for a given property are also available and immediately comparable, then the combined use of the two types of diagram can be quite useful.

The considerable development in computer technology in recent years has provided an additional aid to material selection. This is considered further in the next section.

32.4.1 Computer-aided Selection

One important use of a computer is to provide a data base for information storage and retrieval. Such a data base may be restricted to a particular organisation or it may have world-wide application. Many thousands of the latter data bases now exist, and these can be accessed via *data base hosts*. The catalogue of one such host lists over 6000 data bases in its catalogue.

There are about a dozen data bases specifically about plastics.² Two of the best known and largest are *Rapra Abstracts*, issued by the Rubber and Plastics Research Association of Great Britain*, with about 400 000 entries, and the *KKF* data base of the Deutsche Kunststoff-Institut, with some 300 000 records in 1993. Such data bases provide a huge source of information on all aspects of plastics, and considerable expertise is necessary to extract pertinent information efficiently.

More specifically, data bases are now available which are designed as aids to plastics material selection. One estimate in 1993 was that there were 300–400 systems in the field.³ Systems vary as to whether they are limited to the products of a particular company, to a particular area of activity and to the depth of coverage over a broad area.

One well known system is *Plascams* offer by Rapra Technology Ltd as part of their *KBS (Knowledge-based system) Plastics* package which also incorporates an abstracts database, a topic base (including the 6th edition of this book) and a number of other so-called activity modules. The system is frequently updated but even one of the earliest productions provided data on approaching 600 types of material spread over 84 generic types of material. Thus in addition to data on basic polymer grades data is also given on important 'sub-species' such as flame-retardant grades, UV stabilised grades, toughened grades, fibre-reinforced grades and so on.

In this system the user starts by listing the requirements that are essential to the application and then adding those that are desirable. The essential items are then stepped through one by one in single searching. With each step there is a progressively shorter number of suitable materials. By then entering all the desirable features in a combined search, the shortlist is ranked in descending order of suitability.

The materials on the shortlist may be further investigated by use of the associated data bank in the *Plascams* system, which not only provides a precis of the materials properties and a property data bank but also information on material cost. Such a system cannot, however, be expected to include all of the factors

* Now known as RAPRA Technology Ltd.

considered in the specification. Further study of potential materials will be required, perhaps by use of this book and also by obtaining from suppliers their recommendations for specific grades and current price information.

An alternative approach is to provide a system such as *Campus* or *Polymat PC* of the Deutsches Kunststoff-Institut, which provides data on a large number of specific grades, for example up to 12 000 grades in the latter case. This will give much more specific data and could indeed be used in a supplementary way for the more basic system by making specific grade suggestions. My reservation about these systems is that users may be discouraged from reading around about the materials under consideration and could lose out on useful information from the lack of contact with suppliers. It is also important that, like the user of any pocket calculator, the operator should be able to appreciate whether or not the result or recommendation looks sensible; and this does presuppose some understanding of the subject.

32.5 A SIMPLE MECHANISTIC NON-COMPUTER SELECTION SYSTEM

A crude approximation to computer-based systems can be achieved by considering tables of properties of plastics materials such as those published annually in the *Modern Plastics Encyclopaedia*. Since the tables are to be marked, the following exercise should be carried out on photocopies!

The first stage is to select one of the more demanding requirements and go through the tables, ringing the sub-generic groups that appear to meet this requirement. A second requirement is then taken and the materials that passed the first stage are ringed in a second colour if they appear to meet the second requirement. After a few stages only a shortlist of materials is likely to remain.

When this stage has been reached, the materials on the shortlist can be investigated further, checking suppliers, grades available, prices, processability and further details of the material properties, such as, for example, surface finish and scuff resistance, which do not normally feature in property tables.

32.6 A SIMPLE PATHWAY-BASED NON-COMPUTER SELECTION SYSTEM

In this section a selection procedure will be developed for injection moulding, since this process is used for the widest range of materials. The choice available for other processes such as, for example, compression moulding, filament winding and vacuum forming, is much more restricted. The approach described will be less mechanistic than the systems described in the two previous sections, requiring the prospective user to be aware of the properties of the various materials available. Because the approach is somewhat different, it would be instructive to run it parallel to the above processes and compare the results.

The basic approach will be to select one generic type initially, with a knowledge of its advantages and limitations. If this material is not suitable, different pathways will be followed depending on the deficiencies of the first material.

It is suggested that the first material to be considered is *polypropylene*. The polymer has a number of desirable properties, as discussed in Chapter 11. These include low density, reasonable toughness, flexibility and strength at normal room temperatures, good resistance to hot water for a moderate period, low water absorption, translucency and good surface finish. Furthermore, it is one of the cheapest materials currently available.

If polypropylene is *too hard* for the purpose envisaged, then the user should consider, progressively, polyethylene, ethylene-vinyl acetate and plasticised PVC. If more rubberiness is required, then a vulcanising rubber such as natural rubber or SBR or a thermoplastic polyolefin elastomer may be considered. If the material requires to be rubbery and oil and/or heat resistant, vulcanising rubbers such as the polychloroprenes, nitrile rubbers, acrylic rubbers or hydrin rubbers or a thermoplastic elastomer such as a thermoplastic polyester elastomer, thermoplastic polyurethane elastomer or thermoplastic polyamide elastomer may be considered. Where it is important that the elastomer remain rubbery at very low temperatures, then NR, SBR, BR or TPO rubbers may be considered where oil resistance is not a consideration. If, however, oil resistance is important, a polypropylene oxide or hydrin rubber may be preferred. Where a wide temperature service range is paramount, a silicone rubber may be indicated. The selection of rubbery materials has been dealt with by the author elsewhere.⁴

If polypropylene is *too soft* and a more rigid product is required, polystyrene will probably be the first material to consider. If this is too brittle, then toughened polystyrene, styrene-acrylonitrile and styrene-maleic anhydride will be assessed. In many instances the demand will be for a rigid, tough, good-finish material with a higher softening point than polystyrene. For a wide range of applications ABS is the appropriate material. Where dimensional stability and good dielectric properties over a range of temperatures and higher deflection temperatures under load are to be taken into account, a blend based on polyphenylene oxide may be preferred.

Where *transparency* is required, a range of polymers is available. Polystyrene is the least expensive but polymethylmethacrylate has an outstanding high light transmission combined with excellent weathering properties. Also to be considered are the polycarbonates, glass-clear polyamides, SAN, butadiene-styrene block copolymers, MBS polymers, plasticised PVC, ionomers and cellulose esters such as cellulose acetate.

For many applications a polymer with *good load-bearing* properties is required. This will call for one of the so-called engineering plastics. In this case nylons 6, 66 and, perhaps, 46 will be assessed first, but if a lower water absorption is required the properties of such polyamides as nylon 69, nylon 610, nylon 11, or nylon 12 should be taken into account. Where enhanced stiffness, creep resistance, stiffness and water resistance is required, glass-filled grades may solve the problem, but if low coefficient of friction and/or good moulding appearance are important, then a polyacetal may be considered. Where rigidity and creep resistance are particularly important, then fibre-reinforced polymers, particularly glass-fibre-reinforced polyamides, will be of interest.

There is a frequent demand for materials suitable for *housings* for computer, domestic, electrical and automotive equipment. In these applications toughness, excellent surface finish, surface durability, reasonable rigidity, dimensional stability, good weathering behaviour and low water absorption are common requirements. In these applications ABS is frequently considered first but its limited deflection temperature and heat aging resistance may lead to other

materials being considered, such as ASA, AES and ACS polymers (Section 16.9), PPO derivatives such as Noryl, polycarbonates (PC), polybutylene terephthalate (PBT) and related materials, and alloys such as ABS-PC and PC-PBT. Selection here can be helped in that some suppliers market several of these materials and they produce data which makes comparisons easier than they might have been.

Over the years polymers have been produced suitable for use at progressively *higher temperatures*. Where this is a requirement, it is usual first to decide whether a rubbery or a rigid material is required. If the former, this has been dealt with by the author elsewhere.⁴ If the latter, it is usually convenient to look in turn at polycarbonates, PPO-based materials, polyphenylene sulphides, polysulphones, polyketones such as PEEK and PEK, polyamide-imides, polyphthalamides, fluoropolymers, liquid crystal polymers and polyimides.

Where *fire retardancy* is of importance, then reference should be made to *Tables 5.13–5.15*, which will indicate the intrinsic fire retardancy of the polymer. It will, however, be noted that many polymers may be modified to enhance fire retardancy properties so that fire retardant grades of such polymers may be considered. It is to be noted that such enhanced fire retardancy may be associated with adverse effects on other properties.

Where plastics are to be used for electrical applications, then *electrical properties* as well as mechanical and other properties need to be considered. Whilst properties such as resistivity, power factor and dielectric constant are important, they may not be all-important. For example, although polyamides and many thermosetting plastics may show only moderate values for the above properties, they have frequently been used successfully in low-frequency applications. Perhaps more important for many purposes are the tracking and arcing resistance, which are frequently poor with aromatic polymers.

Occasionally, *water-soluble* plastics are required. Poly(vinyl alcohol) is commonly the first to be considered but some cellulose ethers, polyethylene oxides, poly(vinyl pyrrolidone) and *N*-substituted polyamides are among many possible alternatives.

Consideration of the above factors will cover most applications but polymers are employed in an enormous range of applications, so that many other properties may have to be taken into account. This may result in the use of some of the more esoteric materials but this is somewhat beyond the scope of this section.

References

1. ALLEN, E. O. and VAN PUTTE, D. A., *Plastics Engineering*, **30**, 37 (1974)
2. MAIER, C., *British Plastics and Rubber*, November (1993)
3. MAIER, C., *British Plastics and Rubber*, April (1993)
4. BRYDSON, J. A., *Rubbery Materials and Their Compounds*, Elsevier Applied Science, London and New York (1988) (Title now held by Chapman and Hall, London)

Appendix

A Short List of Additional Information Sources

There is a substantial literature on polymers and plastics and many monographs are listed at the end of individual chapters. In addition the following provide excellent comprehensive source material:

Encyclopedia of Polymer Science and Engineering, 2nd edition, Wiley, New York

Consisting of 17 volumes which were produced between 1985 and 1990 these provide the most comprehensive source of information generally on plastics and polymers. This replaced the *Encyclopedia of Polymer Science and Technology* published during the 1960s which although clearly more dated is in the writer's view more comprehensive.

Polymer Science Dictionary (2nd edn) by Mark Alger, Chapman & Hall, London, 1996

Polymer Technology Dictionary by Tony Whelan, Chapman & Hall, London, 1993

Each of these two complementary books (written by ex-colleagues of the author) contains over 10 000 entries

Of the many journals devoted to the subject the following deserve particular mention

Journal of Polymer Science

Journal of Applied Polymer Science

Kunststoffe (with translations in English)

Modern Plastics International

European Plastics News

The first two comprise original papers while the latter three are more concerned with practical aspects as well as providing information concerning commercial developments of plastics materials.

Mention should also be made of the data collections made available by Rapra Technology Ltd, Shawbury, Shrewsbury, Shropshire on CD-ROM. Subject to frequent upgrading these provide an outstanding database.

Index

- ABS plastics, 443–9
 - processing, 447–8
 - production, 444–8
 - properties and applications, 328, 449, 464, 895
- ABS/PVC blends, 447
- Acetal–polyurethane alloys, 544
- Acetal resins, 8, 49, 515–28, 533–44
 - additives, 543–4
 - applications, 544–6
 - electrical insulation properties, 540
 - mechanical properties, 538–40
 - polymerisation of formaldehyde, 533–6
 - processing, 542–3
 - structure and properties, 533–6
 - thermal properties, 538–42
- Acetone, 17
- Acetylene, 9
- Acetyl tributyl citrate, 333
- Achieve range, 248
- Acid hardening systems, 758–61
- Acrilan, 416
- Acry-ace, 399
- Acrylate rubbers, 417–18
- Acrylic plastics, 398–424
 - acrylate rubbers, 417–18
 - acrylic adhesives, 419–20
 - chloroacrylate polymers and copolymers, 421–3
 - hydrophilic polymers, 420
 - methacrylate and chloroacrylate polymers and copolymers, 421–3
 - methacrylate polymers and copolymers, 421–3
 - nitrile resins, 415–17
 - poly(methacrylimide), 420–21
 - poly(methyl methacrylate), 390–415
 - thermosetting acrylic polymers, 418–19
- Acryloid, 399
- Acrylonitrile, 10
- Acsum, 302
- Activators, 279
- Acyclic aliphatic resins, 766–7
- Addition polymerisation, 33–7
 - see* Polymerisation, addition
- Additive method, 91
- Additives, 124–57
 - acetal resins, 543–4
 - anti-aging, 124, 135–45, 798
 - antistatic, 232, 238
 - blowing agents, 124, 150–53, 279, 280
 - colorants, 124, 149–50, 797
 - coupling agents, 128–31
 - cross-linking agents, 124, 153–4
 - epoxide resins, 768–72
 - fillers, 124, 126–9, 279, 280, 798
 - flame retarders, 104–109, 124, 145–9, 229, 496, 497
 - flow promoters, 124, 132–4
 - fungicides, 496
 - heat stabilisers, 496, 497
 - isotactic polypropylene, 260–61
 - light stabilisers, 496, 497
 - lubricants, 124, 132–4, 496, 497
 - nucleating agents, 496, 497
 - 2-Oxazolines, 155–8
 - photodegradants, 154–5
 - plasticisers, 124, 131–2, 284, 496, 497
 - polish, 826
 - polyamides, 436–8
 - polyethylene, 228–32
 - poly(methyl methacrylate), 409
 - polypropylene, 258–9
 - polytetrafluoroethylene (PTFE), 371–2
 - poly(vinyl chloride), 342
 - reinforcing fillers, 496, 497
 - softeners, 124, 131–2, 279, 280
 - structure control, 839
 - see also under specific types*

- Adhesives:
 acrylic, 419–20
 hot setting, 688
 polyurethane, 805
 resorcinol–formaldehyde, 662
 urea–formaldehyde resins, 677–8
- Adipic acid, 9, 21, 480
- Adiprene C, 787, 788
- Aerodux, 189, 662
- Aflas, 382
- Aflon, 374
- AFT-2000, 515
- Aggregation states, 43–58
 cross-linked structures, 53–5
 crystalline polymers, 49–53
 linear amorphous polymers, 43–9
 polyblends, 55–9
- Aging, 76, 99, 231, 342, 878
- Agriculture, 14
- Air-dried sheet (ADS), 282
- Alcoholysis, 390
- Alcryn, 879
- Aldehydes, 5, 546, 639
- Algoflan, 364
- Aliphatic hydrocarbons, 85
- Aliphatic olefin rubbers, 294–9
 thermoplastic polyolefin rubbers, 298–9
- Aliphatic polyalkenamers, 300–301
- Aliphatic polyamides, 480–6
 adipic acid, 480
 ω -aminobenzoic acid, 484–5
 ω -aminoundecanoic acid, 483–4
 azelaic acid, 481–2
 caprolactam, 482–3
 dodecanolactam, 485–6
 hexamethylenediamine, 481
 intermediates for, 480–86
 polymerisation, 486–7
 sebacic acid, 481–2
 structure and properties, 487–90
- Aliphatic polyolefins, 247–303
 aliphatic olefin rubbers, 299–302
 copolymers containing ethylene, 273–6
 diene rubbers, 281–5
 poly-(4-methylpent-1-ene), 268–71
 polybut-1-ene, 266–7
 1,2-polybutadiene, 303
 polyisobutylene, 267–8
 polypropylene, 247–66
 rubbery cyclo-olefin (cyclo-alkene)
 polymers, 300–302
 thermoplastic diene rubbers, 292–304
see also Polyethylene
- Alkali metals, 35, 36
- Alkon, 531
- Alkyd moulding compositions, 711–2
- N*-Alkyl compounds, 505
- Alkyl, 2-cyanoacrylate, 419
- Alkylene oxides, 546–7
- n*-Alkyl groups, 59
- Alkyl lithium, 36
- Allyl resins, 708–709
- Alphanol, 79, 331
- Alternating copolymers, 27
- Aluminium chloride, 34
- Aluminium hydroxide, 127
- Aluminium stearate, 337
- Aluminium triethyl, 209
- Amber, 2, 19, 870–1
 composition and properties, 870–1
- Ambroid, 871
- Amine flexibilisers, 770–1
- Amine hardening systems, 753–7, 761
- Amines, 140, 143
- Aminocrotonates, 330
- ω -Aminoanthracic acid, 484–5
- Aminoplastics, 24, 668–90
 aniline–formaldehyde resins, 689–91
 melamine–formaldehyde resins, 680–89
 melamine–phenolic resins, 689
 thiourea resins, 690–91
 urea–formaldehyde resins, 669–80
- ω -Aminoundecanoic acid, 483–4
- Amorphous density, 93
- Amorphous non-polar polymers, 81, 85
- Amorphous polar polymers, 81, 85
- Amorphous polyarylene sulphides, 596
- Amorphous polymers, 44, 48
 cooling rates, 174–5
 density, 73
 elastic moduli, 72–3
 glass transition temperature, 64–6, 100, 190
 impact strength, 73–4
 linear, 43–9
 orientation, 47–9
 optical properties, 121
 solubility, 94
 yield strength, 72–3
- Amorphous resins, 57
- Anaerobic acrylic adhesives, 420
- Aniline–formaldehyde resins, 689–91
- Anisotropic behaviour, 48
- Anti-aging additives, 124, 135–45, 798
- antioxidants, 134–43
 antiozonants, 143
 stabilisers against dehydrochlorination, 143
 ultraviolet absorbers and related materials,
 143–7
- Anti-blocking agents, 229
- Antimony oxide, 148–9, 342, 701
- Antioxidants, 98, 134–43, 230–31, 279, 866
 chain-breaking, 135–42
 in polypropylene, 156, 258
 preventive, 135, 140
- Antiozonants, 134, 279, 284
- Antiplastification, 89
- APE, 731
- Apec HT, 565
- Applications:
 ABS plastics, 448
 acetal resins, 544–6
 bis-phenol A polycarbonates, 575–8
 casein, 859
 cellulose acetate, 626–7

- cellulose nitrate, 621
 epoxide resins, 772–5
 flexible foams, 799–800
 furan resins, 812–13
 isotactic polypropylene, 263–5
 melamine–formaldehyde resins, 688–9
 nylons, 502–505, 784, 879, 897
 phenol–formaldehyde moulding powder, 652–4
 phenolic laminates, 658–61
 phenolic resins, 659–61
 polyacetals, 544–6
 polyamides, 502–505
 poly-(2,6-dimethyl-*p*-phenylene oxide) (PPO), 580
 polyethylene, 241–5, 896
 poly(methyl methacrylate), 411–13
 poly-(4-methylpent-1-ene), 271
 polypropylene, 265–7, 878, 894–5
 polysulphones, 601–2
 polytetrafluoroethylene, 372–3
 polyurethane rubbers, 788–9
 poly(vinyl alcohol), 395, 882, 898
 poly(vinyl chloride) (PVC), 355–8
 shellac, 869–70
 silicone fluids, 826–8
 silicone resins, 829–32
 silicone rubbers, 838–9
 styrene-based plastics, 461–3
 styrene-butadiene rubber (SBR), 863
 thermoplastic elastomers, 878–80
 urea–formaldehyde resins, 675–7, 679–80
 vinyl chloride polymers, 355–8
 Aramid fibres, 9, 514–15, 773
 Arc resistance, 110, 122
 Ardel, 729
 Ardil, 9, 860
 Armetal, 528
 Arnite, 607
 Armitel, 738
 Arnite PBTP, 724
 Arnite PETP, 720, 721
 Aromatic diamines, 787
 Aromatic polyamide fibres, 514–15
 Aromatic polycarbonates, 72
 Aromatic polyester, 55
 Aromatic polyimides, 72
 Arrhenius equation, 167
 Arylef, 608, 731
 Arylon T, 447, 602, 731
 Aryloxa, 589
 Asbestos, 338, 647
 Asphaltites, 871
 A-stage resins, 24, 641–2
 Asterite, 411, 413
 ASTM D1525, 188
 ASTM D2863–74, 105
 ASTM D495, 516
 ASTM D5209, 886
 ASTM D635–74, 105
 ASTM D648, 188
 Astrel, 374, 596
 Atactic structures, 68, 251
 A-Tell, 734
 Auto-acceleration effect, 402
 Automotive industry, 13, 591, 652, 654, 803, 878
 Autoxidation, 139, 141
 Average kinetic chain length, 30
 Azelaic acid, 481–2
 Azodi-isobutyronitrile, 25

 B 6805, 360
 Bakelite, 635
 Balanced process, 313
 Balata, 866
 Barex, 416, 417
 Barytes, 338
 BASF process, 456
 Basic lead carbonate (white lead), 327
 Bayblend, 447, 578
 Baymid, 808
 Baypren, 295
 BDS K-resin, 438
 Bead processes, 456–7
 Beckamides, 506
 Bell test, 226
 Benzene, 9, 10, 112
 Benzene rings, 95, 562, 572
 Benzoates, 328
 Benzoyl peroxide, 25
 Benzyl cellulose, 632
 Beta-conidendrol, 535
 Biapen, 589
 Biaxial orientation, 192
 Biaxial stretching, 48, 52, 257, 460, 719
 Binary copolymers, 27
 Biocellat, 627
 Bioceta, 627
 Biodegradable plastics, 13, 880
 Biodegradation, 153, 880–84
 Biomax 881, 886
 Biopol, 883, 885, 886
 Birefringence methods, 48
 Bis-phenol A polycarbonates, 51, 72, 86, 557, 558
 alloys based on, 577–8
 applications, 575–7
 glass transition temperature, 62, 114
 Bitumen, 1–2, 19, 871–2
 Bituminous plastics, 871–2
 Biuret links, 785, 790, 794
 Bleeding, 125, 140, 150
 Block copolymers, 27, 36, 54, 63, 384, 451–2, 579–80
 Blocking, 229, 235
 Blooming, 125, 140, 150
 Blowing agents, 124, 150–53, 229
 Blow moulding, 233, 244, 264, 350
 Blown film processes, 261
 Blow-up ratio, 235
 Bond bending, 195
 Bond dissociation energies, 96

- Bond stretching, 195
 Boron trifluoride, 34
 Bouncing putty, 834
 Branching, 67, 70, 73, 213–15
 Brownian motion, 169
 BS, 1524 softening point, 452, 626
 BS, 2782 flow test, 188, 650
 BS, 771, 650
 B-stage resins, 641–2
 Buna N., 294
 Buna S., 287
 Burning rate, 106
 Buss Ko-Kneader, 673
 Butachlor, 295
 Butacite, 393
 Buta-1,3-diene, 20
 Butadiene, 10, 54, 62
 Butadiene–Pentadiene rubbers, 296
 Butadiene–styrene block copolymers, 451–2
 Butadiene–styrene resins, 128
- Cadmium–barium systems, 328
Cadon, 450
 Calcium carbide, 9
 Calcium carbonate, 127, 338
 Calcium oxide, 9
 Calcium silicate, 127
 Calcium stearate, 337
 Calendering, 49, 158, 160, 237, 348
 Camphor, 4, 88
Campus system, 895
 Capacitance, 112
 Capacity factor, 93
 Caprolactam, 9, 22, 482–3
 Carbanions, 34
 Carbon black, 98, 127, 141, 143, 186
 as conductive filler, 889
 in polyethylene, 227–31, 239
 as ultraviolet absorber, 156, 258
 Carbon fibres, 128
 Carbonic ester polymers, 580–82
 Carbonium ions, 34, 35
 Carbon tetrachloride, 26, 81, 87, 112, 119
 Carbowax, 546
 Carboxyl groups, 54
 Cariflex TR, 297, 298
 Carilon, 279
 Casein, 5, 9, 853–9
 applications, 859
 chemical nature, 854–5
 isolation from milk, 855–6
 production, 856–8
 properties, 858–9
 Casting processes, 184
 Cast phenolic resins, 659
 Catalysts, 37
 Celanex, 724
 Celanix, 608
 Celcon, 531, 532, 533, 536, 540
 Cellidor B, 628
 Cell nucleating agents, 152
 Cellophane, 633, 672
 Cell stabilisers, 152
 Celluloid, 3–4, 5
 structure and properties, 619–21
 Cellulose, 3, 19, 23, 87
 regenerated, 632–4
 Cellulose acetate, 5–6, 23, 621–7
 applications, 625–7
 biodegradable compounds, 627
 compounding, 623–4
 preparation, 621–3
 primary, 622
 properties, 624–5
 secondary, 623
 Cellulose acetate-butyrate (CAB), 628
 Cellulose acetate-propionate, 628
 Cellulose caprate, 628–9
 Cellulose esters, 617–29
 cellulose acetate, 621–7
 cellulose acetate-butyrate (CAB), 628
 cellulose acetate-propionate, 628
 cellulose caprate, 628–9
 cellulose nitrate, 617–622
 cellulose propionate, 628
 Cellulose ethers, 629–32
 ethyl cellulose, 629–31
 Cellulose nitrate, 4, 88, 617–22
 applications, 621
 manufacture of celluloid sheets, 617–19
 preparation, 616–17
 structure and properties of celluloid, 619–21
 Cellulose plastics, 613–34
 cellulose esters, 617–29
 cellulose ethers, 629–30
 ethyl cellulose, 629–29
 nature and occurrence of cellulose, 613–16
 regenerated cellulose, 632–4
 vulcanised fibre, 634
 Cellulose propionate, 628
 Cellulosics, 9
 Chain branching, 64, 72
 Chain coiling, 44–5
 Chain degradation, 97
 Chain ends, 62–3
 Chain flexibility, 59, 72
 Chain growth, 27, 28, 34
 Chain mobility, 62, 64
 Chain separation, 62
 Chain stiffness, 70
 Chain transfer, 26
 Chain transfer agents, 26, 209
 Chain uncoiling, 44–5, 47, 172, 195, 202
 Charpy test, 192–4
 Chelating agents, 140–41
 Chemical blowing agents, 153
 Chemical bonds, 76–80
 Chemical nature of plastics, 19–39
 addition polymerisation, 24–37
 condensation polymerisation, 20, 21, 23, 24, 37–9
 thermoplastic and thermosetting behaviour, 23–4

- Chemical properties, 76–109
 - aging and weathering, 99
 - chemical bonds, 76–80
 - chemical reactivity, 95–6
 - diffusion and permeability, 100–103
 - effects of thermal, photochemical and high-energy radiation, 96–8
 - fire and plastics, 104–109
 - polymer solubility, 80–94
 - toxicity, 103–104
- Chemical reactivity, 95–6
- Chewing gum, 866
- Chicle, 866
- Chill-roll process, 237, 261, 262
- Chipboard, 678
- Chloroendic anhydride, 760
- Chloroacrylate polymers and copolymers, 421–3
- Chlorofluorocarbons (CFCs), 417, 797
- Chloroform, 119
- Chloroprene rubbers (CR), 295–6
- Chlorosulphonated polyethylene (Hypalon), 23, 241
- Chlorosulphonated polyethylenes, 297
- Clausius–Clapeyron equation, 90
- Clausius–Mosotti equation, 117
- Clays, 127
- Coal tar, 9, 10
- Coatings, 805
- Cobalt naphthenate, 703
- Cocatalysts, 34
- Cohesive energy density, 81
- Coining, 179
- Coke, 9
- Cold cure process, 284
- Cold-drawing process, 52, 219
- Cold flex temperature, 131
- Cold forming, 179
- Cold moulding process, 799
- Collodion, 3, 4
- Colorants, 124, 149–50
- Colour-forming groups, 149
- Combustion, 105
- Comonomers, 217, 325
- Composites, 128
- Compression moulding, 233, 350, 649, 651, 674–5, 775
- Computer-aided material selection, 889–6
- Condensers, 111, 112
- Conduction charge, 112
- Congo red test, 327
- Constant-viscosity rubbers, 282
- Constrained geometry homogeneous catalysts, 210, 211
- Contact resins, 7
- Continuous Use Temperature Rating or Index, 186
- Cooling rates, 174–5
- Copolymerisation, 33, 64, 67
 - with ethylene, 273–6
 - poly(methyl methacrylate), 413–15
- Copolymers, 357–8
 - butadiene–styrene, 451–2
 - chlorine-containing, 302
 - ethylene, 374
 - ethylene–acrylic acid, 274
 - ethylene–carbon monoxide, 276
 - ethylene–ethyl acrylate, 274
 - ethylene–styrene, 308–309
 - ethylene–vinyl alcohol, 394–5, 417, 470
 - hexafluoroisobutylene–vinylidene fluoride, 379
 - multiblock, 875
 - polychlorotrifluoroethylene, 374
 - polyhydroxybutyrate–valerate (PHBV), 883–6
 - poly(vinyl chloride) (PVC), 354–5, 360
 - styrene–acrylonitrile, 74, 441
 - styrene–butadiene, 63
 - styrene–maleic anhydride, 450
 - tetrafluoroethylene–ethylene (ETFE), 374
 - tetrafluoroethylene–hexafluoropropylene, 373
 - triblock, 54, 55, 875
 - vinyl chloride–vinyl acetate, 858
 - vinylidene chloride–vinyl acrylonitrile, 470
 - vinylidene chloride–vinyl chloride, 476–80
- Co-ordinate bonds, 77
- Cotton linters, 613, 617
- Coumarone–indene resins, 471–2
- Counter-current mixing, 804
- Coupling agents, 127–31
- Covalent bonds, 77
- Cracking, 10, 56, 207
- Crack propagation, 438
- Crastin, 724
- Crazing, 56–7
- Creep, 198, 559, 567
- Creep curves, 197–8
- Creep–temperature relationships, 198
- Cresols, 638–9, 645
- Crinothene, 237
- Critical point, 173
- Critical shear rate, 173
- Critical shear stress, 173
- Cross-linked structures, 53–5, 91, 98
- Cross-linking, 23–4, 44, 70, 76, 176–9, 225
 - cast polyurethane rubbers, 786–7
 - heat-fugitive, 875
 - rate, 178
 - silicone rubbers, 837–8
- Cross-linking agents, 124, 153–4, 230
- Crystal densities, 121
- Crystalline aromatic polyamides, 513–16
- Crystalline melting point, 70–71
- Crystalline polymers, 44, 49–50
 - liquid crystal polymers, 53
 - orientation and crystallisation, 52–3
- Crystallinity, 52, 72, 73, 185, 203
 - polyethylene, 294–5
- Crystallisation, 49–53, 219
 - factors affecting, 62, 64–70, 73, 233
- Crystallisation rate–temperature curve, 51
- Crystallites, 49
- C-stage resins, 24, 641–2

- Cumene process, 636, 637
 Cyclic aliphatic resins, 764–6
 Cyclohexanone peroxide, 703
 Cyclohexane, 10
 Cycoloy, 447, 894

 Dacron, 584, 607, 695, 713
 Dai-el, 384
 Debye equation, 118
 Decomposition, 104
 Deflection temperature under load test, 188
 Deformation, 158, 195, 201
 Deformation–time curves, 196
 Degradable plastics, 880–83, 886
 polyhydroxybutyrate-valerate copolymers
 (PHBV), 883–6
 Degradation, 76, 105, 275
 Degree of substitution, 615
 Dehydrochlorination, 134, 143, 325
 Dehydrochlorination stabilisers, 134
 Dehydrogenation, 428
 Delrin, 531, 533, 536, 540
 Density, 74, 877
 Dentures, 411
 Derakane vinyl esters, 419
 Deretron, 608
 Deroton, 724
 Dexsil, 834
 Diacryl, 105, 419
 Diakon, 399, 404
 Diakon MX, 415
 Diallyl isophthalate (DAIP), 712
 Diallyl phthalate (DAP), 24, 333, 412
 Diamar, 590
 Diamines, 21, 380
 Diaminophenyl sulphone, 755
 Diaphanyl phthalate (DAP), 331
 Diazomethane, 206
 Dibasic acid, 21
 Dibasic lead phosphite, 327
 Dibasic lead phthalate, 327
 Dibasic lead stearate, 328, 337
 Dibenzyl ether, 88
 Dibutyl phthalate, 88, 331, 463
 Dibutyl sebacate (DBS), 333
 Dibutyltin di-iso-octylthioglycollate, 329
 Dibutyltin dilaurate, 329
 Dibutyltin maleate, 329
 Dicumyl peroxide, 239
 Dielectric constant, 15, 110–19, 226, 229
 Dielectric constant–frequency curve, 114
 Dielectric constant–temperature curve, 115
 Dielectrics, quantitative relationships, 117–19
 Dielectric strength, 110
 Diels–Alder reactions, 301, 302, 504, 698
 Diene rubbers, 85, 95, 130, 186, 276–92
 butadiene-pentadiene rubbers, 292
 chloroprene rubbers (CR), 290–92
 natural rubbers, 280–85
 nitrile rubber (NBR), 88, 289–90
 ozone degradation, 143
 polybutadiene, 286–7
 styrene–butadiene rubber (SBR), 287–9
 synthetic polyisoprene, 285–6
 thermoplastic, 292–4
 Die swell, 172
 Diethylaminopropylamine, 753
 Diethylenetriamine, 753
 Diethyl hexyl phthalate, 64
 Diethyl phthalate, 624
 Differential scanning calorimetry (DSC), 161
 Diffusion, 76, 100–103
 Diglycidyl ether resins, 763, 765
 Dihalides, 22, 552
 Di-isobutyl phthalate, 331
 Di-isocyanates, 22, 153
 Di-isodecyl phthalate, 331
 Di-iso-octyl phthalate (DIOP), 89, 100, 331
 Dilatancy, 324
 Diluents, 699–701
 Dimers, 178
 Dimethacrylates, 420
 Dimethylaminopropylamine, 753
 Dimethyl phthalate (DMP), 87, 88, 624
 Dimethylsilicone rubbers, 832
 DIN, 53460, 188
 DIN, 53461, 188
 Dinonyl phthalate (DNP), 331
 Dioctyl sebacate (DOS), 89, 132, 333
 Diols, 22
 1,3-Dioxolane, 97
 Diphenylmethane di-isocyanates, 779–82
 Diphenylurea, 330
 Dipole forces, 79, 85, 89
 Dipole moments, 119
 Dipole orientation, 113–14
 Dipole polarisation, 113, 117, 118
 Dispersion forces, 79, 85
 Dissipation factor, 114, 122
 Distortion, 202–204
 Disubstituted ethylenes, 98
 Ditrdecyl phthalate, 329
 Divinylbenzene, 37
 Dodecanolactam, 485–6
 Dodecylsuccinic anhydride, 760
 Dodecyl mercaptan, 26
 Doping, 120, 887–8
 Dorlastan, 790
 Dormagen process, 622
 Dough moulding compounds, 709–11
 Dow ‘Log’ process, 456
 Dow–Taga process, 261
 Draw-down ratio, 235
 Duracon, 531, 535
 Durel, 731
 Durethan U, 783
 Dyflor, 376
 Dylarc, 450
 Dymotape, 341
 Dynagen XP-139, 548

 Ebonite, 3, 4, 860–63
 Ecoflex, 882
 Ekkcel, 608

- Ekkcel C-1000, 730
 Ekkcel I-2000, 730
 Ekonol P-3000, 730
 Ekonol T-4000, 730
 Ektar PCTG, 730
 Elastic deformations, 172
 Elasticity, 171
 Elastic moduli, 72–3
 Elastic turbulence, 223
 Elastomer-modified thermoplastics, 258 *see*
 also Thermoplastic elastomers
 Electrical insulation properties, 15, 110, 116,
 226, 373, 565
 acetal resins, 540
 Electrically conductive polymers, 120
 Electrical properties, 898
 polyethylene, 163, 207, 224, 226, 244
 Electrical testing, 122
 Electronegativity values, 78
 Electronic applications of polymers, 119–20
 Electron polarisation, 111, 113
 Electrovalent bonds, 78
 Elvanol, 390
 Elvax, 273
 Engel process, 237
 Engineering plastics, 502, 896
 Entanglements, 44, 62, 72, 167, 168, 185
 Enthalpy, 161–2
 Entropy, 94
 Entropy change, 84
 Entropy of fusion, 72
 Environmental stress cracking, 225–6, 253,
 263, 595
 EPDM rubbers, 295, 303, 449, 504
 Epichlorhydrin rubbers, 548
 Epoxide resins, 7, 24, 329, 369, 606, 744–76
 acyclic aliphatic, 766–7
 additives, 768–72
 applications, 772–6
 curing of glycidyl ether resins, 751–61
 cyclic aliphatic, 764–6
 diluent, 768–72
 flexibilisers, 768–72
 hardening systems, 753–61
 miscellaneous, 761–8
 nitrogen-containing, 767–8
 non-glycidyl ether, 764–8
 preparation from bis-phenol A, 745–50
 structure and properties, 772
 Epoxidised oils, 328, 333, 767
 Estane, 790
 Ester exchange, 558–60
 Ester linkage, 21
 Ethanol, 81
 Ethyl acrylate, 97
 Ethyl alcohol, 9, 88, 113
 Ethylbenzene, 427–8
 Ethyl cellulose, 629–31
 Ethylene–cyclo–olefin copolymers, 280
 Ethylene, 9, 10, 54, 210
 chlorinated, 297
 copolymerisation, 273–6
 copolymers, 374–5
 monosubstituted, 93
 polymers, 208
 Ethylene–acrylic acid copolymers, 274
 Ethylene–carbon monoxide copolymers, 274,
 278–9
 Ethyl phthalyl ethyl glycolate, 624
 Ethylene dichloride, 10
 Ethylene–ethyl acrylate copolymers, 274
 Ethylene glycol, 10, 551
 Ethylene oxide, 10, 22, 97
 Ethylene–propylene rubbers, 8, 73, 229–30,
 243, 878
 Ethylene–styrene copolymers, 308–309
 Ethylene–styrene interpolymers (ESIs),
 308–309
 Ethylene–vinyl acetate (EVA) plastics, 227,
 361, 386, 394, 897
 Ethylene–vinyl alcohol (EVOH) copolymers,
 394–5, 417, 470
 Extenders, 89, 132, 786
 poly(vinyl chloride), 336
 Extrusion, 48, 49, 158, 233–6
 Extrusion moulding, 159, 160, 233, 350
 Eypel F, 383

 Falling weight tests, 192, 194
 Fibre-resin preform mouldings, 660
 Fibrides, 245
 Fillers, 124, 126–31, 355, 672
 inert, 126, 140, 279, 280
 particulate, 126–7, 279, 280
 polyethylene, 228–9
 polypropylene, 258
 poly(vinyl chloride), 337–58
 reinforcing particulate, 127, 284
 Film, 236–7
 Film extrusion processes, 235
 Film tapes, 262–3
 Finaclear, 440
 Fire, 104–109
 Firelighters, 679
 Firemaster, 592
 Fire retardants, 130, 140, 141, 593, 895
 FKM rubbers, 379–80
 Flame retarders, 104–109, 124, 145–9, 445,
 564, 595
 in foams, 797–8
 in nylon, 496, 497
 in polyethylene, 227, 229
 Flammability performance standards, 105
 Flexible foams, 792–801
 one-shot polyester foams, 792–74
 polyether foams, 795–9
 polyether prepolymers, 793–4
 properties and applications, 799–801
 Flow path ratio, 170–71
 Flow promoters, 124, 132–4
 Flow properties, 159, 163–73
 effects of environmental and molecular
 factors, 167–70

- Flow properties—*continued*
 elastic effects in polymer melts, 171–3
 in injection mould, 170–1
 terminology, 164–6
- Flow temperature, 44, 626
- Fluidised-bed techniques, 237, 349, 550, 572
- Fluon, 364
- Fluorel II, 382
- Fluorine-containing polymers, 363–84
 ethylene copolymers, 374–5
 fluorine-containing rubbers, 379–83
 hexafluoroisobutylenevinylidene fluoride
 copolymers, 379
 polychlorotrifluoroethylene copolymers,
 374–5
 polytetrafluoroethylene, 364–73
 poly(vinyl fluoride), 376
 poly(vinylidene fluoride), 376–7
 tetrafluoroethylene–ethylene copolymers,
 374
 tetrafluoroethylene–hexafluoropropylene
 copolymers, 373
- Fluoro compounds, 797
- Fluoroelastomers, 380–82
- Fluoroprene, 379
- Fluororubbers, 363, 379
- Fluorosilicones, 833
- Foams
 flexible, 791–800
 rigid and semi-rigid, 800–804
 urea-formaldehyde resins, 678–9
- Footwear, 14
- Forafon, 376
- Formaldehyde, 5, 10, 20, 97, 857–8
 polymerisation, 533–6
 preparation, 532
- Formica, 688
- Formolisation, 857–9
- Formvar, 392
- Forticel, 628
- Fortron, 593
- Fracture initiation stress, 57
- Free energy change, 84
- Free energy equation, 94
- Free radicals, 239, 283
 addition polymerisation, 25–34, 36
- Freeze-line distance, 235–6
- Friedel–Crafts agents, 34, 475, 663
- Friedel–Crafts and related polymers, 635,
 662–6
- Fringed crystallite theory, 50
- Fringed micelle theory, 50
- Frozen-in stress, 202, 204, 574
- Fumaric acid, 698
- Functionality, 38, 177
- Fungicides, 496
- Furane plastics, 9
- Furan resins, 810–13
 applications, 812–3
 preparation of intermediates, 810–11
 properties of cured resins, 812
 resinification, 811–12
- Furfural, 810–13
- Furfuryl alcohol, 678, 810–13
- Furukawa process, 240
- Gasoline, 10
- Gauche* form, 60
- Gelatine, 28
- Gel effect, 402
- Gel point, 39
- Gelvatol, 390
- Generic Temperature Index, 187
- Gilsonite, 871
- Glass-clear polyamides, 509–13
- Glass fibre, 189, 258, 498
- Glass-like polymers, 45, 64
- Glass transition temperature, 44–58, 70–71,
 185, 196
 amorphous polymers, 100, 104, 784
 and dipole polarisation, 114–17
 factors affecting, 59–64, 70, 72, 73, 88
 nylons, 493
 polyethylene, 62, 212
 poly(ethylene terephthalate) (PET), 62, 114
- Glassy resins, 56
- Glassy state, 44
- Gloss, 121, 235
- Glycerol, 23
- Glycidyl adducts, 754
- Glycidyl ether resins, 751–61
 acid hardening systems, 758–61
 amine hardening systems, 753–7, 761
 curing, 751–61
 miscellaneous, 761–4
- Glycols, 20, 127, 546–7
- Graft polymers, 27, 360
- Gramophone records, 867, 868, 869
- Granule characteristics, 159–61
- Graphite, 133
- Greases, 827
- Grignard method, 815, 818–20
- Grilamid ELY, 527
- Grilamid TR55, 511
- Growth–temperature curve, 51
- GR–S (Government Rubber–Styrene), 287,
 425
- Gutta percha, 2, 4, 7, 70, 865–6
 related materials, 865–6
- Halar, 375
- Halon, 375
- Halophosphates, 148
- Hardening systems, 641–3, 753–61
- Haze, 121, 133, 235, 434
- Heat deflection temperature under load test
 (HDT test), 188
- Heat distortion temperature test, 188, 524,
 565
- Heat stabilisers, 496, 497
- Heat stability, 96
- Henecke machine, 793–4, 798

- Henry's law, 102
 Herclor C, 548
 Herclor H, 548
 Heterogeneous nucleation, 52
 Hexafluoroisobutylene-vinylidene fluoride copolymers, 379
 Hexahydrophthalic anhydride, 750
 Hexamethylenedipamide, 70-71
 Hexamethylenediamine, 9, 21, 481
 Hexamethylenesecbacamide, 70-71
 Hexamethyleneterephthalamide, 70-71
 High-energy radiation, 76, 96-8, 99
 High-frequency heating, 161
 High-impact polystyrene (HIPS), 7, 8, 56, 57, 426, 437-40
 High-styrene resins, 289
 High-temperature polymers, 841-51, 898
 co-ordination, 850-51
 cross-linked organic, 846-7
 fluorine-containing, 841-2
 inorganic, 842-4
 ladder, 848-50
 linear with *p*-phenylene groups and other ring structures, 847-8
 spiro, 848-50
 High-vinyl polybutadienes, 291
 Hipertuf, 723
 Hitachi process, 240
 Hivalloy, 248
 HM-50, 512
 Homogeneous nucleation, 50
 Homopolymers, 27, 53, 63, 70, 226
 Horticulture, 14
 Hostaflon C2, 375
 Hostaflon ET, 374
 Hostaflon PFA-N, 377
 Hostaflon TF, 364
 Hostaflon TFB, 374
 Hostaflon TFM, 378
 Hostaform, 531, 535
 Hostalit LP HT 5060, 361
 Hostamid, 511
 Hostatec, 404
 Hot melt compositions, 353
 Hot moulding process, 799
 Housings, 897
 H-resin, 585
 Hycar 2121X38, 416
 Hycar 4021, 416
 Hydrin, 548
 Hydrocarbon radicals, 134-5
 Hydrofluoric acid, 15
 Hydrogenated nitrile rubbers, 294-5
 Hydrogenated SBS triblock polymers, 294
 Hydrogen bonding, 54, 60, 79-80, 85, 89, 91, 875
 Hydrogen bonding theory, 132
 Hydrolysis, 95, 156, 881
 Hydrophilic polymers, 420
 Hydroquinone, 26, 27
 Hydroxethyl cellulose, 632
p-Hydroxybenzoic acid, 53
 Hydroxyethylmethyl cellulose, 632
 Hydroxyl groups, 95
 primary, 796
 secondary, 796
 Hydroxypropyl cellulose, 632
 Hydroxypropylmethyl cellulose, 632
 Hygroscopic behaviour, 159
 Hypalon, 23, 67, 224, 241, 297
 Hytrel, 55, 695, 737, 790, 879
- Icdal Ti40, 516
 IEC 69-2-1 Glow Wire Test, 107
 IEC 695-2-2 Needle Flame Test, 107
 Igamid IC, 515
 Igepal CA, 226
 Ignition, 104, 105
 I-Gummi, 790
 Impact modifiers, 134, 338-9, 496, 497
 Impact strength, 45, 74-5, 216, 413-15, 567
 assessment of, 192-5
 Impact tests, 192-4
 Impingement mixing, 804
 Impurities, 127
 Induction forces, 79, 85, 89
 Injection moulding, 15, 49, 158, 160, 233, 373
 and compression moulding, 651, 674-5
 cooling rates, 174-6
 flow process, 170-1, 202
 PMMA, 409-10
 polypropylene, 263
 polystyrene, 455
 PVC, 350
 Inorganic resin, 258, 845
 Intensity factor, 93
 Interchain attraction, 59
 Intermolecular forces, 70, 75, 79-81
 International Electrotechnical Commission (IEC), 122
 International Standards Organisation (ISO), 122
 Interpenetrating polymer networks, 808
 Intrinsically electrically conducting polymers (ICPs), 887-9
 Ionic bonds, 77
 Ionic cross-linking, 54, 875
 Ionic polymerisation, 33-7
 Ionomers, 275-6, 875
 Iron dithiocarbamate, 153
 ISO 306, 188
 ISO 75, 188
 Isocyanates, 779-82, 808
 Iso-free volume, 47
cis, trans Isomerism, 70
 Isophthalic acid (IPA), 699, 718
 Isoprene, 20, 54
 Isopropenyl, 2-oxazoline (IPO), 155
 Isopropyl tri(dioctyl pyrophosphate) titanate, 131
 Isotactic polypropylene, 252-9
 additives, 258-9
 applications, 263-5

- Isotactic polypropylene—*continued*
 processing characteristics, 260–63
 properties, 252–7
 Isotactic structures, 68, 249, 251
 Ivoride, 4
 Ixef, 518
 Izod impact strength, 454, 573, 895
 Izod test, 191–4, 374, 567
- Jelutong, 866
- Kaladex, 724
 Kalrez, 382
 Kamex, 415
 Kapton, 516, 518
KBS Plastics package, 894
 Kel-F, 375
 Kematal, 531
 Kermel, 522
 Ketonex, 279
 Kevlar, 514–15
 KF, 376
 Kinel, 516
KKF data base, 895
 Klucel, 632
 Knife handles, 623
 Kodar, 719
 Kodar PETG, 730
 Kodel, 719
 Kraft papers, 653, 657, 688
 Kraton G, 298
 K-resins, 37
 Krytox, 384
K-values, 320–21
 Kynar, 376
 Kynol, 666
- Lac, 2, 867–9
 Ladder polymers, 848–50
 Laminates, 654–8, 807–8, 829–30
 Lanital, 859
 Latices, 2, 158, 181, 231–2, 355, 866
 Lead orthosilicates, 328
 Lead salicylate, 328
 Lead silicate, 328
 Lead stearate, 328, 337
 Levapren, 273
 Levapren 450, 301
 Lewis acid, 210
 Lexan, 557
 Light energy, 98
 Light magnesium carbonate, 338
 Light screens, 144, 145
 Light stabilisers, 496, 497
 Lignin, 19
 Limiting oxygen index (LOI) test, 105–6
 Linear aromatic polyesters, 607–609, 730–38
 Liquid crystal polyesters, 695, 734–8
 Liquid crystal polymers, 53, 734
- Load-bearing plastics, 897
 Lopac, 416
 Loss factor, 114
 Lubricants, 124, 132–4, 336–7, 827
 external, 133, 337
 internal, 133, 337
 nylon, 496, 497
 poly(vinyl chloride), 336–7
 Lucite, 399
 Luran S, 449
 Luranyl, 590
 Lutamer, 887
 Luvican, 472, 473
 Lycra, 790
 Lyotropic mesomorphism, 53
- Machining operations, 158
 Macroblend, 579
 Macromolecules, 19
 Magnesium stearate, 337
 Makrolons, 557, 580
 Maleic anhydride, 760
 Margard, 577
 Markets for plastics, 11–14
 Martens test, 189, 472
 Mass colouration, 149–50
 Material selection, 891–8
 computer-aided selection, 895–6
 data sources, 893–6
 economic factors affecting choice, 892–3
 establishing operational requirements, 892
 non-computer systems, 896
 Maximum service temperature, 186–70
 MBS polymers, 448–9
 Mechanical properties
 acetal resins, 538–42
 polyethylene, 217–20
 Medical applications, 17
 Melamine, 680–83
 Melamine-formaldehyde resins, 5, 7, 669,
 680–89
 applications, 688–9
 laminates, 687–8
 melamine, 680–3
 moulding powders, 683–7
 resinification, 682–3
 Melamine-phenolic resins, 689
 Melinar, 607
 Melinex, 52, 607, 695, 713, 719
 Melt flow index (MFI), 210, 216, 220, 226,
 254–6
 Melt fracture, 172
 Melting point, 40–1, 47, 70–71, 644
 crystalline, 72, 84, 86
 Melt processing of thermoplastics, 159–76,
 223
 crystallisation, 159, 175
 flow properties, 159, 163–73
 granule characteristics, 159–61
 hygroscopic behaviour, 159
 orientation and shrinkage, 159, 175–6

- thermal properties affecting cooling, 159, 174–5
- thermal properties influencing polymer melting, 159, 163–4
- thermal stability, 159, 163
- Melt processing of thermosetting plastics, 176–9
- Melt viscosity, 73, 222–3, 235, 564
- Mercaptans, 26
- Merlon T, 565
- Mesomorphic materials, 53
- Metal deactivators, 140, 141, 142
- Metalocene catalysis, 8–9, 38, 206, 207, 248, 251, 268
 - ethylene–styrene copolymers, 308–309
 - polyethylenes (m–PE), 211, 216, 217, 227–8, 248
 - linear low density (m–LLDPE), 228
 - very low density (m–VLDPE), 228
 - polypropylenes, 249, 251
 - isotactic, 259
 - syndiotactic, 259, 268
 - polystyrenes
 - syndiotactic, 424, 433
- Metal stearates, 328
- Meta-phenylenediamine, 754
- Methacrylate polymers and copolymers, 62, 421–3
- Methacrylato-chrome chloride treatments, 129
- Methanol, 532
- Methocel, 632
- Methyl cellulose, 632
- Methylaluminoxane (MAO), 251, 454
- 4,4'-Methylenedianiline, 755
- Methylene dichloride, 86
- Methyl ethyl ketone peroxide (MEKP), 702
- Methyl methacrylate, 20, 97, 208
- Methyl nadic anhydride VI, 760, 762
- Methylsuccinic acid, 60, 61
- Mica, 870
- Mica marks, 159
- Micelles, 28, 33
- Microfibrillation, 56
- Millable gums, 788
- Mindel, 602
- Modern Plastics Encyclopaedia*, 896
- Modifiers, 26
- Molar attraction constants, 91–2
- Molecular weight distribution (MWD), 40, 216–7, 243, 252
- Molecular weights, 40–1, 43–4, 62–4, 73, 87, 167–74
 - PTFE, 179
- Molecules, 40
- Moltopren, 792
- Molybdenum disulphide, 133, 372
- Molybdenum oxide, 211
- Monomers, 20, 25–8, 36
 - preparation, 207, 386–8, 390–91, 426–9
- Moplen, 247
- Mouldability index, 170
- Moulding compositions, 128, 709–12, 831, 872
- Moulding materials, 720–22
- Moulding powders, 5, 645–54, 672–5, 683–7
- Moulding shrinkage, 203, 256, 262, 501, 575
- Mowiol, 390
- Mowital, 392
- Multiblock systems, 55
- MXD-6, 513
- Mylar, 607, 695, 713, 719
- Nafion, 384
- Naphthalene, 9
- National Bureau of Standards (NBS) smoke chamber test, 109
- Native asphalt, 871
- Natural rubber, derivatives, 860–65
- Natural tack, 284
- n-Butane, 10
- N-Cyclohexylmaleimide, 360–1
- Neoflon, 373
- Neoprene, 295
- Newtonian liquids, 164–6, 169, 325
- Ni-Kieselguhr catalysts, 863
- Nitrile resins, 88, 415–17
- Nitrile rubber (NBR), 88, 281, 294–5, 416, 442
- Nitrogen-containing resins, 767–8
- Nitrosofluoroelastomers, 382
- Nomex, 514, 666
- Non-Newtonian liquids, 169
- Nonox WSP, 230
- Norbornene, 304
- Norsorex, 306
- Noryl, 589–92, 894, 897
- Notched impact strength, 566, 579
- Notch sensitivity, 192, 194
- Novolak resins, 122, 290, 639–46, 762
- NR-16, 416
- Nucleating agents, 496, 497, 886
- Nucleation, 50–51
- Nucleation-temperature curve, 51
- Number average degree of polymerisation, 30
- Number average molecular weight, 32, 174, 206, 215, 236, 702
- Nylon-6, 62, 478, 480, 486–94, 505
 - applications, 502–504, 879, 896
 - chemical nature, 854
 - in glass-filled compositions, 500
 - nucleating agent, 497
 - processing, 505
- Nylon-7, 478, 487, 488
 - applications, 505
- Nylon-9, 461, 485
 - applications, 505
- Nylon-11, 478, 480, 487, 488, 494, 505
 - applications, 402–504, 784, 879, 896
 - chemical nature, 854
 - processing, 500
- Nylon-12, 478, 485, 487, 505
 - applications, 502, 503, 879, 896
 - processing, 500
- Nylon-46, 478, 486, 487, 489, 493, 494
 - applications, 502, 896
 - processing, 500

- Nylon-56, 488
 Nylon-66, 21, 48, 49, 86, 478, 480
 applications, 502–504, 879, 896
 in glass-filled compositions, 500
 nucleating agent, 497
 polymerisation, 486
 processing, 500, 501
 structure and properties, 487–94, 505
 tensile strength, 783
 Nylon-66/610, 478
 applications, 503
 Nylon-66/610/6, 478, 490, 507
 applications, 503
 Nylon-69, 478, 486, 896
 Nylon-76, 487
 Nylon-610, 486, 487, 494, 505
 applications, 502, 503, 879, 896
 processing, 500
 Nylon-611, 487, 494
 Nylon-612, 478, 486, 494
 Nylons, 7, 9, 86, 478–9, 486–96, 502–503
 applications, 502–503
 general properties, 500–506
 glass-filled, 497–500
 glass transition temperature, 493
 processing, 500–505
 Nyrim, 505, 527
- Octo-1-ene, 217
 Octoates, 328
 Olefin addition method, 820
 Olefins, 10, 37, 207
 Oppanol, 269
 Optical properties, relation to structure,
 120–22
 Orevac, 395
 Organochlorosilanes, 820–21
 Organometallic compounds, 8, 35
 Organosols, 351, 352
 Organo-tin compounds, 329
 Orientation, 47–9, 52, 175–6
 biaxial, 49, 52, 57
 monaxial, 49, 57
 Orientation time, 45
 Orlon, 416
 Oroglas, 399
 Oroglas DR, 415
 2-Oxazolines, 155–9
 Oxetane polymers, 549–51
 Oxidation, 134, 224, 226, 881
 Oxidation retarders, 135–6
 Oxychlorination reaction, 313
 Ozone attack, 134
 Ozone effects, 288, 866
 Ozone layer, 798
- P13N, 522
 Packaging materials, 12–13, 16, 100, 154, 395,
 627
 pharmaceuticals, 886
- Paints, 565
 Palmitates, 328
 Pantalast L, 360
 Paraffins, 95
 Paraffin wax, 85
 Parel, 548
 Parkesine, 3–4, 131, 288
 Parkes process, 288
 Particle shape, 126–7
 Particle size, 126
 Partitioning, 85
 Parylene C, 586
 Parylene N, 586
 Paste injection moulding, 354
 Paste-processes, 322
 Pastes, 322–4, 350–54
 Pebax, 527
 Penton, 549–51
 Perlon U, 778, 783
 Permeability, 76, 100–103, 257, 271
 Peroxide cross-linking, 239, 240
 Peroxide decomposers, 140, 141, 142
 Peroxides, 153
 Perspex, 6, 72, 399
 Petrochemical industry, 10
 Phenol–aldehyde resins, 5
 Phenol–formaldehyde moulding powder
 applications, 652–4
 compounding, 646–9
 processing, 649–51
 properties, 652
 Phenol–formaldehyde mouldings, 5
 Phenolic laminates, 654–8
 applications, 658–61
 properties, 656–8
 Phenolic resins, 5, 9, 24, 635–66
 applications, 659–61
 chemical aspects, 639–61
 fibres, 666
 foams, 659
 Friedel–Crafts and related polymers, 662–6
 hardening, 641–3
 manufacture, 643–5
 moulding powders, 645–54
 phenolic laminates, 654–8
 raw materials, 635–9
 resorcinol-formaldehyde adhesives, 662
 Phenols, 5, 9, 140, 143, 230, 636–8
 Phenoxy resins, 606–7
 Phenylene groups, 62
 2-Phenylindole, 330
 Phillips polymers, 214, 216
 Phillips process, 8, 206, 208, 210–11, 217, 275
 Phosgenation process, 560–61
 Phosphates, 144
 Phosphites, 140
 Photochemical processes, 144
 Photochemical radiation, 96–8
 Photoconductivity, 15, 472
 Photodegradants, 154–5, 881
 Photophysical processes, 144
 Photoresists, 395–6

- Phthalates, 148
 Phthalic acid, 23
 Phthalic anhydride, 9, 759
 Piezoelectric properties, 376
 Pigments:
 diene rubbers, 284
 nylon, 496
 polyethylene, 228, 229
 polypropylene, 260, 261
 PVC, 338
 urea-formaldehyde moulding powders, 671, 673
 Pifofilm, 853
 Pitches, 871
 Plascams system, 894
 Plastic crystals, 53
 Plasticisers, 87–9, 116, 124, 131–2, 159, 742
 in moulding powders, 673
 nylon, 496, 497
 poly(vinyl chloride), 191, 318, 330–36
 rubbers, 284
 Plastics:
 characteristics, 15
 degradable, 880–86
 developments 1900–1930, 4–6
 developments since 1939, 7–9
 fire and, 104–109
 future for, 14–17
 markets for, 10–14
 natural, 1–3
 raw materials, 9–10
 vinyl, 6–7
 Plastigels, 351–3
 Plastisols, 351–2
 Plate-out, 337, 338
 Plex 8535-F, 415
 Plexidur, 413
 Plexiglas, 397
 Plexigum, 397
 Pleximid, 415
 Pluronic, 796
 PNF rubber, 383
 Pocan, 724
 Polar carboxyl groups, 60
 Polar groups, 62
 Polarisation charge, 112
 Polarity of bonds, 77–8, 85
 Polar materials, 117
 Polar theory, 132
 Polectron, 472
 Polish additives, 826
 Pollution, 16
 Poly-IF4, 379
 Poly-2F4, 379
 Polyacetal (polyformaldehyde) resins, 97
 Polyacetals, 20, 51, 84, 105, 163, 531–54
 acetal resins, 533–46
 aldehyde polymers, 546
 applications, 544–6
 oxetane polymers, 549–51
 polyethers from glycols and alkylene oxides, 546–7
 polysulphides, 551–4
 preparation of formaldehyde, 532
 Polyacetylines, 120
 Poly(acrylic acid), 423
 Polyacrylonitrile, 96
 Polyaddition, 22
 Polyalkenamers, 305–306
 Polyamide-imides, 524–5
 Polyamides, 9, 21, 478–516
 additives, 496–8
 applications, 502–505
 aromatic, 509–16
 crystalline aromatic, 513–16
 elastomeric, 526–8
 enhanced solubility, 505–507
 general properties of nylons, 490–496
 glass-clear, 509–13
 glass-filled nylons, 498–500
 intermediates for aliphatic polyamides, 490–96
 low molecular weight, 769
 polymerisation for aliphatic polyamides, 486–7
 processing of nylons, 490–492
 structure and properties of aliphatic polyamides, 487–90
 Polyarylates, 695
 Polyaryl ether ketones, 502–506
 Poly-*p*-benzamide, 53
 Polybenzoxazines (PBZs), 667–7
 Poly(γ -benzyl-L-glutamate), 53
 Poly-3,3-bischloromethyloxacyclobutane, 46
 Polyblends, 55–7, 74, 294
 Polybut-1-ene, 268–9
 atactic, 269
 Polybutadiene, 35, 128, 290–91
 1,2-Polybutadiene, 307–308
 1,4-Polybutadiene, 20
 cis-1,4-Polybutadiene, 62, 440
 Poly(butylene terephthalate) (PBT), 107, 695, 724–7, 897
 Polycaprolactones, 741, 793
 Polycarbodi-imide resins, 807–808
 Polycarbonate/ABS grades, 107
 Polycarbonate/polyether-imides, 107
 Polycarbonate-polybutylene teraphthalate alloys (PC-PBT), 579
 Polycarbonate-polyethylene teraphthalate alloys (PC-PET), 579
 Polycarbonates, 8, 62, 86, 114, 556–61
 alloys based on bis-phenol A polycarbonates, 578–9
 applications of bis-phenol A polycarbonates, 575–8
 carbonic ester polymers, 580–82
 commercial grades, 564–7
 ester exchange, 558–60
 general properties, 568–73
 phosgenation process, 560–61
 polyester carbonates and block copolymers, 579–80
 polymer preparation, 558–61

- Polycarbonates—continued
 processing characteristics, 573–5
 production of intermediates, 557–8
 structure and properties, 561–8, 897
- Poly(carborane siloxanes), 834
- Polychloroacrylates, 104
- Polychlorotrifluoroethylene copolymers (PCTFE), 363, 374–5
- Polycrystallinity, 49
- Poly-(1,4)-cyclohexylenedimethylene Terephthalate-co-isophthalate), 727–8
- Poly-(1,4)-cyclohexylenedimethylene-terephthalate) (PCT), 727–8
- Polycyclohexyethylene (PCHE), 275
- Poly(2,6-dibromo-1,4-phenylene oxide), 592–3
- Poly(2,6-dimethyl-*p*-phenylene oxide) (PPO), 587–92
 modified, 589–90
 polyamide, 592
 processing and application, 589
 structure and properties, 581–9
 styrenic, 590–2
- Polydimethylsiloxane rubbers, modified, 832–4
- Polyesteramide BAK resins, 882
- Polyester carbonates, 579–80
- Polyester foams, 792–3
 one-shot, 792–3
- Polyester-glass fibre laminates, 703–707
- Polyester resins, 694–742
 allyl resins, 708–709
 curing systems, 702–704
 diluents, 699–701
 fibre-forming, 713–19
 film-forming, 713–19
 glass fibre laminates, 704–708
 highly aromatic linear, 730–38
 laminating, 7
 liquid crystal, 734–8
 moulding compositions, 709–12
 plasticisers, 743
 poly(butylene terephthalate), 724–1
 polycaprolactones, 741
 poly-(1,4)-cyclohexylenedimethylene-terephthalate) (PCT), 728–30
 poly(ethylene terephthalate) moulding materials, 720–22
 poly(pivalolactone), 739–40
 production, 701–702
 raw materials, 696–701
 rubbery, 742
 saturated acids, 698–9
 special materials, 699–701
 structure and properties, 704
 surface coatings, 740–43
 thermoplastic elastomers, 737–9
 unsaturated, 696–709
 water-extended polyesters, 708
- Polyesteramides, 528–9
- Polyesters, 17, 114
 linear aromatic, 9, 20, 55, 607–609, 730–38
 liquid crystal, 695, 734–8
- Polyetheretherketones (PEEK), 521
- Polyether foams, 794–9
 one-shot, 794–9
 quasi-prepolymer, 794
- Polyether-imides, 107
- Polyetherimides, 525–6
- Polyether prepolymers, 793–4
- Polyethers, 546–9
 elastomeric, 547–51
- Polyethylene, 6–9, 19, 20, 37, 49, 205–45
 additives, 228–32
 amorphous density, 93
 applications, 241–5, 896
 branching, 213–15
 brittle point, 221
 characteristics, 241
 chemical properties, 223–6
 chlorinated, 67, 240–1
 chlorosulphonated, 301
 cross-linked, 225, 230, 239–41
 crystallinity, 212, 215, 299
 crystallisation, 50, 67
 density, 215, 220
 electrical properties, 163, 207, 224, 226, 241
 fillers, 228, 229
 flow properties, 222
 glass transition temperature, 62, 212
 grades, 213
 high-density (HDPE), 8, 206–7, 211, 243–4, 266
 high molecular weight, 212, 238
 light stability, 93
 limitations, 241
 linear low-density (LLDPE), 206–7, 211, 215, 216, 222–3, 244
 film, 243
 properties, 227
 low-density (LDPE), 206, 211, 217, 243–4
 low molecular weight, 206, 238
 mechanical properties, 218–20
 melt viscosity, 72, 221–3, 235
 molecular weight differences, 216
 oxidation, 224, 226
 permeability, 102
 polarisation, 112
 polymerisation, 208–11
 high-pressure, 207, 208–9
 interfacial, 561
 making linear low-density polyethylene, 211
 Phillips process, 208, 210–11, 217
 Standard Oil Company (Indiana) process, 210, 211
 Ziegler processes, 208, 209–10, 238
 preparation of monomer, 207
 processing, 163, 232–8
 properties of LLDPE and VLDPE, 227
 solvents for, 84, 219
 structure and properties, 212–17
 thermal properties, 163, 221–3, 232
 ultra-high molecular weight (UHMWPE), 244

- very high molecular weight (VHMWPE), 238
 very low-density (VLDPE), 206–207, 211, 227
 viscosity, 167, 222
 yield strength, 73
 Poly(ethylene naphthalate) (PEN), 723–4
 Poly(ethylene terephthalate) (PET), 52–3, 121, 156, 417, 695, 717–18
 glass transition temperature, 62, 114
 moulding materials, 720–22
 Polyflon, 364
 Polyformaldehydes, 20, 34, 51, 163
 Polyhaloaldehydes, 546
 Poly-1,6-heptadiyne, 120
 Polyhydantoin resins, 609–10
 Polyhydroxybutyrate-valerate copolymers (PHBV), 883–6
 Polyimides, 480, 516–21
 modified, 521–6
 Polyisobutylene (PIB), 34, 112, 229, 269–70
 Polyisocyanurates, 805–808
 1,4-Polyisoprene, 20, 440
Polymat PC system, 895
 Polymer composites, 236
 Polymeric flow promoters, 134
 Polymerisation:
 addition, 20, 21, 23, 24, 27, 37
 free radical, 25–34, 36
 initiation stage, 24–6, 29–30, 32, 36
 termination stage, 24, 25, 29, 32, 33, 35
 aliphatic polyamides, 486–7
 anionic, 34, 35, 36
 bulk, 27, 402–404
 cationic, 34
 condensation, 20, 21, 23, 24, 39–40
 co-ordination, 37, 210
 double bond, 23
 emulsion, 28, 33, 432
 formaldehyde, 533–6
 ionic, 33–7
 living, 37
 mass, 429–30
 number average degree of, 30
 PCTFE, 374–5
 polyethylene, 208–11
 poly(methyl methacrylate), 401–404
 polytetrafluoroethylene, 364–5
 poly(vinyl acetate), 388–9
 poly(vinyl chloride) (PVC), 315–17
 poly(vinyl fluoride), 376
 rearrangement, 22
 ring-opening, 22
 solution, 431
 styrene-based plastics, 429–33
 suspension, 248, 315, 404, 431–2
 vinyl chloride polymers, 315–17
 Polymerisation, addition, propagation or growth stage, 24, 25, 29
 Polymerisation kinetics, 29
 Polymerisation methods, 17
 Polymerisation temperature, 26
 Polymer polyols, 441, 796
 Polymers:
 amorphous, 41, 45, 81, 85
 bimodal, 244, 249
 co-ordination, 850–51
 cross-linked, 91, 846–7
 crystalline, 81, 84, 86
 definition, 19
 dispersion, 369, 371
 electrical conductivity, 110–17, 120
 electronic applications, 119–20
 emulsion, 321
 ethylene, 209
 fluorine-containing, 841–2
 granular, 369, 370
 heat-resisting, 841–51
 high, 19
 high-temperature, 841–51, 897
 inorganic, 842–6
 intrinsically conductive, 886–8
 ionically conductive, 886–8
 ladder, 848–50
 liquid crystal, 53, 734
 living, 36
 mass, 322
 MBS, 448–9
 monodisperse, 36
 non-polar, 77, 84–6
 polar, 81, 85, 86, 89, 110, 114
 polydisperse, 36
 solubility, 80–94
 spiro, 848–50
 stereoregular, 37
 thermosetting acrylic, 418–19
 Poly(methacrylimide), 420–21
 Poly(methyl acrylate), 423
 Polymethylene, 215
 Poly(methyl methacrylate), 6, 20, 43, 48, 49, 400–413
 additives, 409
 applications, 413–17
 copolymerisation, 413–15
 depolymerisation, 96, 163
 dipoles, 114, 116
 general properties, 405–409
 impact strength, 73
 melt viscosity, 72
 plasticised, 88
 polymerisation, 401–404
 preparation of monomer, 400–401
 processing, 181, 409–11
 solubility parameter, 91
 stability, 98, 163
 structure and properties, 405, 896
 thermal degradation rate, 96–7
 viscosity, 167
 Poly(methyl methacrylimides) (PMM), 415
 Poly-(4-methylpent-1-ene) (P4MP1), 270–72
 applications, 273
 general properties, 13, 84, 272
 processing, 273
 structure and properties, 272–3

- Poly(*n*-dodecyl methacrylate), 62
 Polynorborene, 306–307
 Polyolefins, 6, 8, 95
 Polyox, 547
 Polyoxacyclobutane, 46
 Polyoxymethylene, 20, 105
 Poly(parabanic acids), 610–11
 Poly(phenylene oxides), 586
 alkyl substituted, 586–93
 halogenated, 586
 poly(2,6-dibromo-1,4-phenylene oxide),
 592–3
 Polyphenylenes, 584–5
 Poly(phenylene-sulphides), 107, 593–6
 amorphous polyarylene sulphides, 596
 Poly-*p*-phenylene, 120
 Poly-*(p*-phenylene sulphide), 120
 Polyphthalamide plastics, 516
 Poly(pivalolactone), 739–40
 Polypropylene, 8, 37, 53, 247–68
 additives, 260–61
 applications, 243, 244, 265–7, 878–80,
 896
 atactic, 68, 267–8, 289
 chlorinated, 268
 fillers, 260
 isotactic, 8, 68, 73, 249, 253–9
 linear, 67
 optical properties, 121
 preparation of, 248–51
 processing characteristics, 262–5, 273
 solvents for, 84
 stability, 96
 structure and properties, 251–3, 270–71
 syndiotactic, 267–8
 Polypropylene adipate, 333
 Polypropylene sebacate, 333
 Polypyrrole, 120, 888, 889
 Polysiloxane–polyetherimide copolymers,
 840
 Polystyrene, 6, 7, 9, 20, 43, 896
 expanded, 455–60
 high-impact (HIPS), 7, 8, 56, 57, 426,
 437–40
 impact strength, 73
 melt viscosity, 72
 molecular weight, 174
 oriented, 460–61
 processing, 163, 454–5
 solvents for, 81
 stereoregular, 454
 structure and properties, 433–4
 syndiotactic, 426, 433, 454–5
 toughened (TPS), 437–40
 Polystyrol, 426
 Polysulphides, 21, 22, 551–2, 769–70
 Polysulphones, 9, 596–602
 applications, 601–602
 blends, 602
 general properties, 600–1
 processing, 601
 structure and properties, 599–600
 Polytetrafluoroethylene (PTFE), 7, 13, 49, 67,
 72, 364–73
 additives, 371–2
 applications, 372–3
 chemical reactivity, 95
 density, 73
 general properties, 367–9
 molecular weight, 179
 polymerisation, 364–5
 preparation of monomer, 364
 processing, 363, 369–71
 solvents for, 84
 stability, 96, 97
 structure and properties, 365–7
 Poly(trimethylene terephthalate) (PTT), 728
 Polyurethane-acrylic blends, 808
 Polyurethane foam, 13, 14
 Polyurethanes, 22, 54, 778–808
 coatings and adhesives, 845
 crystalline moulding, 783–4
 fibres, 782–4
 flexible foams, 791–800
 polycarbodi-imide resins, 807–808
 polyurethane-acrylic blends, 808
 rigid and semi-rigid foams, 800–804
 rubbers, 784–91
 properties and applications, 788
 self-skinning foams and RIM process,
 803–804
 thermoplastic, 783–90
 Poly(vinyl acetals), 96, 391–4
 poly(vinyl butyral), 393–4
 poly(vinyl formal), 392–3
 Poly(vinyl acetate) and derivatives, 23, 72,
 386–97
 ethylene-vinyl alcohol copolymers, 394–5
 polymerisation, 388–4
 poly(vinyl acetals), 391–4
 poly(vinyl alcohol), 393–5
 poly(vinyl cinnamate), 399–400
 preparation of monomer, 386–8
 properties and uses, 389
 Poly(vinyl alcohol), 23, 28, 67, 69, 87, 389–91
 applications, 391, 882, 897
 structure and properties, 390–91
 Poly(vinyl butyral), 393–4
 Poly(vinyl carbazole), 12, 104, 472–4
 Poly(vinyl chloride) (PVC), 6, 13, 17, 20, 54
 additives, 342
 applications, 355–8
 chlorinated, 359–60
 compounding ingredients, 325–45
 copolymers, 354–5
 copolymers with propylene, 360
 crystalline, 359
 dipoles, 114
 extenders, 336
 fillers, 337–8
 formulations, 342–5
 glass transition temperature, 56
 graft polymers, 360
 impact-modified, 56

- injection moulding, 350
- latices, 355
- lubricants, 336–7
- melt viscosity, 72
- optical properties, 122
- pastes, 350–54
- pigments, 338
- plasticised (PPVC), 73, 86–7, 100, 312, 347–9, 896
- plasticisers, 318, 330–36
- polymeric impact modifiers and processing aids, 338–42
- polymerisation, 315–17
- processing, 181, 346–55
- properties of compounds, 345–6
- solvents for, 86
- stabilisers, 325–30
- stability, 96, 98, 163
- structure, 317–25
- unplasticised (UPVC), 73, 181, 349–50, 356–8
- Poly(vinyl cinnamate), 395–6
- Poly(vinyl ethers), 475–6
- Poly(vinyl fluoride) (PVF), 376
- Poly(vinyl formal), 67, 392–3
- Poly(vinylidene chloride), 53, 62, 73
- Poly(vinylidene fluoride) (PVDF), 12, 376–7
- Poly-*m*-xylylene, 513–14
- Poly-*p*-xylylene, 585
- Postech, 796
- Powder moulding techniques, 237
- Powder processes, 237
- Power factor, 110, 114, 231
- Preforming, 370
- Prepolymers, polyether, 794–5
- Prepolymer systems, 788–91
- Prevulcanisation inhibitors, 283
- Primary bonds, 76, 77
- Printed circuit board components, 120
- Processing:
 - ABS plastics, 447–8
 - acetal resins, 524–3
 - nylons, 500–502
 - phenol-formaldehyde moulding powder, 649–51
 - polycarbonates, 573–5
 - poly-(2,6-dimethyl-*p*-phenylene oxide) (PPO), 589
 - polyethylene, 163, 232–8
 - poly(methyl methacrylate), 181, 409–11
 - poly-(4-methylpent-1-ene) (P4MP1), 273
 - polypropylene, 262–5, 273
 - polystyrene, 454–5
 - polysulphones, 601
 - polytetrafluoroethylene, 363, 369–71
 - poly(vinyl chloride) (PVC), 181, 346–55
 - urea-formaldehyde resins, 774–5
- Processing aids, 284, 342
- Processing techniques, 158–82
 - casting processes, 182
 - melt processing of thermoplastics, 159–76
 - melt processing of thermosetting plastics, 176–9
 - poly(vinyl chloride), 181, 346–55
 - in rubbery state, 179–82
 - solution processes, 181
 - suspension processes, 181
- Processing temperatures, 161, 163, 167–8, 369, 371
- Product design, 184–204
 - distortion, voids and frozen-in stress, 202–204
 - recovery from deformation, 184, 201–202
 - rigidity of plastics materials, 184–90
 - stress-strain-time behaviour, 195–201
 - toughness, 184, 190–95
- Propiofan, 397
- Propylene, 360
 - copolymers with *N*-cyclohexylmaleimide, 360–61
- Propylene glycol, 696
- Propylene oxide, 796
- Protein plastics, 19, 860
- Proton acceptors, 86, 89, 132
- Proton donors, 86
- Pseudo-elastic design approach, 200
- Pseudoplasticity, 324
- Pyre ML, 516, 518
- Pyro-Chek 68 PB, 452
- Pyroelectric properties, 376
- Pyromellitic dianhydride IV, 760
- Quacorr RP100A, 813
- Questa, 454
- Quiana, 515
- Quinone, 27
- Rabinowitsch equation, 165
- Radel, 596
- Radiation cross-linking, 239
- Rafaelite, 871
- Rainwear, 14
- Rapra Abstracts*, 894
- Raschig process, 636, 637
- Rate constant, 45
- Rate of flow, 178
- Raw materials, 9–10
- Reaction injection moulding (RIM) process, 182, 501–505, 779, 804
- Reaction rate, 29–30
- Recovery from deformation, 184, 201–202
- Reflectance, 121
- Refractive index, 120–21, 565
- Regulators, 26
- Reinforced reaction injection moulding (RRIM) process, 804
- Reinforcement, 126
- Reinforcing fillers, 496, 497
- Relative permittivity, 110, 112, 122
- Relative temperature index (RTI), 186–7
- Relaxation time, 236

- Release agents, 826
 Rennet, 855
 Repulsion effect, 60
 Resin XP5272, 450
 Resitol, 641
 Resols, 641, 643–6, 661
 Resorcinol-formaldehyde adhesives, 662
 Rexene, 268
 Rheopexy, 324
 Rhodoviol, 390
 Ribbed smoked sheet (RSS), 286
 Ricinoleates, 328
 Ricinoloxazolimalleinate, 155
 Rigid foams, 801–804
 Rigidity of plastics materials, 184–90
 assessment of maximum service
 temperature, 186–90
 Rilsan N, 512
 Ring products, 96
 Ring structures, 62
 Rohacell, 421
 Rossi–Peakes flow test, 626, 650
 Rotation about bonds, 59–60
 Rotational casting methods, 354
 Rotational energies, 59
 Rotational moulding, 237–8, 244
 Rubber-bridge theory, 56
 Rubber hydrochloride, 863
 Rubbers, 2–3
 acrylate, 417–18
 aliphatic olefin, 299–305
 brominated butyl, 302
 butadiene-acrylonitrile, 128
 butadiene-pentadiene, 296
 butyl, 34, 229, 302
 cast polyurethane, 785–7
 chlorinated, 302, 864–5
 chloroprene, 295–6
 cold, 292
 constant-viscosity, 287
 cyclised, 278, 863
 diene, 281–96
 dimethylsilicone, 832
 epichlorhydrin, 548
 ethylene-propylene, 8, 73, 229–30, 243,
 878
 fluorine-containing, 379–83
 hot, 292
 liquid silicone, 839–40
 milkable gums, 788
 modified polydimethylsiloxane, 832–4
 natural, 19, 52, 81, 96, 285–9, 860–65
 nitrile, 88, 281, 294–5, 416, 442
 polybutadiene, 290–91
 polypropylene, 260
 polyurethanes, 784–90
 silicone, 837–8
 styrene-butadiene, 127, 128, 281, 291–5,
 425, 438–9
 synthetic, 7, 35
 synthetic polyisoprene, 289–90
 terpolymer, 277
 thermoplastic, 9, 37
 thermoplastic diene, 296–9
 thermoplastic polyolefin (TPORs), 302–4,
 878
 thermoplastic polyurethane, 790–91
 Rubber-to-metal bonding, 863–4
 Rubbery cyclo-olefin (cyclo-alkene) polymers,
 304–307
 aliphatic polyalkenamers, 305–306
 chlorine-containing copolymers, 307
 polynorbornene, 306
 Rubbery materials, 9, 64, 67, 127–8, 227,
 874–5
 Rubbery polymers, 45, 100
 Rubbones, 865, 881
 Rucodor, 360
 Runaway reactions, 208
 Rynite, 608, 694, 721
 Ryton, 593
 Ryurex X-15, 450

 Saflex, 393
 Salicylic esters, 98
 SAN polymers, 416, 441, 453
 Santonox, 230
 Saran, 53, 466, 470
 Saran-wrap, 469
 Saturated hydrocarbons, 10
 Schatzki crankshaft effect, 47, 539
 Screw-preplasticising, 233
 Sebacates, 333
 Sebacic acid, 481–2
 Secondary bonds, 76
 Secondary valence forces, 76
 Seedlac, 867, 868
 Sekisui process, 240
 Self-skinning foams, 804
 Semiconductors, 120
 Semi-rigid foams, 800–804
 Setting operations, 158
 Sharkskin, 216, 223, 235
 Shear modulus, 198
 Shear rates, 164–9, 172–3, 221
 Shear strains, 198
 Shear stress, 164–5, 173
 Shear thinning, 324
 Sheet moulding compounds, 711
 Shellac, 2, 4, 9, 19, 869–70
 applications, 869–70
 chemical composition, 868
 occurrence and preparation, 867–8
 properties, 868–9
 Shrinkage, 176, 233, 370
 Side-chain crystallisation, 421
 Silanes, 129, 130
 Silicas, 338
 Silicates, 338
 Silicone fluids, 823–8
 applications, 826–8
 general properties, 829–30
 preparation, 823–4

- Silicone resins, 828–32
 applications, 829–32
 laminates, 829–31
 moulding compositions, 831
 preparation, 828
 properties, 828–9
 Silicone rubbers, 832–40
 compounding, 836–37
 cross-linking, 837–8
 dimethylsilicone, 832
 fabrication, 837–8
 liquid, 839–40
 modified polydimethylsiloxane, 832–4
 polysiloxane-polyetherimide copolymers, 840
 properties and applications, 838–9
 Silicones, 72, 814–40
 direct process, 818–20
 Grignard method, 818
 nomenclature, 815–16
 olefin addition method, 820
 preparation, 816–17, 821–23
 preparation of intermediates, 817–21
 properties, 816–17, 821–23
 rearrangement of organochlorosilanes, 820–21
 silicone fluids, 823–8
 silicone resins, 828–32
 silicone rubbers, 832–40
 sodium condensation method, 820
 Sintering, 370–71
 Sioplas process, 239
 Skybond, 522
 Slip additives, 237
 Slip agents, 228, 229, 238
 Slush moulding, 354
 Soamol, 395
 Sodium carboxymethyl cellulose, 632
 Sodium chloride, 22
 Sodium condensation method, 820
 Sodium naphthalene, 35
 Sodium polysulphide, 22
 Softening point, 188–90, 216, 413–15
 Solef, 376
 Solprene, 297
 Solubility of polymers, 76, 80–94
 extenders, 89
 parameters, 81–94, 100, 341
 plasticisers, 87–9
 thermodynamics, 93–4
 Solution processes, 181
 Solvent crazing resistance, 48
 Solvent recovery, 27
 Solvents, 81, 84–7, 572
 Soreflon, 364
 Spandex fibres, 784, 791
 Spanzelle, 790
 Specific inductive capacity, 112
 Spherulites, 50, 52, 121, 217
 Spilac, 419
 Spiro polymers, 848–51
 Spraying techniques, 237
 Stabilisers, 325–30
 Staflen, 211
 Sta-Flow, 360
 Stamping, 179
 Standard Malaysian Rubber (SMR) scheme, 286
 Standard Oil Company (Indiana) process, 205, 210
 Starch, 19
 Steam moulding, 457–9
 Stearic acid, 127, 128, 133
 Stereoregularity, 64, 67, 69, 454
 Stereospecificity, 37
 Steric hindrance, 60, 251
 Sticklac, 867, 868
 Stilan, 403
 Strain softening, 219
 Stress–log time curves, 198
 Stress relaxation, 198
 Stress–strain curves, 198, 219
 Stress–strain–time behaviour, 195–201
 assessment of long-term behaviour, 198–200
 creep curves, 198–200
 WLF equations, 196–8
 Stress-whitening, 341, 342, 360
 Structural foams, 458–60
 Structure and properties, 59–74
 acetal resins, 533–6
 aliphatic polyamides, 487–90
 celluloid, 619–21
 cellulose acetate, 624–6
 chemical properties, 76–109
 electrical properties, 110–22
 epoxide resins, 772
 mechanical properties, 72–4
 nylon-66, 487–94, 505
 optical properties, 120–22
 polycarbonates, 561–3
 poly-(2,6-dimethyl-*p*-phenylene oxide) (PPO), 587–9
 polyester resins, 704
 polyethylene, 212–17
 poly(methyl methacrylate), 405, 896
 poly-(4-methylpent-1-ene) (P4MP1), 270–3
 polypropylene, 251–3, 270–7
 polystyrene, 433–4
 polysulphones, 599–600
 polytetrafluoroethylene, 365–7
 poly(vinyl alcohol), 390–91
 poly(vinyl chloride), 317–25
 shellac, 868–9
 silicone resins, 828–9
 silicone rubbers, 838–9
 silicones, 816–17, 821–3
 thermal properties, 59–71
 urea-formaldehyde resins, 675–7
 Styramic HT, 452
 Styrene, 10, 428–9
 Styrene–acrylonitrile copolymers, 74, 441
 rubber-modified, 448–50

- Styrene-based plastics, 425–62
 - ABS plastics, 441–7
 - applications, 461–3
 - butadiene-styrene block copolymers, 451–6
 - expanded polystyrene, 455–60
 - general properties, 434–7
 - grades available, 432–3
 - oriented polystyrene, 460–61
 - polymerisation, 429–33
 - preparation of monomer, 426–9
 - commercial preparation, 427–9
 - laboratory preparation, 426–7
 - processing of polystyrene, 454–9
 - properties and structure of polystyrene, 433–4
 - stereoregular polystyrene, 454
 - styrene-acrylonitrile copolymers, 441
 - styrene-maleic anhydride copolymers, 450
 - styrene purification, 428–9
- Styrene–butadiene copolymers, 63
- Styrene–butadiene rubber (SBR), 127, 128, 282, 291–4, 425, 438–9
 - applications, 863
 - high-styrene resins, 291
- Styrene–isoprene–styrene (SIS) triblocks, 298–9
- Styrene–maleic anhydride copolymers, 450
- Styron, 426
- Sulphonated EPDM, 305
- Sulphonation process, 636
- Sulphonyl chloride, 67
- Sunlight, 97
- Supec, 593
- Surface coatings, 149, 741–3, 870
- Surface crystallisation, 235–6
- Surface dyeing, 149
- Surface resistivity, 110, 122
- Surgery, 14, 17
- Surlyn, 278
- Suspension processes, 181
- Suspensions, 27, 158
- Syndiotactic structures, 68, 251, 426, 433, 454–5
- Synergism, 141–2
- Synthetic polyisoprene, 289–90
- Synthetic resins, 128
- Synthetic rubbers, 7, 35

- Tackifiers, 284
- Tacticity, 68
- TAF process, 459
- Talc, 28, 338
- Targor, 248
- Tecnoflon, 380, 382
- Tedlar, 376
- Tedur, 593
- Teflex, 373
- Teflon, 364, 373
- Teflon AF, 378
- Teflon EPE, 378
- Teflon FEP, 373, 377
- Teflon PFA, 377

- Tefzel, 374
- Teklan, 470
- Telomerisation, 484
- Temperature coefficient, 197
- Tenal, 531
- Tenite butyrate, 628
- Tenite PCDT, 603
- Tenite polyterephthalate, 608
- Tenite propionate, 628
- Tenite PTMT, 724
- Tensile creep test, 200
- Tensile impact tests, 192, 194
- Tensile modulus, 198
- Tensile strength, 127, 216
- Terephthalic acid, 10
- Ternary copolymers, 27
- Terpolymer rubber, 277
- Terpolymers, 27
- Tertiary amines, 755
- Tertiary butylcatechol, 27
- Terylene, 52, 584, 607, 695, 713
- Tetrachloromethylbenzene, 37
- Tetraflon, 364
- Tetrafluoroethylene–ethylene copolymers (ETFE), 374
- Tetrafluoroethylene–hexafluoropropylene copolymers, 373–4
- Tetrahydrofuran, 17, 86, 100
- Tetramers, 178
- Tetramethylene terephthalate (4GT), 738–9
- Thermal degradation, 96–7, 184, 186
- Thermal expansion coefficients, 197
- Thermal properties, 159, 161–2, 174–5
 - acetal resins, 538–42
 - polyethylene, 163, 221–3, 232
- Thermal radiation, 96–8
- Thermal stability, 163, 186–7
- Thermodynamic law, 84
- Thermodynamics, and solubility, 93–4
- Thermoelastomers, 87
- Thermoplastic diene rubbers, 296–9
- Thermoplastic elastomers, 737–9, 874–80
 - applications, 878–80
 - costs, 878
 - future, 880
 - polyamide, 879
 - polyester, 879
 - polyolefin, 260
 - polyurethane, 55, 879
- Thermoplastic fluoroelastomers, 383–4
- Thermoplastic polyolefin rubbers (TPORs), 302–304, 878
- Thermoplastics, 23–4
 - melt processing, 159–76
- Thermosetting acrylic polymers, 418–19
- Thermosetting composition, 177
- Thermosetting plastics, 2, 3, 23–4, 81, 87–9
 - melt processing, 176–9
- Thermosetting resins, 7
- Thermotropic materials, 53
- Thermotropic mesomorphism, 53
- Thiokol A, 552

- Thiokol FA, 552, 553
 Thiokol ST, 552, 553
 Thiourea resins, 5, 691–2
 Thixotropy, 324
 Ticona, 244
 Tipped polyols, 796
 Tipping, 796
 Titanium coupling agents, 131
 Titanium halide, 8
 Titanium tetrachloride, 8, 34, 209
 Toluene, 9, 77
 Toluene di-isocyanate (TDI), 779–82, 786, 797
 Topanol CA, 230
 Topas, 280
 Torlon-2000, 518, 524
 Torlon, 516, 524
 Total flow, 178
 Tough-brittle transition, 191
 Toughness, 184, 190–95, 215
 assessment of impact strength, 192–5
 Toxicity, 27, 76, 103–104
 TQ (tubular quench) process, 263
 Tracking, 110, 122, 652, 687
 Tradlon, 610
 Transesterification process, 560
 Transfer agents, 31
 Transfer moulding, 120, 651
trans form, 60
trans isomer, 69
 Transition point, 253
 Transitions, 65
 Transmittance, 121
 Transparency, 121, 271, 707, 896
 Triacetin, 624
 Tribasic lead sulphate, 327
 Triblock copolymers, 54, 55, 875
 Tricel, 627
 Trichlorethylene, 26
 Trichloromethylbenzene, 37
 Triethylenetetramine, 753
 Trifunctional monomers, 42–43
 Triglycidyl isocyanurate, 767
 Tri-isopropylphenol phosphates, 333
 Trimellitates, 333
 Trimellitic anhydride V, 760
 Trimers, 178
 Trioxane, 22
 Triphenyl phosphate, 624
 Trisnonyl phenyl phosphite, 328
 Tritolyl phosphate (TTP), 54, 87–9, 132, 148, 331, 863
 Trixylyl phosphate (TXP), 148, 331
 Trogamid T, 478, 509, 511, 512
 Tromsdorff effect, 402
 Tubular processes, 235–6
 Typly, 863

 Udel, 596, 599, 602
 UL, 746B Relative Temperature Index Test, 186, 187
 UL94–5VA rating, 106
 UL94–5VB rating, 106–7
 UL94–5V rating, 594
 UL94 flammability ratings, 105–8, 149, 516
 UL94-V1 rating, 513
 UL94-V2 rating, 573
 UL94-VO rating, 573, 593
 Ultem Siltem STM1500, 526, 840
 Ultradur, 724
 Ultraform, 531
 Ultranyl, 592
 Ultrapek, 604
 Ultraviolet absorbers and related materials, 98, 134, 140–47, 567, 573
 light screens, 144, 145
 photochemical processes, 144
 photophysical processes, 144
 quenching agents, 144, 145
 Ultraviolet attack, 134
 Ultraviolet light transmission, 15
 Underwriters Laboratories, 105, 149, 186, 594, 732
 continuous use temperature index, 513
 Unzipping reactions, 97
 U-Polymer, 731
 Urea, 5
 Urea–formaldehyde resins, 669–80
 adhesives, 677–8
 applications, 676–7, 679–80
 firelighters, 679
 foams, 675
 moulding materials, 671–7
 processing, 674–5
 properties, 676–7
 raw materials, 669
 resinification theories, 670–71
 Urepan, 619, 788
 Urethane foams, 22

 Valox, 310SEO, 107
 Valox, 338, 107, 608, 724
 Vamac, 277, 301
 Van der Waals forces, 75
 Vaporisation, 79, 90
 Vectra, 579, 736
 Vedril, 399
 Versamids, 503
 Vertifoam process, 793
 Verton, 499
 Vespel, 516, 518
 Vestan, 719
 Vestenamer, 305
 Vestolit BAU, 360
 Vestoran, 590
 Vicat softening point (VSP), 188, 189, 415, 421, 442–3, 565
 polycarbonates, 578, 579
 Viclan, 466, 470
 Victrex, 596, 603, 604, 606
 Victrex SRP, 735
 Vinnol K, 360
 Vinoflex MP400, 476

- Vinyl, evolution, 6-7
Vinyl acetate, 10
Vinyl chloride polymers, 6, 9, 10, 12, 20, 311-60
 applications, 355-8
 commercial, 320-25
 compounding ingredients, 325-45
 polymerisation, 315-17
 preparation, 313-15
 processing, 346-54
 PVC compounds, 345-6
 structure of poly(vinyl chloride), 317-25
Vinyl chloride-vinyl acetate copolymers, 867
Vinylidene chloride, 466-70
Vinylidene chloride-vinyl acrylonitrile copolymers, 470
Vinylidene chloride-vinyl chloride copolymers, 466-70
Vinyl monomer, 24
Vinyl plastics, 6
Vinyl silane cross-linking, 239
Vinyl thermoplastics, 466-77
 coumarone-indene resins, 471-2
 poly(vinyl carbazole), 472-4
 poly(vinyl ethers), 475-6
 poly(vinyl pyrrolidone), 474-5
 vinylidene chloride polymers and copolymers, 466-70
Vinyltrichlorsilane, 129
Viscosity, 164-9, 177, 178, 197-8
Viscous deformation, 172, 195-6
Viscous flow, 202
Viscous slippage, 198
Vistanex, 269
Viton GLT, 380
Voids, 202-204, 322
Volan, 129
Volume resistivity, 110, 122
Vulcanisation, 2, 3, 24, 153, 282, 288, 303
 dynamic, 302, 880
 elastomeric polyethers, 548
 FKM rubbers, 380
 natural rubber derivatives, 860-66
 polysulphides, 553
Vulcanisation accelerators, 282
Vulcanised rubber, 81, 87-9
Vulcanite, 3
Vulcaprene, 529, 742
Vulkollan rubbers, 784, 787, 791, 794
Vyrene, 790
Warerite, 688
Water-extended polyesters, 708
Water repellants, 826-7
Water-soluble plastics, 897
Weak links, 97
Weathering, 76, 99, 231, 371, 373, 577, 878
Weight average molecular weight, 32, 168, 216, 218, 366
Williams, Landel and Ferry equation (WLF equation), 197-8
Woodflour, 647, 672, 676
Work function, 93
Wurtz-Fittig reaction, 584
Wurtz reaction, 820
X4006, 526
Xenoy, 579
XR3808, 526
XR-resin, 384
Xydar, 735, 737
Xylenols, 645
Xylok resins, 663
Xylonite, 4, 621
Xyron, 590
Yield strength, 74
Zalak, 382
Zein, 860
Ziegler-Natta catalysts, 37-8, 248, 270, 273, 292, 294, 359, 585
 development, 8, 289, 290, 299, 304, 305
Ziegler processes, 8, 206, 209-10, 211, 216, 238
Ziegler-type catalysts, 247, 248, 485
Zinc oxide, 127