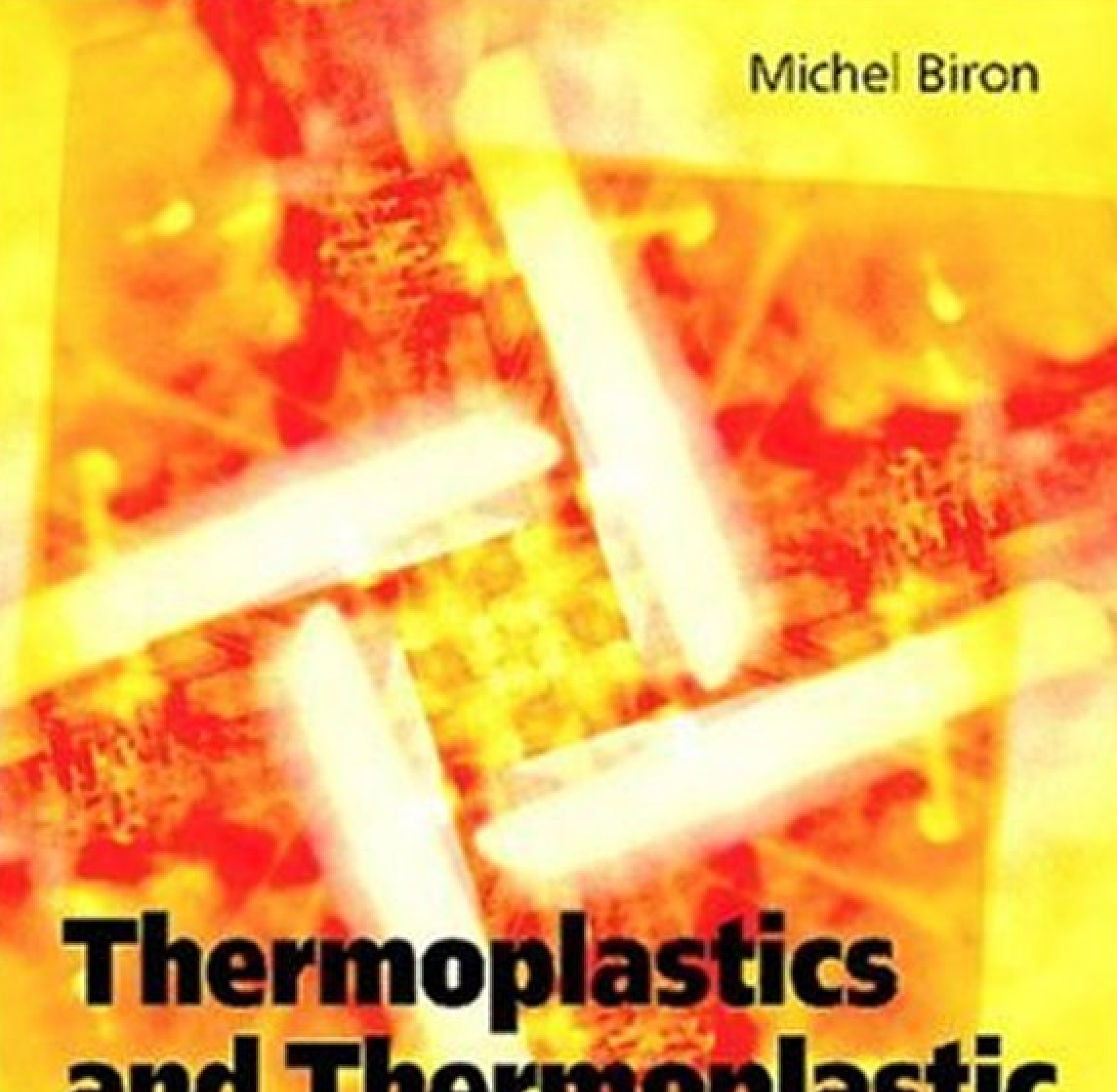
Michel Biron



Thermoplastics and Thermoplastic Composites

Technical Information for Plastics Users

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List of Tables and Figures

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Disclaimer

All the information contained in this book was collected from reliable documentation and verified as far as possible. However, we cannot accept responsibility for the accuracy of the data.

The characteristic data, economic figures, general assessments and indications concerning all the properties are not guaranteed and cannot be used for calculations, computations or other operations to determine design, cost-effectiveness or profitability.

Readers must verify the technical data and economic figures with their own suppliers of raw materials or parts, and other current technical and economic sources. Prototypes and tests under operating conditions are essential.

Acronyms and abbreviations

5V	UL fire rating
AAGR	Average Annual Growth Rate
ABS	Acrylonitrile-Butadiene-Styrene
ACM-V	Vulcanized acrylate rubber
ACS	Acrylonitrile Chlorinated polyethylene Styrene
AES or AEPDS	Acrylonitrile EPDM Styrene
AMC	Alkyd Moulding Compound
ArF or AF	Aramid Fibre
ASA	Acrylonitrile Styrene Acrylate
ASTM	American Society for Testing and Materials
ATH	Aluminium TriHydrate
BF	Boron Fibre
BMC	Bulk Moulding Compound
BMI	BisMaleImide
BOPP	Bi-axially Oriented PolyPropylene
CA	Cellulose Acetate
CAB	Cellulose AcetoButyrate
CAD	Computer Aided Design
CBT	Cyclic polyButadiene Terephthalate
CE	Cyanate Ester
CF	Carbon Fibre
CFC	ChloroFluoroCarbon
CIC	Continuous Impregnated Compound
CM or CPE	Chlorinated PolyEthylene
CNT	Carbon NanoTube
COC or COP	Cyclic Olefin Copolymers or Cyclic Olefin Polymers
CONC	Concentrated solution
COP or COC	Cyclic Olefin Polymers or Cyclic Olefin Copolymers
COPE or TPEE	COPolyEster TPE
CP	Cellulose Propionate

CPE or CM	Chlorinated PolyEthylene
CPVC or PVC-C	Chlorinated PVC
CS	Compression Set
CUT	Continuous Use Temperature under unstressed state
Cy	PolyCyanate
DAP	DiAllyl Phthalate
DCPD	Poly(DiCycloPentaDiene)
DMC	Dough Moulding Compound
DMTA	Dynamic Mechanical Thermal Analysis
DRIV	Direct Resin Injection and Venting
DSC	Differential Scanning Calorimeter
DTA	Differential Thermal Analysis
EB	Elongation at Break
EBA, EGMA, EMAH, EEA, EAA	Ethylene-acid and ethylene-ester copolymers, e.g. Ethylene-ButylAcrylate
ECTFE	Ethylene monoChloroTriFluoroEthylene
EE, E&E	Electrical & Electronics
EMA	Ethylene-MethAcrylate ionomers
EMI	ElectroMagnetic Interference
EP	EPoxy
EPDM rubber	Terpolymer ethylene, propylene, diene
EPS	Expandable (or Expanded) PolyStyrene
ESC	Environmental Stress Cracking
ESD	ElectroStatic Discharge
ETFE	Ethylene-TetraFluoroEthylene
EVA, E/VAC, EVAC, VAE, EVM	Ethylene-VinylAcetate copolymers
EVOH	Ethylene-Vinyl alcohol copolymers
F-PVC	Flexible PVC
FEP	Fluorinated Ethylene Propylene
FR	Fire Retardant
GF	Glass Fibre
GFRP	Glass Fibre Reinforced Plastic
GMT	Glass Mat Thermoplastic
HB	UL fire rating
HDPE or PE HD	High Density PolyEthylene
HDT	Heat Deflection Temperature

HPGF	High-Performance short Glass Fibre reinforced polypropylene
HSCT	High Speed Civil Transport (aircraft)
HTPC	Hybrid ThermoPlastic Composite
HTV	High Temperature Vulcanization
ILSS	InterLaminar Shear Strength
IMC	In-Mould Coating
IMD	In-Mould Decoration
IPN	Interpenetrating Polymer Network
IRHD	International Rubber Hardness
IRM	International Referee Material
ISO	International Standardization Organization
LCP	Liquid Crystal Polymer
LCTC	Low Cost Tooling for Composites
LDPE or PE LD	Low Density PolyEthylene
LEFM	Linear Elastic Fracture Mechanics
LFRT	Long Fibre Reinforced Thermoplastic
LFT	Long Fibre reinforced Thermoplastic
LGF	Long Glass Fibre
LIM	Liquid Injection Moulding
LLDPE	Linear Low Density PolyEthylene
LRTM	Light RTM
LSR	Liquid Silicone Rubber
LWRT	Light Weight Reinforced Thermoplastic
MABS	Methylmethacrylate-Acrylonitrile-Butadiene-Styrene
MBS	Methyl methacrylate-Butadiene-Styrene
MDPE	Medium Density PolyEthylene
MF	Melamine
MPR	Melt Processable Rubber (TPE)
NB	No Break
NVH	Noise Vibration Harshness
O&M	Organization & Methods department
OPET	Oriented PET
OPP	Oriented PP
PA	PolyAmide
PA-T	Transparent amorphous PolyAmide
PAA	PolyArylAmide
PAI	PolyAmide Imide

PAEK	PolyArylEtherKetone
PAN	PolyAcryloNitrile
PAS	PolyArylSulfone
PB	PolyButene-1 or PolyButylene-1
PBI	PolyBenzImidazole
PBO	PolyphenyleneBenzoOxazole
PBT or PBTP	PolyButyleneTerephthalate
PC	PolyCarbonate
PCB	Printed Circuit Board
PC-HT	PolyCarbonate – High Temperature
PCL	PolyCaproLactone
PCT	PolyCyclohexylene-dimethylene Terephthalate
PCTA	Terephthalate/Isophthalate
PCTFE	PolyChloroTriFluoroEthylene
PCTG	PolyCyclohexylene-dimethylenediol/ethyleneglycol Terephthalate
PE	PolyEthylene
PEAR	PolyEtherAmide Resin
PEBA	PolyEther Block Amide
PEEK	PolyEtherEther Ketone
PEG	PolyEthylene Glycol
PEI	PolyEtherImide
PEK	PolyEtherKetone
PEN	PolyEthylene Naphthalenedicarboxylate
PES or PESU	PolyEtherSulfone
PET or PETP	PolyEthylene Terephthalate
PETG	PolyEthyleneGlycol/cyclohexylene-dimethylenediol Terephthalate
PETI	PhenylEthynyl with Imide Terminations
PEX	Crosslinked PolyEthylene
PF	Phenolic resin
PF1Ax	PF general purpose, ammonia free
PF2Cx	PF heat resistant, glass fibre reinforced
PF2Dx	PF impact resistant, cotton filled
PF2E1	PF mica filled
PFA	PerFluoroAlkoxy
PGA	PolyGlycolic Acid
PHA	PolyHydroxyAlkanoate
PHB	PolyHydroxyButyrate

PI	PolyImide
PK	PolyKetone
PLA	PolyLactic Acid
PMI	PolyMethacrylImide
PMMA	Poly MethylMethAcrylate
PMP	PolyMethylPentene
PO	PolyOlefin
POM	PolyOxyMethylene or Polyacetal
PP	PolyPropylene
PPA	PolyPhthalAmide
PPE	PolyPhenylene Ether
PP/EPDM	Unvulcanized EPDM blended with polypropylene or block copolymerized PP-EPDM (reactor TPO) – (TPE) (TPO)
PP/EPDM-V	Vulcanized EPDM dispersed in polypropylene (TPE) (TPV)
PP/IIR-V	Vulcanized butyl rubber dispersed in polypropylene (TPE) (TPV)
PP/NBR-V	Vulcanized nitrile rubber dispersed in polypropylene (TPE) (TPV)
PPO	PolyPhenylene Oxide
PPS	PolyPhenylene Sulfide
PPSU	PolyPhenyleneSulfone
Prepreg	Preimpregnated
PS	PolyStyrene
PSU	PolySulfone
PS-X or XPS	Crosslinked PolyStyrene
PTFE	PolyTetraFluoroEthylene
PTMT or PBT	PolyTetraMethylene Terephthalate or PolyButyleneTerephthalate
PTT	PolyTrimethylene Terephthalate
PUR	PolyURethane
PV	Pressure*Velocity
PVA or PVAL or PVOH	PolyVinyl Alcohol
PVAC	PolyVinyl ACetate
PVAL or PVA or PVOH	PolyVinyl ALcohol
PVB	PolyVinyl Butyrate
PVC	PolyVinyl Chloride
PVDC	PolyVinyliDene Chloride
PVC-C or CPVC	Chlorinated PVC
PVC-U	Unplasticized PVC

PVDF	PolyVinyliDene Fluoride
PVF	PolyVinyl Fluoride
PVOH or PVAL or PVA	PolyVinyl Alcohol
RF	Radio Frequency
RFI	Resin Film Impregnation
RH	Relative Humidity or Hygrometry
RIM	Reaction Injection Moulding
RIRM	Resin Injection Recirculation Moulding
RP	Reinforced Plastic
RRIM	Reinforced Reaction Injection Moulding
RT	Room Temperature
RTM	Resin Transfer Moulding
RTP	Reinforced ThermoPlastic
RTV	Room Temperature Vulcanization
SAN	Styrene AcryloNitrile
SATUR	Saturated solution
SB	Styrene Butadiene
SBC	Styrenic Block Copolymer
SBS	Styrene-Butadiene-Styrene (TPE)
SCRIMP	Seeman's Composite Resin Infusion Moulding Process
SEBS	Styrene Ethylene/Butylene Styrene (TPE)
SEPS	Styrene Ethylene/Propylene Styrene (TPE)
SGF	Short Glass Fibre
Si	Silicone
SIS	Styrene Isoprene Styrene (TPE)
SMA	Styrene Maleic Anhydride
SMC	Sheet Moulding Compound
SMMA	Styrene-Methyl MethAcrylate
SN curve	Plot of stress or strain (S) leading to failure after N cycles of repeated loading
SOL	Solution
SP-polyimides	Condensation polyimides
SPC	Statistical Process Control
SPDF	Super Plastic Diaphragm Forming
SRRIM	Structural (Reinforced) Resin Injection Moulding
TAC	TriAllyl Cyanurate
TDI	Toluene-2,4-DiIsocyanate
TFE	TetraFluoroEthylene

TGA	ThermoGravimetric Analysis
TGV	High-speed train
TMC	Thick Moulding Compound
TP	ThermoPlastic
TPE	ThermoPlastic Elastomer
TPE/PVC	PVC-based TPE, alloys of PVC and rubber (TPE) (TPO or TPV)
TPEE or COPE	ThermoPlastic Elastomer Ester
TPO	ThermoPlastic Olefin
TPR	ThermoPlastic Rubber
TPS	ThermoPlastic Styrenic
TP/Si-V	TPV of a vulcanized silicone rubber dispersed in a thermoplastic phase
TPU	ThermoPlastic polyUrethane
TPV	ThermoPlastic Vulcanizate
TR	Temperature-Retraction procedure
TS	Tensile Strength
UD	UniDirectional composite
UF	Urea-Formaldehyde
UHMWPE or PE-UHMW	UltraHigh Molecular Weight PE
UL	Underwriters Laboratories
Unkn.	Unknown
UP	Unsaturated Polyester
UV	UltraViolet
V0 to V2	UL fire rating
VAE	Ethylene-VinylAcetate copolymers
VARI	Vacuum Assisted Resin Injection
VARTM	Vacuum Assisted RTM
VE	VinylEster
VIP	Vacuum Infusion Process
VST	Vicat Softening Temperature
WPC	Wood Plastic Composite
XLPE	Crosslinked LDPE
XPE or PEX	Crosslinked PolyEthylene
XPS or PS-X	Crosslinked PolyStyrene
ZMC	A highly automated process using Moulding Compounds

Chapter 1

Outline of the actual situation of plastics compared to conventional materials

No engineer or designer can be ignorant of plastics, but the decision to use a new material is difficult and important. It has both technical and economical consequences. It is essential to consider:

- the actual penetration of the material category in the industrial area
- the abundance or scarcity of the material and the process targeted
- the functionalities of the device to be designed
- the characteristics of the competing materials
- the cost
- the processing possibilities
- the environmental constraints.

The goal of the facts and figures that follow is to help clarify quickly the real applications for thermoplastics and thermoplastic composites and the relative importance of the various material families and processes involved.

1.1 Polymers: the industrial and economic reality compared to traditional materials

1.1.1 Plastic and metal consumption

Usually, material consumption is considered in terms of weight (Table 1.1), but it is also interesting to examine:

- the consumption or production in terms of volume (Table 1.2), which is the most important for fixed part sizes
- the consumption linked to the rigidity of the engineering materials (Table 1.3).

In this last case, if the reference material, of unitary section area and unitary length, is M_0 (volume $V_0 = 1$) with Young's modulus E_0, it can be replaced with material M_1 with unitary

Table 1.1 World consumption or production by weight (million tonnes)

Year	Plastic	Steel	Aluminium
1970	30	595	10
1975	40	644	13
1980	48	716	16
1985	68	719	17
1990	92	770	19
1995	122	752	20
2000	147	848	24
2003	160	884	26
2005 (prediction)	170	918	28

Table 1.2 World consumption or production in terms of volume (million m^3)

Year	Plastic	Steel	Aluminium
1970	30	76	4
1975	40	82	5
1980	48	92	6
1985	68	92	6
1990	92	99	7
1995	122	96	7
2000	147	109	9
2003	160	113	10
2005 (prediction)	170	116	11

Table 1.3 World consumption at equal tensile stress (million $m^3 \times$ Young's modulus)

Year	Plastic	Steel	Aluminium
1970	60	15 000	300
1975	80	16 500	375
1980	96	18 500	450
1985	136	18 500	450
1990	184	20 000	525
1995	244	19 000	525
2000	294	22 000	675
2003	320	22 500	750
2005 (prediction)	340	23 000	800

length, section area S_1, and Young's modulus E_1. For the same tensile stress:

$$S_1 * E_1 = 1 * E_0$$

S_o:

$$S_1 = E_0 / E_1$$

The volume of M_1 with the same rigidity as M_0 is:

$$V_1 = S_1 * 1 = V_0 * E_0 / E_1$$

Therefore:

$$V_1 * E_1 = V_0 * E_0$$

Table 1.3 compares the rigidity-modified data for consumption expressed as volume (million m^3)× Young's modulus (GPa). The elastic tensile modulus is arbitrarily fixed at 2 for plastics, 200 for steel and 75 for aluminium.

The annual consumption of plastics is:

- intermediate between those of steel and aluminium in terms of weight, that is, roughly a sixth of the consumption of steel and six times the consumption of aluminium for recent years
- higher than those of steel and aluminium in terms of volume in recent years: roughly 1.4 times the consumption of steel and 15 times that of aluminium
- lower than those of steel and aluminium if we reason in terms of equal rigidity: plastic consumption is equivalent to roughly 1% of the steel consumption and half that of aluminium.

The average annual growth rate over the past 35 years is:

- 5.1% for plastics
- 1% for steel.

Over the 15 years from 1985 to 2000, the average annual growth rates are confirmed for plastics and steel (Table 1.4). Polymer composites also show a progression exceeding that of metals. For the period 2000–2005, plastics slow down slightly and steel slightly accelerates but the gap between annual growth rates is not significantly affected.

Figure 1.1 displays these normalized changes in world consumption.

1.1.2 Mechanical properties

1.1.2.1 Intrinsic mechanical properties

Expressed as Vickers hardness, the hardnesses of the engineering materials cover a vast range, broader than 1 to 100. The handful of example figures in Table 1.5 does not cover the hardnesses of rubbers, alveolar polymers and flexible thermoplastics.

Table 1.4 Growth in world consumption*

Year	Plastics	Polymer composites	Aluminium	Steel
1985	100	100	100	100
1990	135	150	112	107
1995	179	160	118	104
2000	216	190	141	115
2005 (Prediction)	265	200	165	130

* Normalized on 100 for reference year 1985

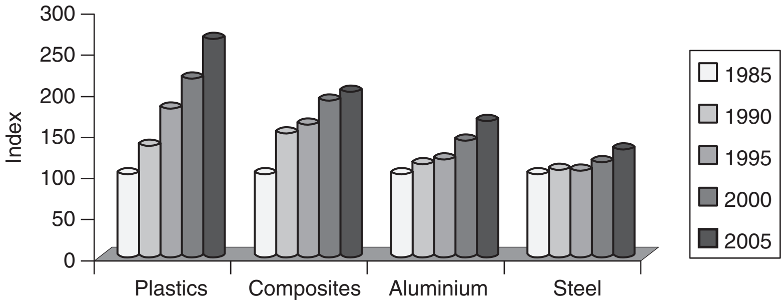


Figure 1.1. Evolution of world consumption – base 100 for 1985

Table 1.5 Examples of material hardnesses

	Aluminium	PMMA	Steel	Tungsten	Glass	Tungsten carbide
Hardness	15	22	150	350	540	2400

Figure 1.2 visualizes the hardnesses of a broad range of materials.

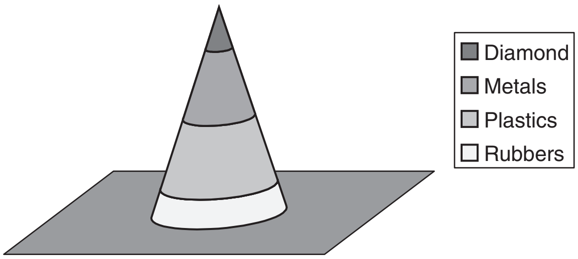


Figure 1.2. Hardness of some materials

Table 1.6 indicates the tensile characteristics of some traditional materials (metals, glass, wood) and polymers in various forms:

- unidirectional composites, highly anisotropic
- SMC (sheet moulding compound), 2D quasi-isotropic
- LFRT (long fibre reinforced thermoplastics), more or less quasi-isotropic
- short fibre reinforced plastics, 3D isotropic

- neat polymers, 3D isotropic
- alveolar polymers.

The indicated figures are examples and do not constitute exhaustive ranges.

Figures 1.3 and 1.4 and Tables 1.6 and 1.7 show that:

- unidirectional composites in the fibre direction can compete with existing metals and alloys. However, it is necessary to moderate this good classification by taking into account the high anisotropy of these composites, with low resistance and modulus in the direction perpendicular to the fibres;
- the highest-performance engineering plastics compete with magnesium and aluminium alloys.

Table 1.6 Examples of tensile properties of various materials

	Tensile strength (MPa)		Yield stress (MPa)		Tensile modulus (GPa)
		Metals & alloys			
	Min.	Max.	Min.	Max.	
Steel	300	1800	200	1700	210
Titanium	1000	1000			105
Aluminium	75	700	30	550	75
Magnesium	85	255	43	190	44
		Glass			
Bulk glass	40	300			
Fibre glass	2000	3500			55–85
		Wood			
Wood	5	16			11
		Polymer composites			
Unidirectional CF	1800	3000			260
Unidirectional ArF	1400	1500			87
Unidirectional GF	800	800			28
SMC CF	280	350			50
SMC GF	48	285			21
		Long glass fibre reinforced polymers			
Epoxy (EP) LGF	90	90			16
		Short glass fibre reinforced polymers			
EP GF & mineral	50	100			14
PEEK 30% CF	210	210			17
PEEK 30% GF	165	165			10
		Neat polymers			
PEEK	80				4
EP	70	90			4
		Foamed polymers			
Expanded & foamed plastics	0.05	16			0.02–0.5

ArF: aramid fibre; CF: carbon fibre; GF: glass fibre; LGF: long glass fibre; UD: unidirectional

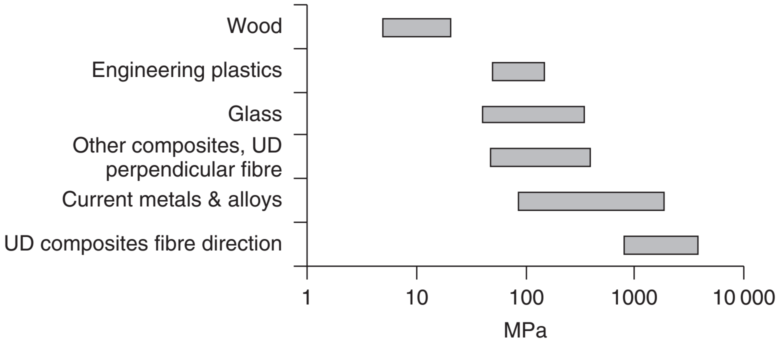


Figure 1.3. Tensile strength (MPa) of various materials

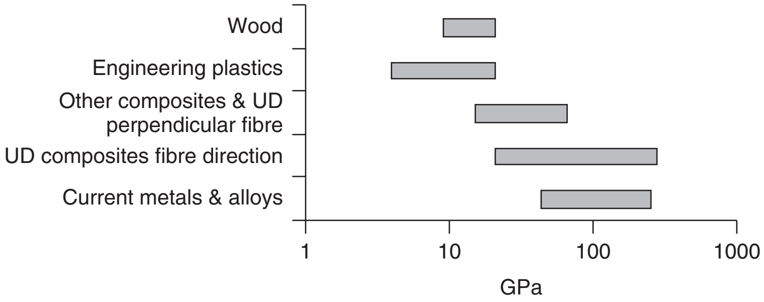


Figure 1.4. Tensile modulus (GPa) of various materials

1.1.2.2 Specific mechanical properties

The specific mechanical properties take account of the density and consider the performance to density ratio (performance/density).

Due to the high densities of metals, the resulting classification (Table 1.7 and Figures 1.5 and 1.6) is different from that of the mechanical properties alone.

Figures 1.5 and 1.6 and Table 1.7 show that:

- unidirectional composites in the fibre direction can compete with existing metals and alloys and some have the highest performances. However, it is necessary to moderate this good classification by taking account of their high anisotropy, with low resistance and modulus in the direction perpendicular to the fibres;
- the best of the other engineering plastics cannot match the high performance of the magnesium and aluminium alloys in terms of rigidity.

1.1.3 Thermal and electrical properties

Metals are characterized by their low coefficients of thermal expansion and their strong thermal and electric conductivities, whereas wood (except where there is excessive moisture), and neat polymers have high coefficients of thermal expansion and are electrical and thermal insulators.

The loading or reinforcement of the polymers changes these characteristics:

- the coefficients of thermal expansion decrease
- carbon fibres, steel fibres and carbon blacks lead to more or less conducting polymer grades.

Table 1.7 Specific tensile properties of various materials

	Density	Specific tensile strength (MPa)		Specific tensile modulus (GPa)
Metals & alloys				
		Min.	Max.	
Steel	7.8	38	231	27
Titanium	4.5	220	222	23
Aluminium	2.8	27	250	27
Magnesium	1.75	49	146	25
Glass				
	2.5	16	120	
Wood				
	0.4–0.75	12	21	13–27
Polymer composites				
Unidirectional CF	1.56	1154	1923	167
Unidirectional ArF	1.37	1022	1095	64
Unidirectional GF	1.9	421	421	15
SMC CF	1.5	187	233	33
SMC GF	1.8	27	158	3–12
Long glass fibre reinforced polymers				
EP LGF	1.8	50	50	9
Short glass fibre reinforced polymers				
EP GF & mineral	1.9	26	53	5–9
PEEK 30% CF	1.44	146	146	12
PEEK 30% GF	1.52	109	109	7
Neat polymers				
PEEK	1.3	62	62	3
EP	1.2	58	75	3
Foamed polymers				
Expanded & foamed plastics	0.02–0.9	2	17	0.4–0.6

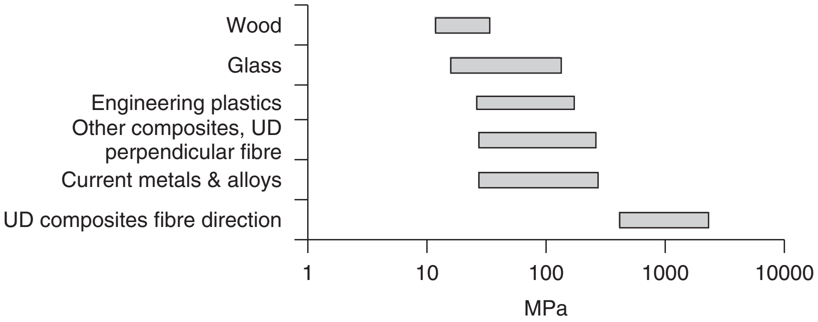


Figure 1.5. Specific tensile strength (MPa) of various materials

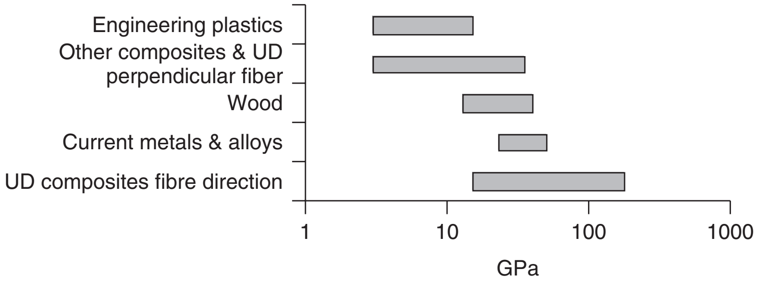


Figure 1.6. Specific tensile modulus (GPa) of various materials

Table 1.8 displays some thermal and electrical characteristics of polymers and conventional materials.

Table 1.8 Physical and electrical properties of various materials

	Coefficients of thermal expansion (10^{-6})	Thermal conductivity (W/m.K)	Electrical resistivity ($\log_{10}$)
Metals & alloys			
Copper	16–20	115–394	−7 to –8
Aluminium	20–25	237	−7 to −8
Glass			
	8.8	1.2	12–15
Wood			
		0.1–0.2	5: High RH 8: for 12% moisture
Polymer composites			
Unidirectional CF			
Fibre direction	−0.04	50	
Perpendicular to the fibre direction	38	1	
Unidirectional GF			
Fibre direction	12	0.4	11–15
Perpendicular to the fibre direction	22	0.2	11–15
SMC CF	3		
SMC GF	11–20		11
Short fibre reinforced polymers			
Epoxy CF	3–12	0.6–1.1	
Epoxy GF	12–20	0.6–1.2	14
PEEK 30% CF	15–40	0.9	5
PEEK 30% GF	15–20	0.4	15
Neat polymers			
Epoxy	60	0.2	15
PEEK	40–60	0.25	16
Foamed polymers			
Plastics		0.025–0.120	

1.1.4 Durability

Metals and glass generally support higher temperatures than polymers, which present a more or less plastic behaviour under stresses, leading to:

- an instant reduction of the modulus and ultimate strength
- a long-term creep or relaxation.

Polymers are sensitive to thermo-oxidation and, for some, to moisture degradation. Provided they are not subject to moisture degradation, polymers, unlike current steels, are not sensitive to corrosion.

The thermal behaviour of the polymers can be characterized:

- immediately, by the HDT (heat deflection temperature) under a 1.8 MPa load. For the chosen examples (Table 1.9), the values vary between 150°C and 320°C;
- in the long term, by the CUT (continuous use temperature) in an unstressed state. For the examples chosen, the values vary from 130°C to 320°C.

Table 1.9 displays some thermal characteristics of polymer and conventional materials.

Metals have minimum melting points higher than 400°C and often higher than 1000°C, whereas:

- thermoplastics melt in the range of 120°C for polyethylene to 350°C for high-performance thermoplastics
- thermosets, because of the crosslinking, cannot melt but decompose without melting as the temperature increases.

Polymers are sensitive to a greater or lesser degree to photo-degradation, which can limit their exterior uses. On the other hand, many polymers, including the commodities, are resistant to the chemicals usually met in industry or at home and displace the metals

Table 1.9 Thermal properties of various materials

	Melting point (°C)	Long-term resistance temperature in an unstressed state (°C)	Heat deflection temperature, HDT 1.8 MPa (°C)
		Metals	
Iron	1535		
Aluminium	1660		
Magnesium	649		
		Polymer composites	
UD EP/CF	Infusible	150–230	
UD EP/GF	Infusible	150–230	
SMC EP/GF	Infusible	130–230	290
		Short fibre reinforced polymers	
PEEK 30 CF	334	250	320
PEEK 30 GF	334	250	
EP/CF	Infusible	130–230	
EP/GF	Infusible	130–230	290
		Neat polymers	
PEEK	334	250	150
Epoxy	Infusible	130–230	

previously used for these applications: galvanized or cast iron and steel for domestic implements, gas and water pipes, factory chimneys, containers for acids and other chemicals.

Polymers, like other materials, are sensitive to fatigue. Figure 1.7 plots some examples of fatigue test results according to the logarithm of the number of cycles leading to failure.

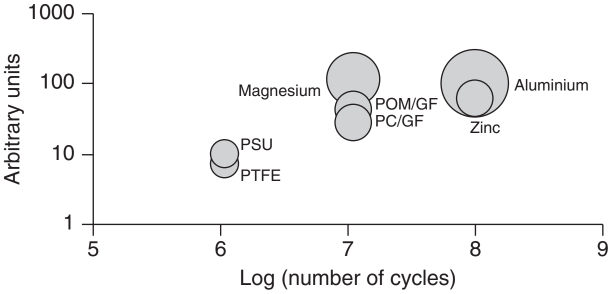


Figure 1.7. Examples of fatigue failure

To compensate for their handicaps in terms of properties compared to the traditional materials, polymers have effective weapons:

- manufacturing in small quantities or large series of parts of all shapes and all sizes, integrating multiple functions, which is unfeasible with metals or wood
- possibility of selective reinforcement in the direction of the stresses
- weight savings, lightening of structures, miniaturization
- reduction of the costs of finishing, construction, assembling and handling
- aesthetics, the possibilities of bulk colouring or in-mould decoration to take the aspect of wood, metal or stone, which removes or reduces the finishing operations
- durability, absence of rust and corrosion (but beware of ageing), reduction of maintenance operations
- transparency, insulation and other properties inaccessible for the metals.

1.1.5 Material costs

Obtaining information on prices is difficult and costs are continually fluctuating. The figures in the following tables and graphs are only orders of magnitude used simply to give some idea of the costs. They cannot be retained for final choices of solutions or estimated calculations of cost price.

Usually, the material costs are considered versus weight but it is also interesting to examine:

- the cost per volume, which is the most important for a fixed part size
- the cost linked to the rigidity for the engineering materials.

1.1.5.1 Cost per weight of various materials

Table 1.10 and the graph in Figure 1.8 demonstrate that plastics and polymer composites are much more expensive than metals, even more specialized ones such as nickel.

Table 1.10 Order of magnitude of some material costs (€/kg)

	Minimum	Maximum
Thermoplastics (TP)		
Commodity: polyethylene, PVC, PS. . .	<1	3
Engineering	2	10
Speciality	5	90
Fluoroplastics	14	110
Thermosets (TS)		
Commodities	<2	7
Engineering	3	10
Speciality	20	160
Metals		
Steel	0.2	0.4
Special steel	1.4	2
Aluminium	1	2
Titanium	3	4
Copper	1.5	1.7
Nickel	5	6
Wood		
	0.6	0.8
Polymer composites		
Composite CF	140	
Composite ArF	100	
Composite GF	50	
SMC	2–5	

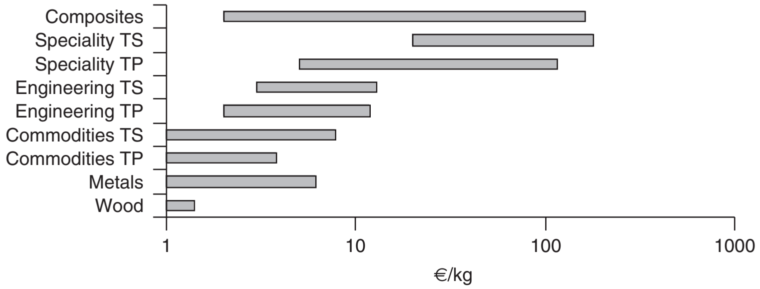


Figure 1.8. Examples of material costs (€/kg)

1.1.5.2 Cost per volume of various materials

As for the specific mechanical properties, the high densities of metals modify the classification (Table 1.11 and Figure 1.9) of the various materials.

According to the cost per volume:

- plastics are competitive: only the very high performance plastics or composites are more expensive than metals
- wood is the cheapest material.

Table 1.11 Order of magnitude of some material costs (€/litre)

	Minimum	Maximum
Thermoplastics		
PE, PVC, PS, PP	0.8	4
ABS, SAN, SMA	3	5
PMMA, PC, PA, POM, PET, PBT, PPE	3	8
Speciality PA	7	12
PPS, PSU	7	30
PEI, PAI	20	40
PTFE	25	50
PEEK, LCP	20	120
ETFE, ECTFE, FEP, PFA	60	220
Thermosets		
DCPD	5	7
Epoxy	4	10
Melamine	3	5
Phenolic	3	10
Polyimide	80	260
Polycyanate	24	60
Polyurethane	4	9
Urea formaldehyde	2	3
Unsaturated polyester	3	7
Vinylester	5	9
Metals		
Steel	1.6	3.2
Special steel	10	16
Aluminium	3	6
Titanium	13	18
Copper	13	15
Nickel	45	54
Wood		
	0.5	0.6
Polymer composites		
Composite CF	220	
Composite ArF	140	
Composite GF	100	
SMC GF	4–10	

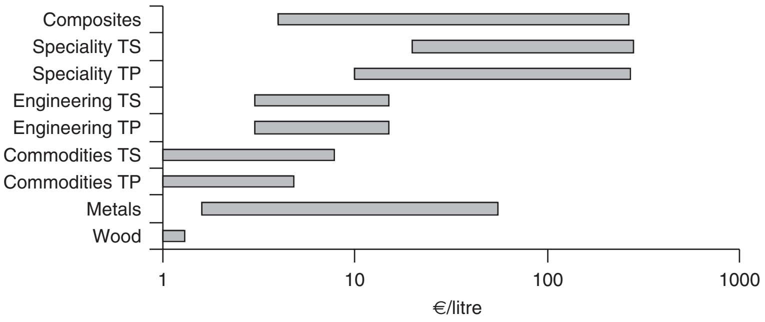


Figure 1.9. Examples of material costs (€/litre)

1.1.5.3 (Performance/cost per litre) ratios of various materials

Table 1.12 and Figures 1.10 and 1.11 confirm that polymer composites are more expensive than metals for the same mechanical performances. It is necessary to exploit their other properties to justify their use.

Table 1.12 [Tensile properties/cost per litre] ratios of various materials

	Tensile strength (MPa per €/litre)		Tensile modulus (GPa per €/litre)
	Metals & alloys		
	Min.	Max.	
Steel	187	562	65–130
Titanium	55	77	7
Aluminium	25	117	17
	Wood		
	10	27	20
	Polymer composites		
Unidirectional CF	8	14	1
Unidirectional ArF	10	11	1
Unidirectional GF	8	8	1
SMC GF	12	28	2–5
	Neat thermoplastics		
Commodity	15	<1	
Engineering	12	<1	
Speciality	5	<1	

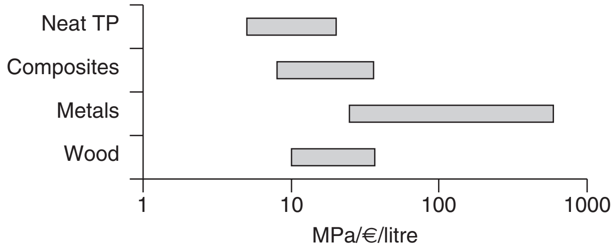


Figure 1.10. Examples of 'tensile strength versus costs per litre' ratios

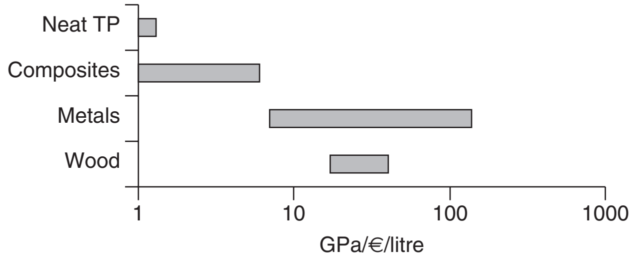


Figure 1.11. Examples of 'tensile modulus versus costs per litre' ratios

1.2 What are thermoplastics, TPE, thermosets, composites and hybrids?

1.2.1 Thermoplastics

Thermoplastics have the simplest molecular structure, with chemically independent macromolecules (Figure 1.12). By heating, they are softened or melted, then shaped, formed, welded, and solidified when cooled. Multiple cycles of heating and cooling can be repeated without severe damage, allowing reprocessing and recycling.

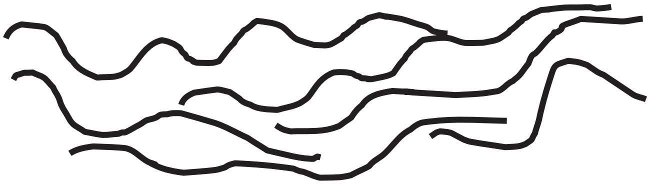


Figure 1.12. Schematic structure of a thermoplastic

Often some additives or fillers are added to the thermoplastic to improve specific properties such as thermal or chemical stability, UV resistance, etc.

Composites are obtained by using short, long or continuous fibres.

Thermoplastic consumption is roughly 80% or more of the total plastic consumption.

Alloys of compatible thermoplastics allow applications to benefit from the attractive properties of each polymer while masking their defects.

Some thermoplastics are crosslinkable and are used industrially in their two forms, thermoplastic and thermoset; for example, the polyethylenes or the vinylacetate-ethylene copolymers (VAE) (the links created between the chains limit their mobility and possibilities of relative displacement).

Advantages

- The softening or melting by heating allows welding and thermoforming.
- The processing cycles are very short because of the absence of the chemical reaction of crosslinking.
- Processing is easier to monitor, because there is only a physical transformation.
- Thermoplastics don't release gases or water vapour if they are correctly dried before processing.
- The wastes are partially reusable as virgin matter because of the reversibility of the physical softening or melting.

Disadvantages

- When the temperature rises, the modulus retention decreases, due to the absence of chemical links between macromolecules.
- For the same reason, the creep and relaxation behaviours are not as good as for the thermosets.
- During a fire, fusibility favours dripping and annihilates final residual physical cohesion.
- There are few materials workable in the liquid state.

The 'pyramid of excellence' (see Figure 1.13) arbitrarily classifies the main families of thermoplastics according to their performances, consumption level and degree of specificity:

- PE, PP, PVC, PS: commodity thermoplastics
- ABS, SAN: copolymers with more specific applications
- PA, PC, PMMA, POM, PPE, PET, PBT. . .: engineering thermoplastics
- PSU, PEI, PPS. . .: engineering thermoplastics with more specific performances
- ETFE, PEEK: high-tech uses, limited consumption
- LCP, PTFE, PFA, FEP, PI: high-tech uses, more limited consumption
- PBI: highly targeted uses and very restricted consumption.

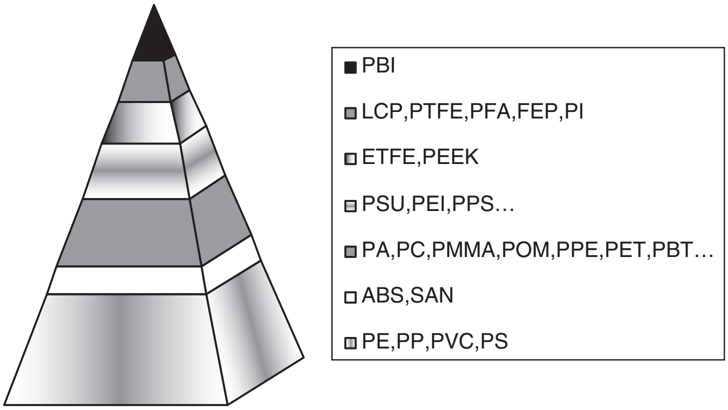


Figure 1.13. Pyramid of excellence for some thermoplastic families

1.2.2 Thermoplastic elastomers (TPEs)

TPEs are copolymers or compounds of thermoplastics and rubber.

The elasticity of TPEs (Figure 1.14 (a), (b) comes:

- either from the structure of the macromolecules with alternating soft and hard segments, the latter gathering together to constitute the nodes of a physical lattice; or
- from a dispersed phase of soft elastomer, vulcanized or not, forming microscopic droplets in a continuous phase of a hard thermoplastic. This structure allows processing in accordance with thermoplastic techniques. The rubber provides elasticity.

TPEs account for roughly 1% of total plastic consumption.

They lead to a combination of interesting properties:

- elasticity in a limited range of temperatures
- ease of thermoplastic processing without curing and, often, without a mixing step
- ease of recycling as for all the thermoplastics.

On the other hand, their mechanical properties decrease as the temperature rises because of their thermoplasticity.

The 'pyramid of excellence' (see Figure 1.15) arbitrarily classifies the main families of TPEs according to their performances, consumption level and degree of specificity:

- SBS, TPE-PVC, TPO: the less elastic TPEs, fair thermal resistance
- SEBS: same elasticity but better thermal behaviour

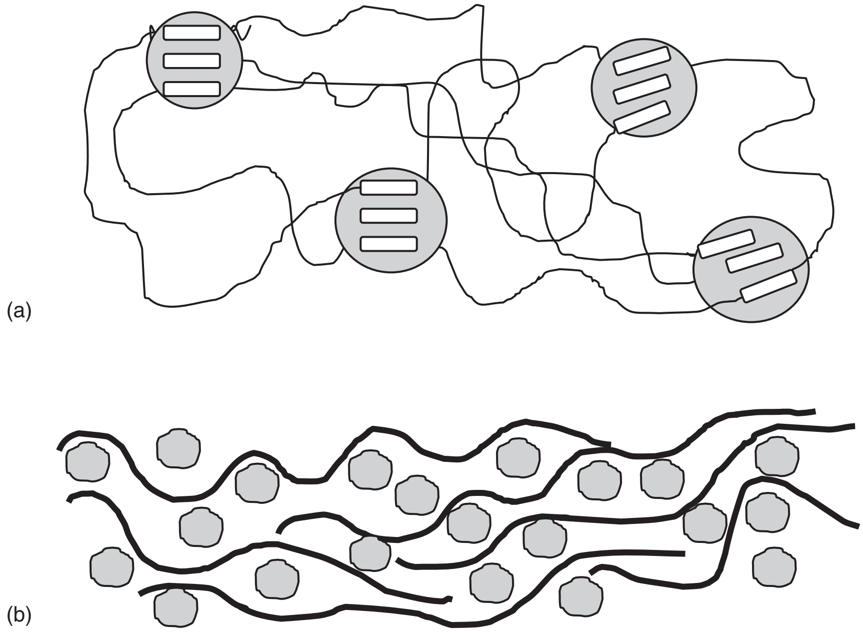


Figure 1.14. Schematic structure of TPEs: (a) Copolymer with hard segments arranged in domains; (b) compound of rubber particles dispersed in thermoplastic matrix

- PP/EPDM-V: better elasticity and good thermal resistance
- PP/NBR-V: same elasticity plus oil resistance
- PP/IIR-V: same elasticity plus gas impermeability
- TPU: high mechanical properties
- COPE, PEBA, TPE/Si-V: high performances but high prices.

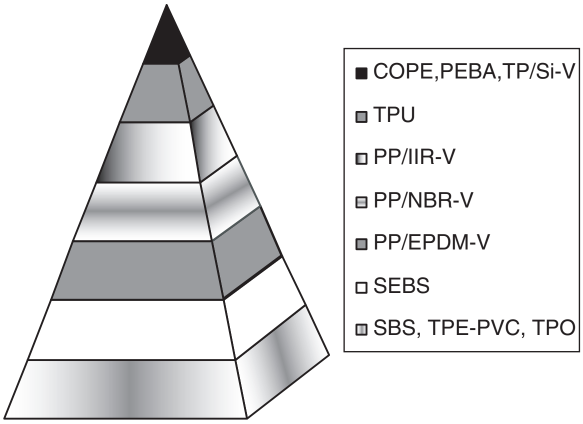


Figure 1.15. Pyramid of excellence for some TPE families

1.2.3 Thermosets

Thermosets before hardening, like thermoplastics, are independent macromolecules. But in their final state, after hardening, they have a three-dimensional structure obtained by chemical crosslinking produced after (spray-up moulding or filament winding) or during the processing (compression or injection moulding, for example).

Figure 1.16 schematizes the molecular arrangements of these polymers.

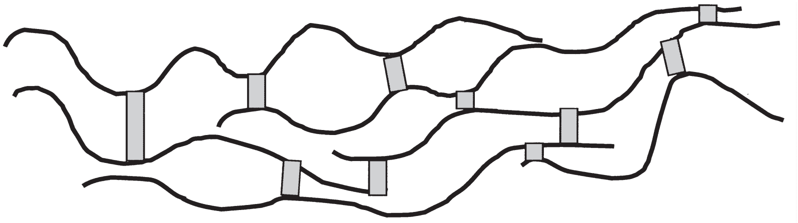


Figure 1.16. Thermoset after crosslinking

Some polymers are used industrially in their two forms, thermoplastic and thermoset; for example, the polyethylenes or the VAE. Thermoset consumption is roughly 12–20% of the total plastic consumption.

The links created between the chains of the thermosets limit their mobility and possibilities of relative displacement and bring certain advantages and disadvantages.

Advantages

- Infusibility: thermosets are degraded by heat without passing through the liquid state. This improves some aspects of fire behaviour: except for particular cases, they do not drip during a fire and a certain residual physical cohesion provides a barrier effect.
- When the temperature increases the modulus retention is better, due to the three-dimensional structure.
- Better general creep behaviour, the links between the chains restricting the relative displacements of the macromolecules, one against the other.
- Simplicity of the tools and processing for some materials worked or processed manually in the liquid state.

Disadvantages

- The chemical reaction of crosslinking takes a considerable time that lengthens the production cycles and, often, requires heating – an additional expenditure.
- The processing is often more difficult to monitor, because it is necessary to take care to obtain a precise balance between the advance of the crosslinking reaction and the shaping.
- Certain polymers release gases, in particular water vapour, during hardening.
- The wastes are not reusable as virgin matter because of the irreversibility of the hardening reaction. At best, they can be used like fillers after grinding.
- The infusibility prevents assembly by welding.

The 'pyramid of excellence' (see Figure 1.17) arbitrarily classifies the main families of thermosets according to their performances, consumption level and degree of specificity:

- urea-formaldehydes (UF): old materials of modest properties
- phenolic resins (PF) and melamines (MF): good thermal behaviour but declining

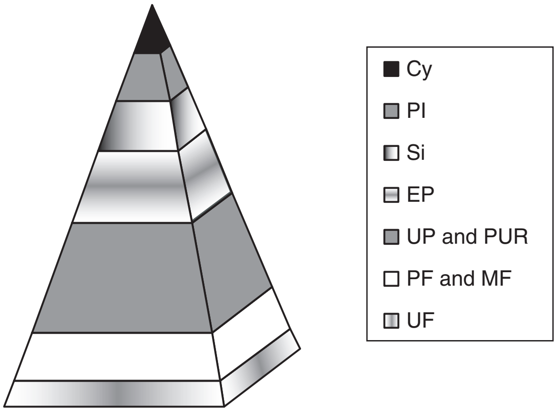


Figure 1.17. Pyramid of excellence for some thermoset families

- unsaturated polyesters (UP) and polyurethanes (PUR): the most used for their general qualities
- epoxy (EP): broad range of properties; some are used for high-tech composites
- silicones (Si): flexibility and high heat resistance; physiologically harmless
- polyimides (PI): high-tech uses, limited distribution
- polycyanates (Cy): highly targeted uses and very restricted distribution.

1.2.4 Polymer composites

Polymer composites are made from:

- a polymer matrix, thermoset or thermoplastic
- a non-miscible reinforcement closely linked with the matrix: fibres of significant length compared to the diameter, yarns, mats, fabrics, foams, honeycombs, etc.

The consumption of composites with organic matrices is a few percent of the total plastic consumption.

The main advantages of these composites are:

- mechanical properties higher than those of the matrix
- the possibility of laying out the reinforcements to obtain the best properties in the direction of the highest stresses.

The development of polymer composites is held back by recycling difficulties, attenuated in the case of the thermoplastic matrices.

The 'pyramid of excellence' (see Figure 1.18) classifies, as arbitrarily as for the previous polymers, the composites according to their performances, consumption level and degree of specificity:

- unsaturated polyesters (UP) reinforced with glass fibres: the most used for their performances and low cost
- phenolic resins (PF) reinforced with glass fibres: fire resistance, good performances and low cost
- epoxy (EP) reinforced with glass fibres that perform better than the UP/GF
- epoxy (EP) reinforced with aramid or carbon fibres or with honeycombs: high-tech and high-cost composites performing better than the EP/GF
- silicone (Si) reinforced with glass fibres: flexibility, heat resistance, chemical resistance and physiological harmlessness

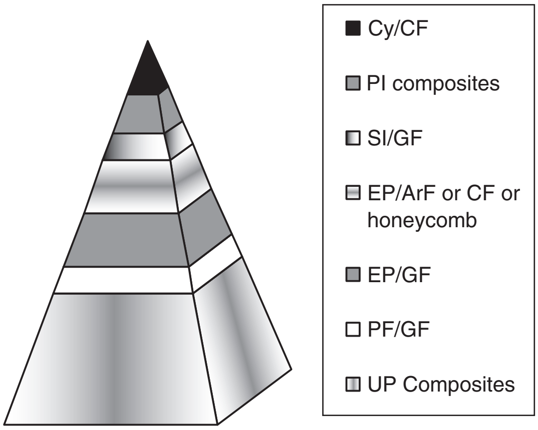


Figure 1.18. Pyramid of excellence for some composite families

- polyimide (PI) reinforced with aramid or carbon fibres or with honeycombs: very high-tech and high-cost composites performing better than the EP composites; the consumption is limited
- polycyanate matrices: very specific uses, high-tech and high-cost composites; very restricted consumption.

1.2.5 Hybrid materials

Hybrid materials are not really a clearly defined material category but result from a design method that associates, by integrating them closely, one or more polymers on the one hand and, generally, one or more other materials, which provide one or more functionalities difficult or impossible to obtain with only one polymer.

The dividing line between hybrid materials and associated materials is rather fuzzy. This definition does not regard as hybrids, for example, those polymers joined after their manufacture onto structures of metal or concrete. On the other hand, overmoulding on structural and functional inserts is regarded as hybrid.

The hybrid techniques often associate polymers and metals and combine the benefits of the two material classes. The metal provides the rigidity and the overmoulded reinforced plastic keeps the shape of the metal and adds numerous functionalities.

There is also a growing interest in the association of elastic polymers, which assume sealing or damping functionalities, with rigid plastics or composites that have the structural role. One of the materials can be overmoulded on the other or the two materials can be co-moulded.

By associating simple and inexpensive plastic processes (injection moulding, for example) with simple and inexpensive metal processes (stamping, embossing, bending), the polymer/metal hybrids allow the integration, thanks to the plastic elements, of the maximum number of functionalities: mountings, fastening points, fixings, cable holders, housings, embossings, eyelets, clips, etc. This leads to:

- the elimination of the assembling stages of the suppressed components
- the reduction of the dimensional defects of the assembled components
- the avoidance or reduction of welding operations that can cause metal deformations.

This principle, in more or less complex versions, is applied to:

- the front-ends of recent cars such as the Audi A6, Ford Focus and VW Polo
- footbrake pedals in metal/plastic hybrid
- wheels of planes in hybrid metal/composite epoxy/carbon
- car doors
- frame-hull (MOSAIC project) in hybrid composite/aluminium.

Inversely, the polymer can sometimes provide the structural functions while the metal ensures a role not easily assumed by the polymer:

- For high-pressure air tanks, a hybrid design gives the best results: a thin metal liner ensures the sealing and is used as a mandrel to make the envelope by the filament winding technique. The aramid or carbon fibres ensure the mechanical resistance. The weight saving is 30–50% compared to all-metal tanks while the costs are optimized.
- The engines of the Polimotor and Ford projects are in hybrid composites of phenolic resins/glass fibres and epoxy/glass fibres with combustion chambers, cylinders and pistons in metal. This permits the direct contact with hot combustion gases that the polymer could not support. The composite provides the rigidity of the engine.
- Certain incinerator chimneys are in hybrid stainless steel with an inner lining in sandwich resin/glass fibres with a core in foamed polyurethane.

The materials associated with the polymers can also be concrete or wood, for example:

- azurel structural panels for individual construction, developed by Dow, made of wood and expanded polystyrene
- rigid elements for the modular design of dwellings made of hollow structures of glass fibre reinforced unsaturated polyester filled with concrete.

1.3 Plastics: an answer to the designer's main problems

Designers are directly or indirectly subjected to economical, technical and environmental constraints. Plastics and composites are well positioned to provide solutions.

1.3.1 Economic requirements

Cost savings on the total life of the parts. A polymer overcost can be compensated for by designing, processing, finishing, assemblage, operating and maintenance costs and by a longer durability.

Plastics and polymer composites offer:

- design freedom: realization of all shape and size parts unfeasible with metals or wood
- integration of several functionalities by using the property versatilities such as structural and other additional properties: damping, shock and noise absorption, heat insulation, electrical insulation, translucence or transparency, rigidity of UD composites or flexibility of some polyurethanes, thermal stability of silicones, polyimides . . .
- the possibility to combine two polymer materials to ensure several functionalities if all the desired characteristics are not brought together in a single polymer. A polyurethane flexible foam and a rigid polyurethane can combine structural and damping properties in the same part
- the possibility of selective reinforcement in the direction of the stresses by selecting particular composites or by part drawing

- the reduction of design and production set-up times
- weight reduction thanks to the good mechanical properties combined with low density. The resulting fuel savings in automotive applications and labour and handling savings in building and civil engineering applications allow reduction of the operating costs
- the aesthetics, the possibilities of bulk colouring or in-mould decoration to take the aspect of wood, metal or stone that remove or reduce the finishing operations
- the integration of functionalities, the large sizes permitted by certain processing methods and the particular processes of assembly lead to cost reductions in assemblage, to smoother surfaces without rivets or weldings favourable to aesthetic quality and to a greater aerodynamic optimization
- the possibility of repairing the composites to permit the recovery of expensive parts after damage.

1.3.2 Technical requirements

Solidity, reliability and permanence of the parts in the face of increasingly harsher environments and higher temperatures . . .

Plastics and polymer composites offer:

- durability, the absence of rust and corrosion (but beware of ageing)
- ease and reduction of maintenance
- good fatigue behaviour, slow damage propagation, and the possibility of targeting a damaged mode to preserve the essential functionalities of the part between two inspections.

1.3.3 Marketing requirements

Aesthetics, comfort, frequent renewal of the product ranges.

Plastics and polymer composites offer:

- design freedom: the realization of all shapes and sizes of parts unfeasible with metals or wood
- adaptation to ‘niche’ products
- production flexibility: processing adaptability from the prototype to mass production
- the possibility to refresh or to renew the product lines more frequently thanks to the easier replacement and modification of tools with plastic than with metals.

1.3.4 Environmental requirements

The standards and regulations limit the pollution and increase the level of recycled wastes.

Plastics and polymer composites offer:

- weight reduction thanks to good mechanical properties combined with low density. This leads to fuel savings in the automotive and transportation sectors, and labour and handling savings in building and civil engineering, which reduce the pollution
- the reduction or suppression of the periodic painting of metals contributes to a reduction in pollution.

The recycling of wastes is difficult for thermosets and composites because of the cross-linking and/or the presence of fibres broken during recycling.

1.3.5 Some weaknesses of polymer materials

Like all materials, polymers also have their weaknesses, general or specific.

To start with, the reader may have noticed that all the quoted advantages are never combined together in the same polymer class. Moreover, polymers meet certain general obstacles as technical materials. Let us quote for example: sensitivity to impact, ageing, low rigidity, thermal behaviour, rate of production, recycling.

1.4 Outline of the technical and economic possibilities of processing

A satisfactory combination of part, polymer and process is of the first importance:

- each process does not allow the fabrication of all types of parts
- polymers are not all suitable for processing by all methods.

It is pointless to select a polymer of high performance if it is not technically and economically suitable for manufacturing the part under consideration.

For the choice of the process according to the part, the following are the main points to be considered:

- the shape: parts of all shapes and limited sizes are, generally, manufactured by moulding by compression, injection, transfer, thermoforming and the derived methods such as rotomoulding, RIM, RRIM, RTM . . . Parts of constant section are, generally, manufactured by extrusion, pultrusion and derived methods
- the size: parts of enormous size are manufactured by boiler-making, hand lay-up, spray lay-up, centrifugal moulding, filament winding. . .
- the aspect: a good aspect on the totality of the part surface is only obtained by moulding. The other processes leave either rough-cut sections or a more or less rough face
- the quantity to produce: the rate of output depends on the process. Injection moulding, RTM and SMC allow mass production whereas boiler-making, hand lay-up or spray lay-up moulding hardly exceed 1000 parts.

1.4.1 Thermoplastic processing

The processes used for thermoplastics are diversified because of the thermoplasticity, which allows:

- easy moulding, extrusion, calendering
- thermoforming
- welding
- assembly and boiler-making.

Just to give an idea of the importance of the various processing methods, the shares of the major processes used for the most used thermoplastic (polyethylene) are roughly:

- extrusion: 35%
- injection moulding: 25%
- blow moulding: 35%
- rotomoulding: >1%
- others: 4%

1.4.1.1 Moulding solid thermoplastics

Injection is by far the most used moulding process but compression and compression-transfer are used for specific cases. Rotomoulding is specifically used for polyethylene and a few other powdered resins. Slush moulding is broadly used for automotive dashboards.

Generally:

- the part sizes are limited by the mould size and the machinery performances
- the parts are isotropic if the compound is isotropic
- the whole surface of the part has a good finish.

Each process presents some particularities:

- Injection moulding:
  - permits the total automation of the process
  - is suited for mass production
  - shot capacities cover a large range, for example, a few grammes up to more than 100 kg
  - over-moulding and co-moulding are usable
  - optimization of the moulding parameters can be difficult and part warpage is sometimes difficult to predict
  - normally, finishing is unnecessary
  - apart from the particular cases of resins filled with fibres and other acicular or lamellar fillers, the parts are isotropic
  - the output rates, the mould and press prices are the highest, and the labour costs are reduced to the minimum
  - for standard, mass-distributed parts it is the cheapest process.
- Injection blow moulding:
  - is suited for the production in large quantities of bottles, similar containers and other hollow objects
  - the aspect and dimensional quality are excellent compared to extrusion blow moulding
  - the outputs are high.
- Rotomoulding:
  - is suited for the fabrication of hollow parts such as containers, dolls, tanks, kayaks...
  - is convenient for the production of small parts and giant ones such as tanks of more than 75 000 litres capacity
  - is used for small and medium output
  - products are essentially stress-free and there are no weld lines
  - finishing is often essential
  - the output rates are low
  - the mould and machinery are relatively inexpensive, and the labour costs are high.
- Compression moulding (not much used for thermoplastics):
  - is suited for small and medium output of unusual shapes
  - finishing is often essential
  - the output rates are low, the mould and press are relatively inexpensive, and the labour costs are high.
- Compression-transfer moulding (not much used for thermoplastics):
  - is suited for medium output
  - finishing is often simple
  - the output rates, mould and press prices, and labour costs are halfway between compression and injection moulding.

- Slush moulding used with thermoplastics in powder form for the fabrication of automotive dashboards:
  - ○ is suited for medium and high output, for example the dashboards of BMW series 7 up to the Polo by VW.
  - ○ the machinery is rather sophisticated.

1.4.1.2 Extrusion and connected processes

Extrusion and derived processing methods are the most used in terms of weight, allowing the fabrication of profiles, cast and blown films, wire sheathing and coating, blow-moulded hollow parts, and expanded materials such as EPS. Generally:

- the output is medium or high, varying from kg/h to tons/h
- the section sizes are limited by the die size and/or the machinery size. The length is unlimited
- arrangements of reinforcements are limited
- the parts are often anisotropic. Properties are different in the machine and the transverse directions
- the aspect is correct for the outer surface but cuts are rough
- several extruders can be arranged to fabricate multi-material profiles
- the cost of the tools and machinery depends on its sophistication. Each tool is appropriate for a single section. Universal screws are not always convenient and some profiles or materials need special screws or special extruders.

1.4.1.3 Calendering

- Calenders are very expensive and specific machines that are used only for high-output production.
- The section sizes are limited by the roller sizes. The length is practically unlimited.
- It is possible to calender thermoplastics onto fabrics to obtain a reinforcing effect.
- The parts are often anisotropic. Properties are different in the machine and the transverse directions.
- The aspect is correct.

1.4.1.4 Blow moulding

This combination of extrusion and moulding:

- is used for large series of bottles, similar containers and other hollow objects
- the aspect and dimensional quality are not as good as injection blow moulding
- the outputs are high.

1.4.1.5 Moulding liquid thermoplastics

The most commonly used liquid thermoplastics are plastisols (pastes of PVC with a high content of plasticizers). There is also a polyamide of very low consumption. Some of the processes can be applied to powders in suspension.

The plastisols can be moulded by:

- Dipping:
  - ○ is suited for small and medium output
  - ○ the part sizes are limited by the size of the former

  - reinforcements can be arranged onto the former before dipping
  - the parts are isotropic with neat resins or with isotropic fillers
  - the aspect is correct for the outer surface. A finishing step is often essential
  - the moulds are inexpensive and the cost of the machinery depends on its sophistication
  - the output rates are low.
- Low-pressure injection moulding, RIM, RRIM for liquid polyamide:
  - are suited for medium output
  - the part sizes are limited by the mould size
  - reinforcements can be arranged in the mould before injection
  - the parts are isotropic with neat resin or with isotropic reinforcements
  - the aspect is well finished for the whole part surface
  - the low-pressure resistant moulds are more expensive than for the casting but cheaper than injection moulds. A press and a mixing/injection unit are necessary but the labour costs are moderate. Provides medium output rates.

1.4.1.6 Secondary processing

- Thermoforming:
  - is convenient from prototype to mass production
  - allows the production of large parts
  - machinery can be simple or sophisticated and consequently the shapes and tolerances can be rough or precise. In the best conditions, fine tolerances and sharp details are obtained and with excellent finishing techniques the thermoformed parts can match injected parts.
- Welding:
  - can be very simple or sophisticated
  - allows small or continuous joining
  - can avoid the design and tooling constraints of complex parts by assembling several pieces of standard production (sheets, tubes, films...) or more simple parts produced with economical tools
  - needs skilled workers
  - machinery is generally relatively inexpensive but there is a lot of labour.
- Machining: practically all the thermoplastics can be machined to some degree by almost all the metal or wood machining methods after adaptation of the tools and processes to a greater or lesser extent:
  - sawing, drilling, turning, milling, tapping, threading, boring, grinding, sanding, polishing, engraving, planing... The low thermal conductivity and the decrease of the mechanical characteristics at elevated temperature limit the machining temperature and it is necessary to cool and reduce the tool feed motion
  - machining is suited for prototypes and low output of complex parts made from blanks whose mould could be simplified; it is also suited to making thick or tight tolerance parts.
- Boiler-making is commonly used for the fabrication of large vessels, piping, etc. thanks to the use of techniques such as welding, forming, machining, bonding of sheets, slabs, pipes, blanks...

  This processing method allows the building of very large size tanks, cisterns, tubing, geomembranes etc. from prototypes up to medium output.

  The workers must be skilled and the labour costs are high.

- Fabrication is also commonly used to build inflatable boats, protective clothing and inflatable structures, particularly those made of soft PVC. The workers must be skilled and the labour costs are high.

1.4.1.7 Brief economic comparison of some processing costs

Table 1.13 illustrates schematically some general economic possibilities of various processes without claiming to be exhaustive. Other values may be recorded for the concerned parameters and not all the processes are examined. These figures are only orders of magnitude used simply to give some idea of the costs. They cannot be retained for final choices of solutions or estimated calculations of cost price.

Table 1.13 Linked processing costs of some thermoplastic processes*

Process	Standard output	Linked processing cost
Injection	1 000 000	1
	1000	14
Blow moulding	1 000 000	1.5
	1000	12
Rotomoulding, sophisticated machinery	1 000 000	2.5
	100	16
Thermoforming	10 000	5
	10	16
Rotomoulding, basic machinery	1000	6
	10	15
Fabrication by machining, cutting, welding, gluing . . .	1000	12
	1	14

* Relative to the processing cost of a standard part injected at 1 million units

All parts are not necessarily producible by all the processes.

The costs are all relative to the processing cost of a standard part injected at 1 million units, which is defined as 1.

1.4.1.8 Repair possibilities: a significant thermoplastic advantage for large parts

Large parts made from thermoplastics have the significant economic advantage of being rather easy to repair.

A good professional can correctly repair the most-common thermoplastic parts, such as piping, geomembranes, inflatable boats and structures, by welding or gluing patches after removal of the soiled and damaged part.

1.4.2 Thermoset processing

The processes used for thermoplastics are modified for the thermosets:

- after obtaining the part shape, it is necessary to heat for a sufficient time to crosslink the thermoset, which solidifies and gains its cohesion and final properties
- due to the irreversible formation of a three-dimensional network during hardening, the thermosets cannot be processed by thermoforming or welding, and boiler-making is very limited.

1.4.2.1 Moulding solid thermosets

They can be moulded by compression, compression-transfer and injection. Generally:

- the part sizes are limited by the mould size and the press power
- the parts are isotropic
- the whole surface of the part has a good finish.

Each process presents some particularities:

- Compression moulding:
  - is suited for small and medium output
  - thick parts are problematic because of the low thermal conductivity of the polymers
  - released gas cannot escape and induces voids and internal stresses
  - inserts are difficult to use
  - finishing is often essential
  - the output rates are low, the mould and press are relatively inexpensive, and the labour costs are high.
- Compression-transfer moulding:
  - is suited for medium output
  - the quality of the thick parts is particularly improved
  - inserts are easy to use
  - finishing is often simple
  - the output rates, the mould and press prices, and the labour costs are halfway between compression and injection moulding.
- Injection moulding:
  - permits total automation of the process
  - is suited for mass production
  - the optimization of the moulding parameters can be difficult and the part warpage is sometimes difficult to predict
  - normally, finishing is unnecessary
  - apart from the particular cases of resins filled with fibres and other acicular or lamellar fillers, the parts are isotropic
  - the output rates, the mould and press prices are the highest, and the labour costs are reduced to the minimum.

1.4.2.2 Moulding liquid thermosets

They can be moulded by:

- Simple liquid resin casting in an open or closed mould:
  - is suited for small and medium output
  - the part sizes are limited by the mould size
  - reinforcements can be arranged in the mould before casting
  - the parts are isotropic with neat resin or with isotropic reinforcements
  - the aspect is correct for one part surface for open moulding, and for the whole part surface for closed moulding. A finishing step is often essential
  - the moulds are inexpensive and there is no press but the labour costs are high. The output rates are low.
- Low-pressure injection moulding, RIM, RRIM:
  - are suited for medium output
  - the part sizes are limited by the mould size

  - reinforcements can be arranged in the mould before injection
  - the parts are isotropic with neat resin or with isotropic reinforcements
  - the aspect is well finished for the whole part surface
  - the moulds are pressure resistant and more expensive than for the casting. A press and a mixing/injection unit are necessary but the labour costs are moderate. The output rates are intermediate.

1.4.2.3 Secondary processing

- Boiler-making is reduced because of the 3D network, which prevents thermoforming and welding. It is possible to use techniques such as machining, bonding of sheets, slabs, pipes, blanks . . . This technique allows the building of very large size tanks, cisterns, tubing, etc. from prototypes up to medium output. The workers must be skilled and the labour costs are high.
- Machining: practically all the thermosets can be machined to some degree by almost all the metal machining methods after adaptation of the tools and processes to a greater or lesser extent:
  - sawing, drilling, turning, milling, tapping, threading, boring, grinding, sanding, polishing, engraving, planing . . . The low thermal conductivity and the decrease of the mechanical characteristics at elevated temperature limit the machining temperature and it is necessary to cool and reduce the tool feed motion
  - machining is suited for prototypes and low output of complex parts made from blanks whose mould could be simplified; it is also suited to making thick or tight tolerance parts.

1.4.3 Composite processing

1.4.3.1 Primary processes

The processes differ according to the nature of the matrix:

- thermoplastics: after obtaining the part shape cooling may be all that is necessary
- thermosets: it is necessary to heat after obtaining the part shape for a sufficient time to crosslink the thermoset, which solidifies and gains its cohesion and final properties.

The processes are numerous and differ in their technical and economic possibilities. Let us quote for example:

- stamping
- atmospheric moulding processes: hand lay-up, spray lay-up
- liquid moulding: RRIM, RTM, impregnation, infusion . . .
- solid-state moulding: compression and injection, SMC, BMC, ZMC . . .
- prepreg systems
- bag moulding
- filament winding
- centrifugal moulding
- continuous sheet manufacture
- pultrusion
- Sandwich composites . . .

The process, the structure of the composites, the design of the parts and the output are interdependent factors that cannot be isolated from each other.

The shape of the parts must be adapted to the material and the process, which dictates certain conditions: for example, the maximum thickness, the thickness variations on the same part, the acceptable radius for the direction changes of the walls (depth of grooves, flanges, ribs...), the possibility of using reinforcement ribs and inserts, the possibility of creating apertures and cavities during the transformation, the aesthetics.

The part sizes are limited by the tool sizes such as moulds, dies, autoclaves or winding machines and by the power and the size of equipment such as presses, bags, pultrusion machines, etc.

Tables 1.14 and 1.15 illustrate some general technical and economic possibilities of the various processes without claiming to be exhaustive. Other values may be recorded for the parameters concerned and not all the processes are examined.

Table 1.14 Examples of the process choice versus the part characteristics

Part size, maximum area (m^2)	Thickness (mm)	Examples of parts	Smooth surface	Method
Virtually unlimited, <300	Unlimited Often 2–10	Ship	1	Hand lay-up
Virtually unlimited	Unlimited Often 2–10	Ship	1	Spray lay-up
Up to 15	1–10	Car body element	2	Resin injection
Up to 15	3–10	Car body element	2	Cold compression moulding
Up to 5	1–6	Car body element	2	Hot compression moulding mats and preforms
Up to 5	2–10	Car body element	2	Hot compression moulding prepregs
Up to 10		Housing	1	RRIM
Limited		Electrical & electronic parts	2	High pressure injection
Up to 20		Aeronautics elements	All	Autoclave
Up to 4		Automobile parts	2	Stamping
Diameter from 5 cm up to 25 m* with specific equipment	1 to 10 and more	Pressurized tank	1	Filament winding
Up to 30	3–15	Tube, pipe	1	Centrifugal moulding
Limited section	3–20	Profile	All	Pultrusion
Limited section	1–4	Roof sheeting	2	Continuous impregnation

* Manufacture from specific material developed for a particular part

Table 1.15 Examples of economic characteristics of some processes

Method	Output (units)	Cycle time	Investment	Labour cost
Hand lay-up	1–1000	30 min to some days	Low	High
Spray lay-up	1–1000	30 min to some days	Low	High
Resin injection	200–10 000	30 min to some hours	Medium	Medium
Cold compression moulding	500–20 000	5–30 min	Medium to high	Medium
Hot compression moulding mats and preforms	Mass production	1–10 min	High	Medium
Hot compression moulding prepregs	Mass production	2–5 min	High	Low
RRIM	1000–250 000			Medium
High pressure injection	>10 000		High	Low
Autoclave	<5000		Medium	Medium
Stamping	Medium output		Medium	Low
Filament winding	<10 000	According to part	High	High
Centrifugal moulding		10 min to some hours	High	Low
Pultrusion	Continuous	Continuous	High	Low
Continuous impregnation	Continuous	Continuous	High	Low

Table 1.14 shows some examples of the process choice versus the part characteristics.
Table 1.15 shows examples of the economic characteristics of some processes.

1.4.3.2 Secondary processing

Machining: practically all the composites can be machined to some degree by almost all the metal machining methods after adaptation of the tools and processes to a greater or lesser extent:

- sawing, drilling, turning, milling, tapping, threading, boring, grinding, sanding, polishing, engraving, planing ... The low thermal conductivity and the decrease of the mechanical characteristics at elevated temperature limit the machining temperature and it is necessary to cool and reduce the tool feed motion
- machining is suited for prototypes and low output of complex parts made from blanks (whose mould could be simplified); it is also suited to making thick or tight tolerance parts.

However, it is necessary to note several points:

- machining destroys the gelcoat if it exists. To avoid the risks of a later attack, it is necessary to re-make a new gelcoat locally.
- for the anisotropic composites, it is not possible to machine in all directions. Drilling, for example, can be done only perpendicularly to layers.
- the carbon and glass fibres are very abrasive and quickly wear away high-speed steel tools. For intensive use, carbide or diamond tools are more suitable.

Assemblage:

- Welding does not apply to the thermosets. For thermoplastics, the presence of fibres disturbs welding, which is not often used.
- Joining does not present particular difficulties and is used to assemble composite with composite or metal. The parts can have structural functions, such as, for example, the assemblage of a metal structure and a composite superstructure on a frigate. Joining avoids damage of the composite by drilling and allows an excellent distribution of the loads.

1.4.3.3 Repair possibilities: a significant composite advantage

Large composite-made parts have the significant economical advantage of being rather easy to repair:

- A good professional can correctly repair the most-common thermoset composites or those of intermediate performance. Surface damage can be repaired by: puttying, sanding, gel-coating or painting. For deep damage, the repair is more complex: removal of the layer soiled by the external medium (for example, water for ships, chemicals for tanks. . .), *in situ* lay-up to replace the destroyed layer, gel-coating or painting
- For the high-performance or sandwich composites, repairs, when they are possible, are always much more delicate. However, race boats are currently repaired after damage.

1.4.4 Hybrid processing

The constituents of a hybrid can be interlocked:

- mechanically: overmoulding of the polymer on the metal, which bears anchorages such as lugs, holes. . .
- chemically: bonding of the polymer to the metal treated with a primer or adhesion of two compatibilized polymers. Certain thermosets such as polyurethane are easily bonded on metals but the adhesion of polypropylene and some other materials is difficult.

1.5 Environmental constraints

The ecological constraints, which vary from country to country, are of two main types:
- toxicity and pollution
- recycling.

1.5.1 Toxicity and pollution

Without entering into details, let us recall some examples. These are far from representing the whole extent of the problem:
- There is an obligation to respect limits of residual monomer rates. For example, after application of urea-formaldehyde resin, the residual rate of formaldehyde is limited according to national regulations
- The use of heavy metals and halogens is more and more disputed
- Solvents, for example styrene, are subject to increasingly severe legal requirements.

1.5.2 The recycling of polymers

Polymer recycling presents technical and economic difficulties and is less advanced, industrially, than that of metals. In the automotive sector, for example, the rate of metal recycling is higher than 95%. For polymers, recycling is only minor with isolated industrial achievements such as battery boxes.

Volvo, for a recent model, has achieved a 9 kg recycled plastic use.

The main ways to recycle polymers are:
- re-use with virgin material in the same or another application
- conversion into basic chemicals by chemolysis or thermolysis
- energy production by combustion.

Recycling the wastes is difficult for the thermosets and composites because of the cross-linking and/or the presence of fibres broken during the recycling.

To be solved, recycling must be considered at the design stage in order to choose the best solutions for the part at the end of its life.

Some general rules, to which there are of course exceptions, can be stated:
- mark parts to make the later identification of the materials easier
- avoid the use of incompatible polymers in the same part or subset
- standardize the polymers used
- choose the assembly methods that lead to the easiest dismantling at the end of the lifetime
- preferably choose a material whose recycling will be possible in the same fabrication . . .

1.6 The final material/process/cost compromise

The final choice of the design team results from many iterations concerning the functional properties, the environmental constraints, the possibilities to produce the part in the required quantities, and the price. The price considered may just be the part cost but can also include assembling, delivery, set up and end-of-life costs, taking account of durability, the savings in maintenance, etc.

Figure 1.19 shows an example of the selection scheme for the material and process.

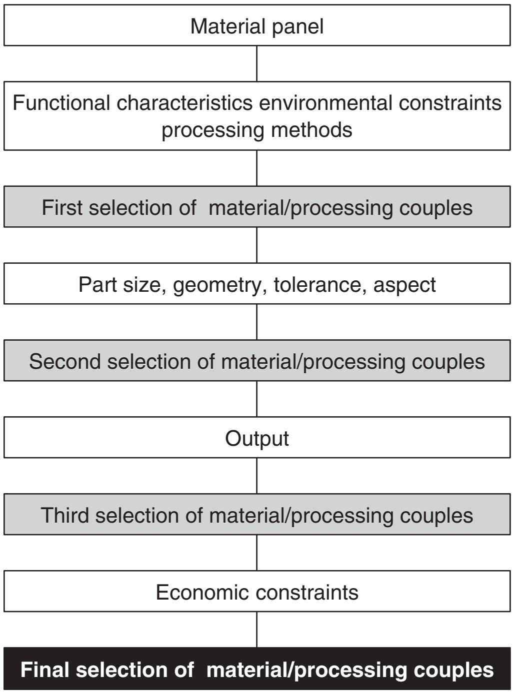


Figure 1.19. Selection scheme of the material and process

References

Websites

Apme.com, plasticseurope, spmp.sgbd.com, worldsteel.org, www.world-aluminium.org

Papers

[1] M. Biron, *Thermosets and Composites – Technical Information for Plastics Users*, Elsevier Ltd (2004)
[2] F. Pardos, *Antec 2002 Proceedings*, p. 2736
[3] F. Szabo, *International Polymer Science and Technology*, Vol. 28, No. 11, (2001), p.T/1
[4] F. Pardos, *Antec 1999 Proceedings*, p. 3034

Chapter 2

The plastics industry: economic overview

The decision to use a new material is difficult and important. It has both technical and economic consequences, making it essential to consider:

- the abundance or scarcity of the material and the process targeted
- the cost
- the actual penetration of the material category in the industrial area.

The goal of the following facts and figures concerning thermoplastics and composites is to help quickly clarify the real applications and the relative importance of the various families and processes. The figures are roughly estimated from professional or government studies and papers or news from technical reviews. These sources can indicate significantly different figures according to the methodology used (applications, whether or not the captive industry is taken into account, etc.).

2.1 Overview of the global plastics industry today and tomorrow

Worldwide plastics consumption is of the order of 170 million tonnes annually in round figures, with a turnover of US$560 billion. Over the past five years, global plastics consumption has grown consistently by an average annual rate of 4%, comparable with steel and aluminium rates.

Table 2.1 and Figure 2.1 indicate the orders of magnitude of global plastics consumption.

Table 2.1 Global plastics consumption

	Million tonnes	%
Commodity	122	72
Engineering	8–9	5
Composites	6–8	3–5
Speciality	<1	<1
TPE	1.1	<1
Environment-friendly	<1	<1
Others	30	18
Total	170	100

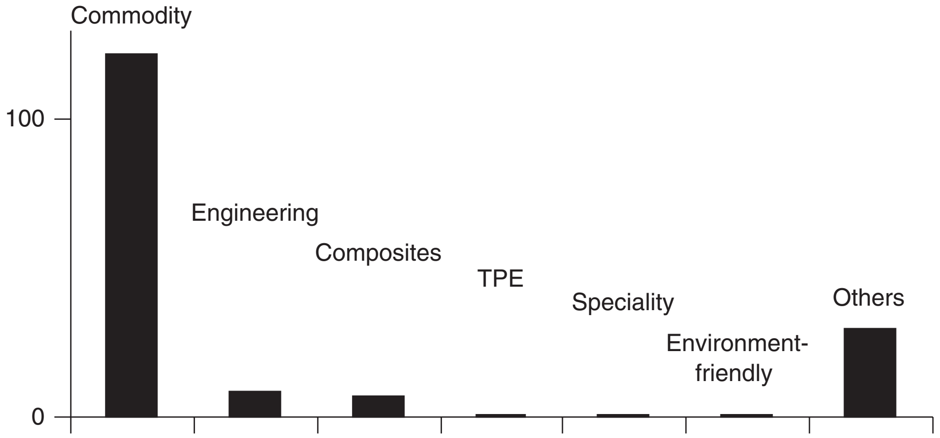


Figure 2.1. World plastic consumption (million tonnes)

Worldwide plastic growth is estimated between 4% and 5.5% per annum for the next few years, leading to a worldwide consumption estimated from 210 up to 260 million tonnes by 2010.

Consumptions and growth rates broadly vary according to the area considered. China and other Asian countries excluding Japan are the leaders for commodity plastics consumption and growth rate, superseding North America and Western Europe, which in return are leaders for engineering and speciality plastics. Table 2.2 and Figure 2.2 display consumption data for 2000 and forecasts for 2010 according to a medium hypothesis of annual growth rate. Consumptions are uncertain and forecasts are more or less subjective. Consequently, other estimations can be found in other sources.

Table 2.2 Consumptions and growth rates for all plastics

	Commodities (million tonnes)	Total plastics (million tonnes)		Annual growth rate (%)
Year:	2000	2000	2010 (forecast)	2010/2000
Asia excluding Japan	34	38	78	7.5
North America	30	48	71	4
Western Europe	27	40	53	3
Japan	8	11	14	2.5
Latin America	8	11	16	4
Africa & Middle East	6	7	12	5.5
Eastern Europe/FSU[†]	4	5	10	7
	117	160*	254	4.8

* This figure is slightly superior to the worldwide consumption generally quoted (150 million tonnes) probably because of distortions concerning the applications considered, with some non-plastics being included in the accounting.

[†] FSU: Former Soviet Union

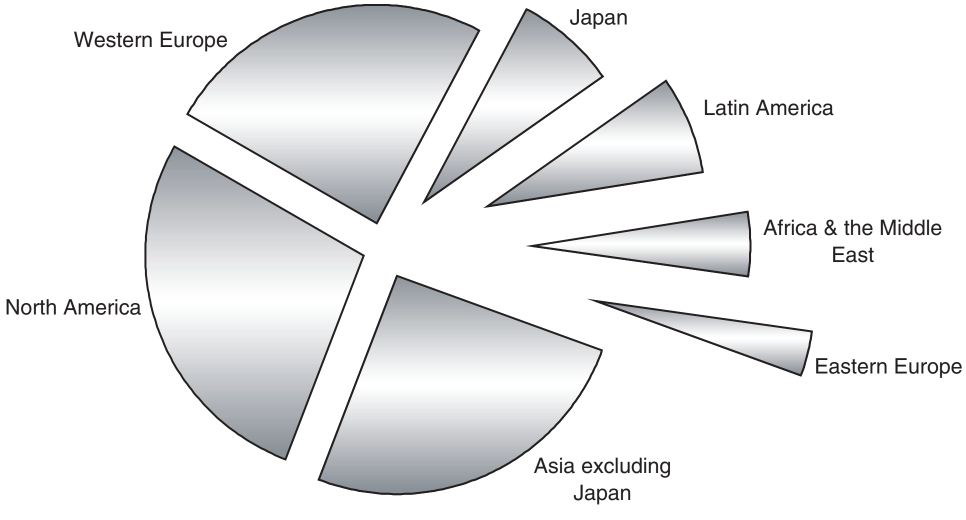


Figure 2.2. Consumptions in 2000 according to area

Table 2.3 Market shares by weight for the main plastics

Thermoplastics	Thermosets	Market share (%)
PE		27–33
PP		15–16
PVC		13–14
PET		7–10
PS		6–8
	Amino resins	3–7
	PUR	2–4
	Unsaturated polyesters	2–3
	Phenolic resins	1
PA		1
Other engineering		3
	Other engineering	1
TPEs		<1
Total thermoplastics		79
	Total thermosets	11
Composites		4
Others		6
Total		100

The market shares for the major families of plastics are estimated in Table 2.3 for industrialized countries; however, other figures can be found in other sources according to the applications taken into account and the areas considered.

For Western Europe, thermoplastics represent 79% of overall plastic consumption. Data for North America is perhaps higher.

The distribution between the families varies from one area to another mainly for polyethylene, thermoplastic polyesters and amino resins. For these, the variation perhaps comes from a problem of identification in the statistics, as some may include significant applications that are outside the framework of this book. However, we can say that the five most used plastic families are thermoplastics.

The market shares (order of magnitude only) for some engineering and speciality plastics were estimated as follows (see Table 2.4).

2.2 Market shares of the various thermoplastic families

Table 2.5 and Figure 2.3 indicate the market shares by weight of the main thermoplastics versus total thermoplastics in the main industrialized countries.

2.3 Market shares of composites

In terms of weight, the share of composites in the total plastics consumption is relatively weak (4–5%), but the share in terms of value is higher: roughly 12%.

The growth rate, 4–7% per year, is greater than that of the plastics industry as a whole.

Table 2.6 and Figure 2.4 show the consumption of composites in North America, Europe and Asia. Approximately 31% of composite matrices are thermoplastics, and 69% are

Table 2.4 Market shares by weight for some engineering and speciality plastics

Thermoplastics	Thermosets	Market share (%)
PET		Several %
	Polyurethanes	Some %
	Amino resins	Some %
	Phenolic resins	Some %
	Unsaturated polyesters	Some %
Polyamides		1% to some %
Polycarbonates		1% to some %
PMMA		1% to some %
Market shares <1%		
	Epoxies	Some ‰
Polyacetal		Some ‰
PBT		Some ‰
PPE		Some ‰
PC/ABS alloys		Some ‰
SAN		Some ‰
Cellulosics		Some ‰
Market shares <1‰		
PTFE		Some ‱
PPS		Some ‱
PA/Polyolefin alloys		Some ‱
PSU, PESU		Some ‱
PEI		Some ‱
Market shares <1‱		
FEP		Some ‱o
LCP		Some ‱o
PEEK		Some ‱o
PFA		Some ‱o

Table 2.5 Market shares by weight for the main thermoplastics

Thermoplastics	Market share (%)
PE	33–38
(LDPE/LLDPE)	(19–22)
(HDPE)	(11–16)
PP	20–21
PVC	15–18
PET	6–10
PS	7–9
Other styrenics	2–4
PA	1–2
PC	1
PMMA	1
Aceta1	<1
Other engineering	6
TPEs	<1
Total thermoplastics	100

thermosets. The unsaturated polyester resins (thermosets) are the most used, followed by polypropylene (thermoplastic). The thermoplastic share is growing fast.

Asian consumption is specifically orientated to glass reinforced plastics (GRP) without a significant production of advanced composites.

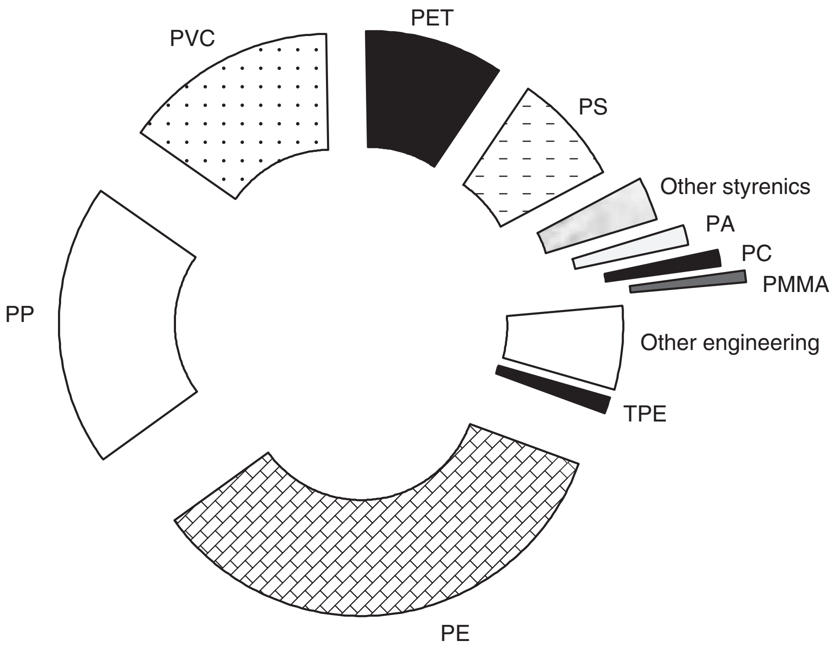


Figure 2.3. Market shares based on total thermoplastic consumption

Table 2.6 Composite consumption in North America, Europe and Asia

	America	Europe	Asia	Others
Composite consumption (million tonnes)	2.5	2.5	2.6	0.5
Share of world composite consumption (%)	31	31	32	6

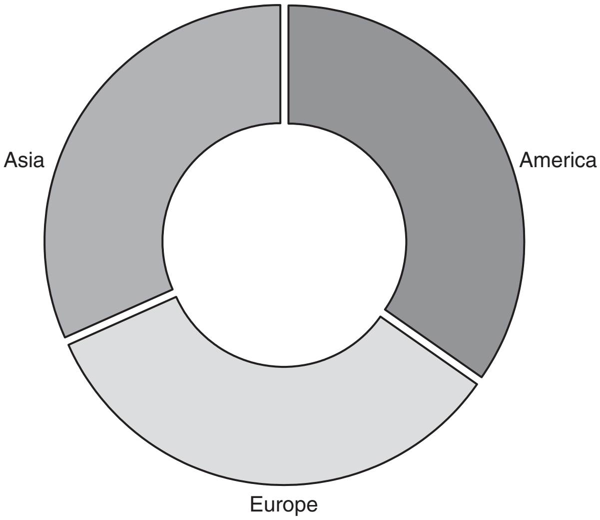


Figure 2.4. Market shares of the three main regions of composite consumption (%)

Figure 2.5 shows the share for polypropylene matrices versus thermoset matrices.

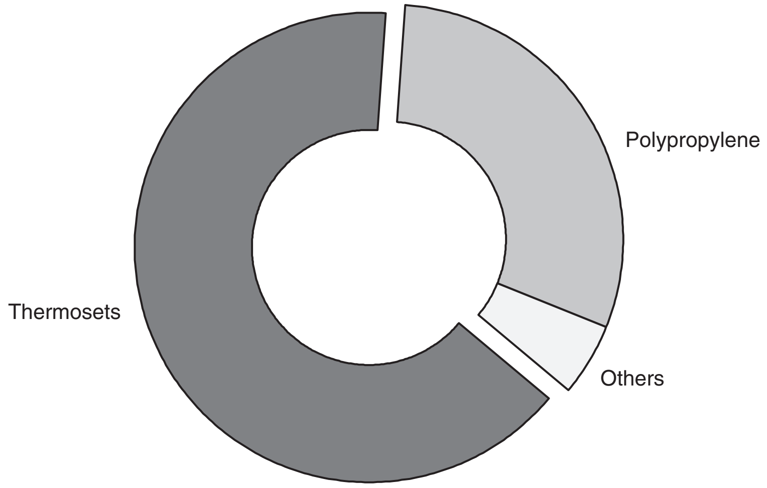


Figure 2.5. Market shares for the two main composite matrices

2.4 Market shares for the main application sectors

Table 2.7 and Figure 2.6 indicate the approximate market shares consumed by different application sectors for plastics as a whole. The figures vary according to geographical regions and may evolve with time.

- Three application sectors – packaging, building & civil engineering, automotive & transportation – consume 70% or more of all plastics.
- The eight application sectors that each consume more than 1% of plastics together account for more than 90% of the total plastics consumption.

Table 2.7 Market shares for the eight main plastic application sectors

Market	%
Packaging	37–39
Building & civil engineering	18–24
Automotive & transportation	8–13
Electrical & electronics	7–9
Sports & leisure	2–5
Furniture & bedding	2–4
Agriculture	2
Medical	1
Others	7–11
Total	100

The consumption of thermoplastics predominates (as indicated by Table 2.3) but the market share distribution of the thermoplastic application sectors (see Table 2.8 and Figure 2.7) is nevertheless somewhat different from that of plastics as a whole. Figures vary broadly according to geographical area.

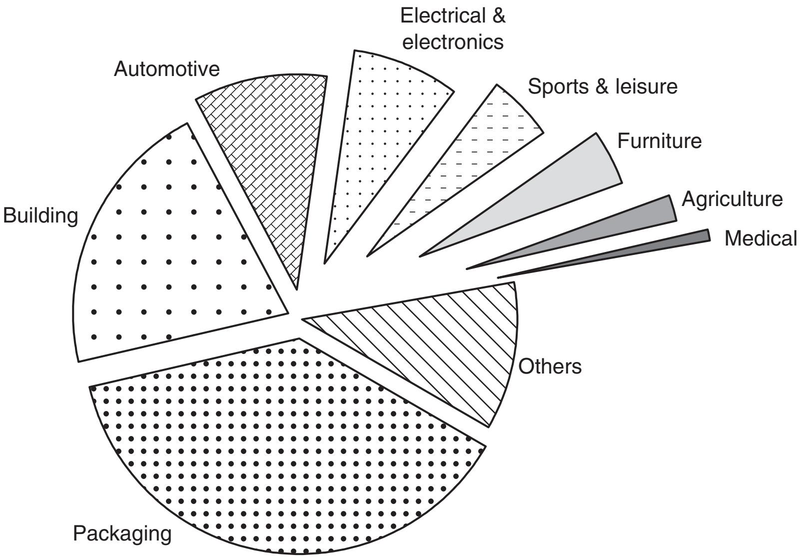


Figure 2.6. Market shares of the eight major plastic application sectors

Table 2.8 Market shares for the eight main thermoplastic application sectors

Market	%
Packaging	33–48
Building & civil engineering	19
Consumer goods	16
Automotive & transportation	5–13
Electrical & electronics	3–8
Furniture & bedding	1–4
Medical	2
Industrial	1
Others	4–6
Total	100

- The packaging sector, which is also a major application area for plastics as a whole, consumes 33% up to 48% of thermoplastics.
- The building & civil engineering sector is also the second-largest market for thermoplastics.
- The consumer goods sector is the third largest market for thermoplastics. (This sector is somewhat ill-defined and in later sections is divided between the household, office and entertainment appliances and sports & leisure sectors.)
- The shares consumed by the automotive & transportation and electrical & electronics sectors vary substantially with the geographical area considered.

The consumption of composites (see Table 2.9 and Figure 2.8) is atypical:

- The building & civil engineering sector is the major consumer.
- The composite market shares taken by the automotive & transportation, electrical & electronics, and sports & leisure sectors are approximately twice the average for plastics as a whole.

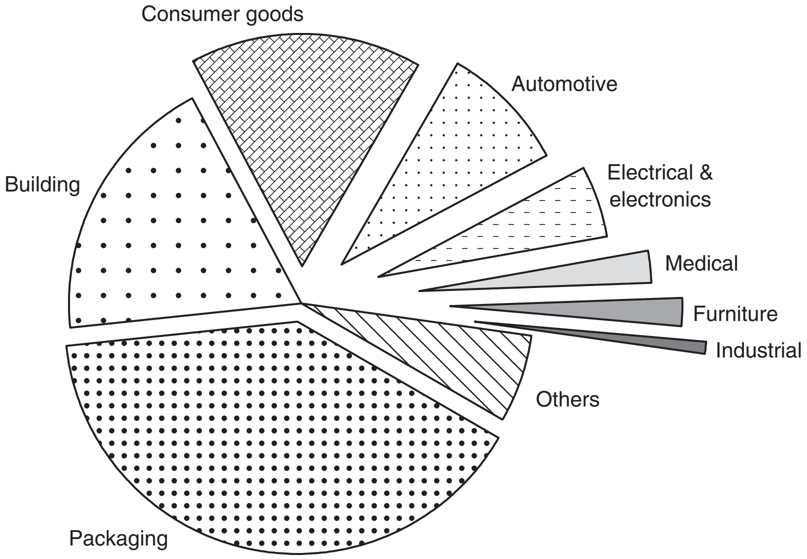


Figure 2.7. Market shares of the eight major thermoplastic application sectors

Table 2.9 Market shares for the nine main composite application sectors

Market	Composite shares
Building & civil engineering	23–39
Automotive & transportation	25–31
Consumer goods	5–13
Electrical & electronics	3–14
Mechanical & industrial	10
Shipbuilding	6
Aeronautics	1–3
Medical	1
Railway	1
Others	3
Total	100

- The shipbuilding sector consumes 6% of composites.
- The aeronautics sector is a significant composite consumer, particularly in terms of turnover, because of the high proportion of advanced composites used with matrices such as epoxies, polycyanates, polyimides, PEEK, and reinforcements such as carbon fibres.
- The packaging sector is absent.

2.5 Importance of the various processing modes

For each type of polymer, there are several possible processing methods from which it will be necessary to choose to best suit the required geometries, production rates, targeted properties and economic context.

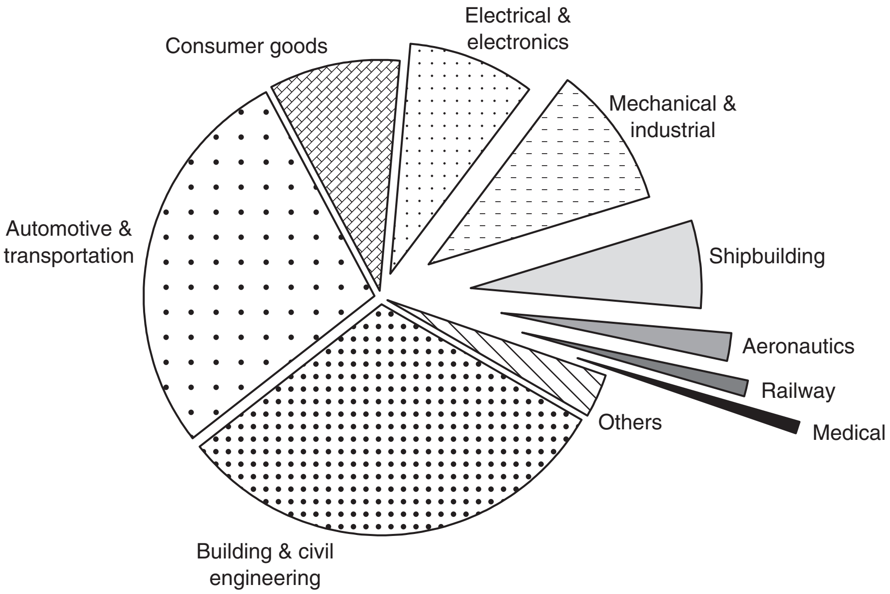


Figure 2.8. Market shares of the nine major composite application sectors

Figure 2.9 gives some indications of the distribution of thermoplastic consumption according to processing method:

- Extrusion is the most used process for films and sheets, tubes & pipes, various profiles . . .
- Injection is used for moulding small to large parts, from micro-switches up to fenders and pallets, etc.
- Blow moulding allows the manufacture of hollow parts, notably bottles.

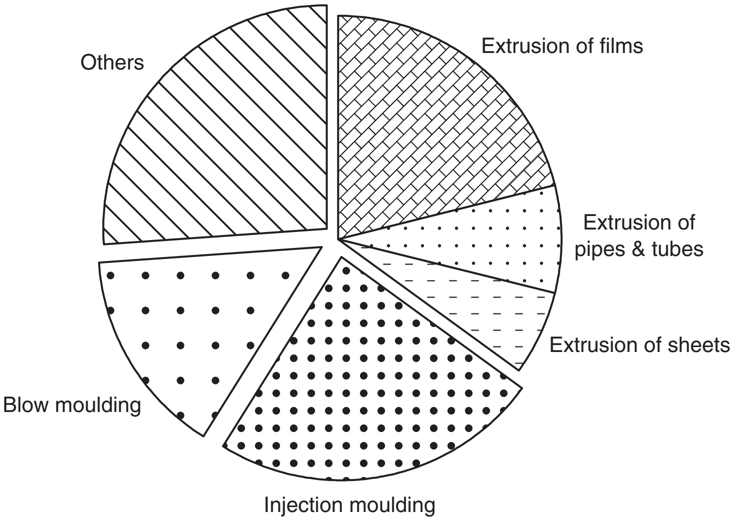


Figure 2.9. Market shares of the main thermoplastic processing methods

- Among the other processes let us quote, for example:
  - ○ calendaring, rotomoulding, casting, slush moulding and powdering for primary processing
  - ○ thermoforming, machining and boiler-making for secondary processing.

Composite processing uses specialized methods. For thermoplastics, glass mat thermoplastic (GMT) is the main method but prepreg, lay-up, tape winding, pultrusion are also used to produce composites. SMC/BMC are the main processes for thermosets but lay-up is currently used for large parts and prepregs are used for high-tech parts.

Figure 2.10 displays examples of market shares for the main composite processing methods.

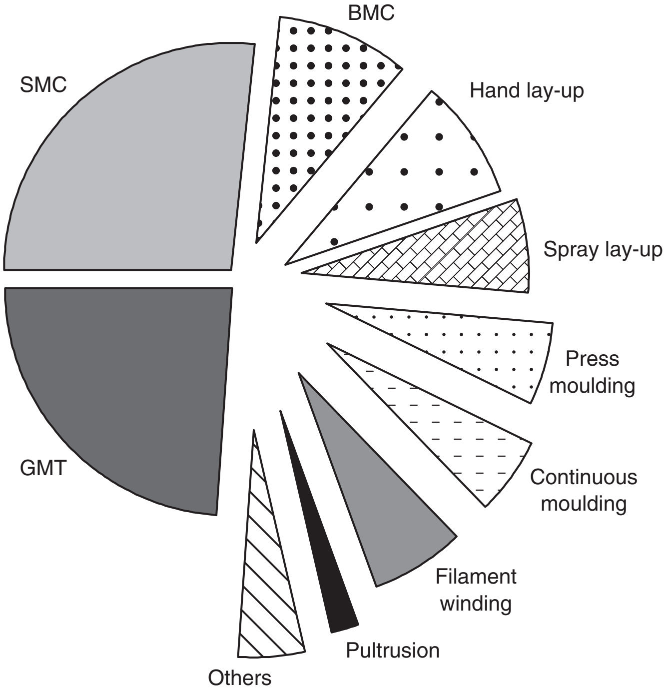


Figure 2.10. Market shares of the main composite processing methods

2.6 Consumption trends

2.6.1 Thermoplastics

Table 2.10 displays the consumption of the major thermoplastics in 2005 for the three main geographic areas, together with market shares and average annual growth rates (AAGR). These identified thermoplastics represent roughly 70% of the overall global consumption of plastics.

- Polyethylene is the most-consumed thermoplastic – 37% of the subtotal of the identified thermoplastics for the three main areas.
- The market share of polypropylene is lower but its annual growth rate is high.
- PVC, the third largest, is handicapped by environmental pressure. Its annual growth rate, mainly due to China, is the lowest.

Table 2.10 Consumption of major thermoplastics in 2005 for the three main areas

	2005 consumption (million tonnes)				Market shares (%)	AAGR (%)
	North America	Western Europe	China	Subtotal for the three areas		
PE	18.7	14.2	11	43.9	37	7
PP	8.8	8.5	9	26.3	22	8
PVC	7.7	5.9	8	21.6	19	6
PET/PBT	4.3	4.2	0.1	8.6	7	7
PS & other styrenics	4.8	4.0	6	14.8	13	6
PA	0.6	1.4	0.2	2.2	2	8
	44.9	38.2	34.3	117.4	100	7.6

- Styrenics are fourth with a moderate annual growth rate.
- Thermoplastic polyesters are atypical with an insignificant consumption in China but a high annual growth rate in Europe and America.

Globalization promotes the transfer of general-purpose thermoplastic processing from Europe or America to Asia.

2.6.2 Composites

The annual growth of composite consumption in industrialized countries is approximately estimated at a few percent. Table 2.11 shows some trends for the USA.

Table 2.11 US market shares for the ten main composite application sectors

	Share of composite consumption (%)	Annual change (%)
Automotive & transportation	31	5
Building & civil engineering	20	2
Corrosion protection	11	5
Shipbuilding	11	5
Electrical & electronics	10	4
Sports & leisure	8	4
Mechanics & Industry	5	2
Railway	1	4
Medical	1	4
Aeronautics	2	3
Total	100	4

2.7 The North American market

Table 2.12 (after statistics from the American Plastics Council) displays some estimations of consumptions, market shares and average annual growth rates (AAGR) for thermoplastics in North America. The American market shares are close to the global values with a steady growth rate, roughly 5–6% per annum.

2.8 The Western European market

Table 2.13 (after PlasticsEurope) displays the Western European consumption of thermoplastics for 2001 and 2005, with market shares and average annual growth rates (AAGR).

Table 2.12 North American market: estimations of consumption and annual growth rates

	Total sales and captive use (kt)		Market shares linked to identified thermoplastic uses (%)	AAGR (%/year)
Year:	2001	2005		
LDPE	3469	4000	9	3.6
LLDPE	4879	5940	13	5.1
HDPE	6898	8720	19	6.0
PP	7325	8810	20	4.7
PVC	6640	7720	17	3.8
Thermoplastic polyester	3165	4310	10	8.0
PS	2825	3180	7	3.0
ABS	597	710	1.6	4.5
SAN	57	65	0.1	3.2
Other styrenics	718	840	1.9	4.0
Nylon	526	600	1.4	3.3
	37 099	44 895	100	5

Table 2.13 Western European market: estimations of consumption and annual growth rates

	Total sales and captive use (kt)		Market shares linked to identified thermoplastic uses (%)	AAGR (% per year)
Year:	2001	2005		
LDPE/LLDPE	7758	8366	22	2
HDPE	5047	5813	15	3.8
PP	7247	8511	22	4.4
PVC	5725	5939	16	1
Thermoplastic polyester	3424	4180	11	5.5
PS	3083	3189	8	1
ABS/SAN	792	814	2	1
Nylon	1305	1351	4	1
	34 381	38 163	100	2.6

The European market shares are close to the global values with a low growth rate, roughly 3% per annum.

2.9 The Chinese market

Statistics are rare and often differ. However, it is generally estimated that:

- China is the main consumer among the Asian countries
- the consumption of commodities is higher than in fully industrialized countries, and
- the annual growth rates are higher, ranging between 7% and 30% according to the material considered and the optimism of the source. China benefits from globalization, which leads to the transfer of commodity processing from industrialized countries.

Table 2.14 displays some estimations without any warranty.

We can observe that the market shares are atypical:

- the share for PVC is a lot higher than the worldwide consumption
- PET/PBT are marginal, far lower than the global consumption
- polyamides have lower consumption than in industrialized countries.

Table 2.14 Chinese market in 2005: estimations of consumption and average annual growth rates

	Consumption (million tonnes)	Market share (%)	Annual change (%)
PE	11	31	7–15
PP	9	26	7–15
PVC	8	23	7–15
PS and other styrenics	6	17	7–15
Subtotal of commodities	(34)	(97)	
PC	0.4	1	10–30
POM	0.2	<1	7–15
PA	0.2	<1	10–20
PET	0.1	<1	10–20
PPE	<0.1	<1	10–30
Subtotal of engineering TP	(1)	(3)	
Grand total	35	100	7–15

2.10 Structure of the plastics processing industry

In Europe, there are approximately 29 000 companies specializing in processing plastics. Together they employ about one million people, and have sales around €100 billion. These figures do not represent the whole of plastics processing. A large number of enterprises are integrated into automotive, electrical/electronics, building, and toys and games firms and are not taken into account in these statistics.

SMEs employing more than 100 workers generate 75% of the plastics processing turnover. The general trend is towards alliances and mergers.

In the USA, there are approximately 13 000 companies specializing in processing plastics, about half the European figure. They employ about 600 000 people, and have sales around €63 billion. A large number of enterprises, integrated into other industries, are not included in these statistics.

In China, it is expected that companies are much smaller than in industrialized countries. For example, China is the leader for PE films but production is shared between about 10 000 companies.

Compared with the USA and Japan (Table 2.15), Europe appears to have:

- Smaller companies than the USA (a smaller ratio of employees versus the number of companies), but larger ones than Japan.

Table 2.15 Structure of plastics processing companies

Processing company and employment statistics			
	No. of companies	No. of employees	Ratio of employees to companies
Europe	29 000	1 000 000	34
USA	13 000	610 000	47
Japan	20 000	447 000	23

Processing turnover statistics			
	Turnover (million €)	Average turnover (million €) per company	Average turnover (million €) per employee
Europe	98 000	3.3	0.1
USA	63 000	4.8	0.1
Japan	86 000	4.3	0.2

- The same order of productivity as the USA, but a noticeably lower productivity than Japanese firms (in terms of average turnover per employee).

2.11 Plastic costs

Polymeric materials are intrinsically expensive, but their use becomes appealing if one takes into account the processing costs, the new technical possibilities that they permit and the total cost at the end of their lifetime.

Figure 2.11 analyses the various cost components.

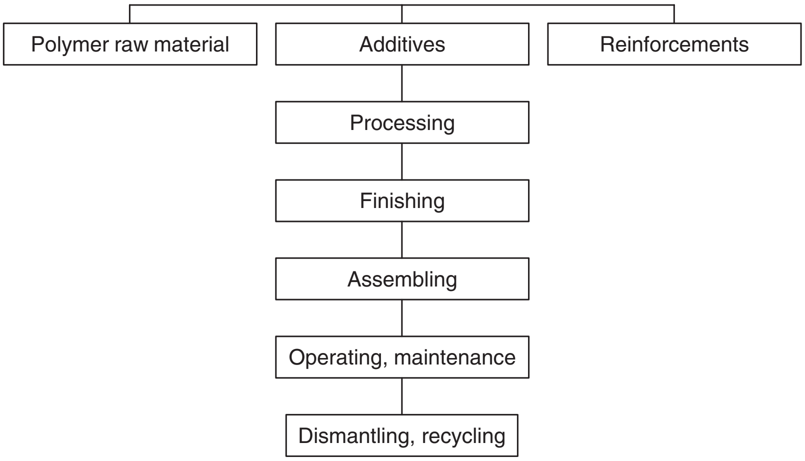


Figure 2.11. End-life cost of the plastic parts

2.11.1 Raw material costs

Most significantly, the price per litre varies from about €1 to more than €100 according to the nature of the polymer itself, the formulation of the grades and the inclusion of high-cost reinforcements including carbon fibres and so on.

The highest prices relate to the polymers with the highest performances, which are also the least used. Figure 2.12 illustrates this situation.

For comparison, the approximate prices per litre of conventional materials are roughly:

- €1.75–€14 for iron and steel
- €1 for wood.

2.11.2 Examples of additive costs

Apart from the reinforcements, the additives are numerous and some are more expensive than the raw polymer. Figure 2.13 displays the main additive categories.

Average prices for overall additives are roughly estimated from €1.6/kg to €2/kg with a broad range of individual prices from less than €1/kg for cheap fillers up to tens of €/kg for speciality additives.

To solve a same problem it is sometimes possible to choose between very different economic routes. For example:

- compatibility between fillers and polymers can be obtained with silanes ranging from €10 up to €20/kg or with functionalized polymers ranging from €3 up to €5/kg

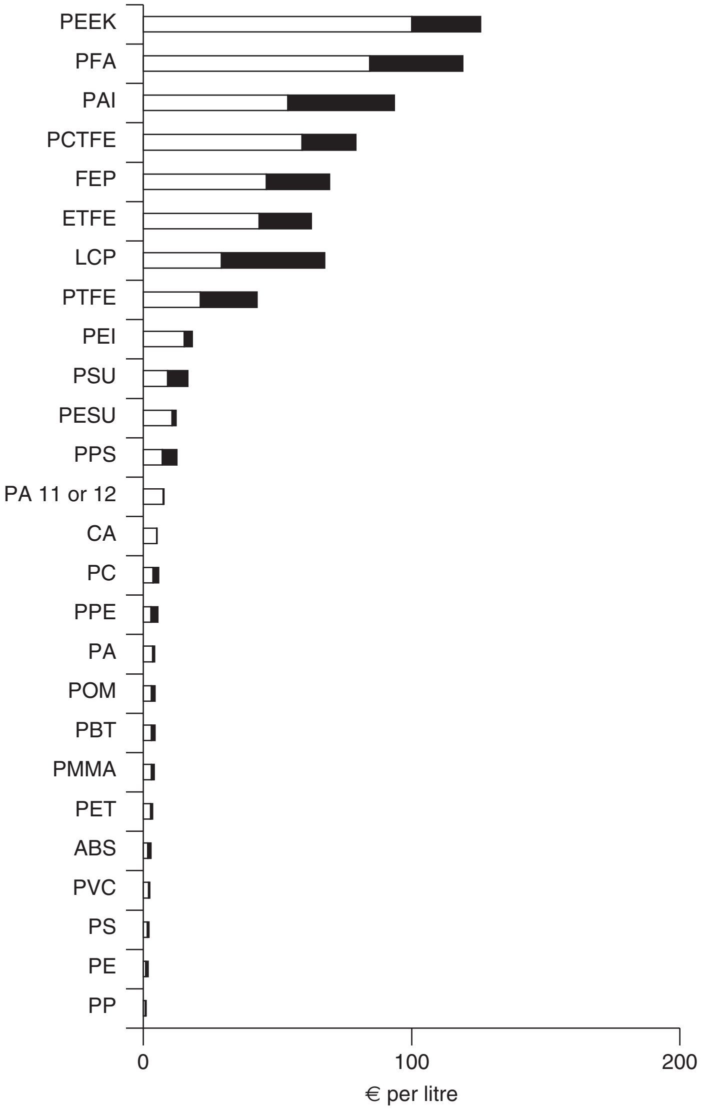


Figure 2.12. Plastic raw materials: costs € per litre

- UV protection can be obtained with cheap carbon blacks (but colour is grey to black) or with expensive photostabilizers.

The final choice depends on the specifications and the end-user's requirements.

2.11.3 Reinforcement costs

For the global advanced composites market, the average cost of high-performance fibre reinforcements (carbon, aramid, high modulus polyethylene, boron, R/S/T-glass and some E-glass) is estimated from €5.5 to €6 per kg. This moderate price is due to the decrease in the carbon fibre price. Some grades could fall to less than €10/kg in the short or medium term.

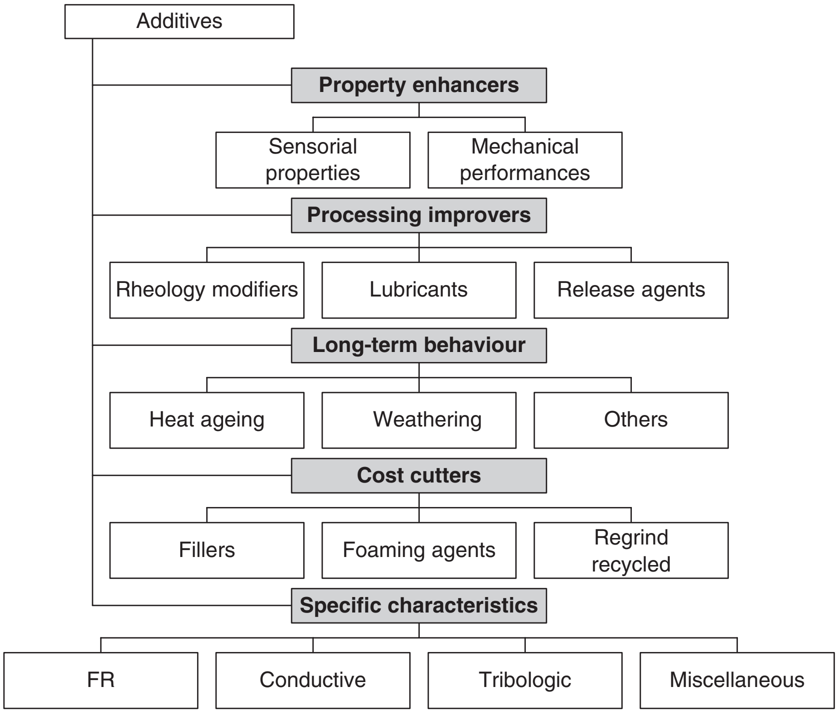


Figure 2.13. Additives for thermoplastics

The price of the fibrous reinforcements (Figure 2.14) depends on the nature of the fibres and the form of the reinforcement: continuous or chopped fibres, mats, rovings, fabrics or unidirectional.

Figure 2.14. Relative costs of various fibre reinforcements

The prices of fibres cover a large range, which partly explains the low consumption of fibres other than those of E-glass.

The prices of sandwich composite cores (Figure 2.15) range from 1 (reference) for balsa to 5 for the aramid honeycombs.

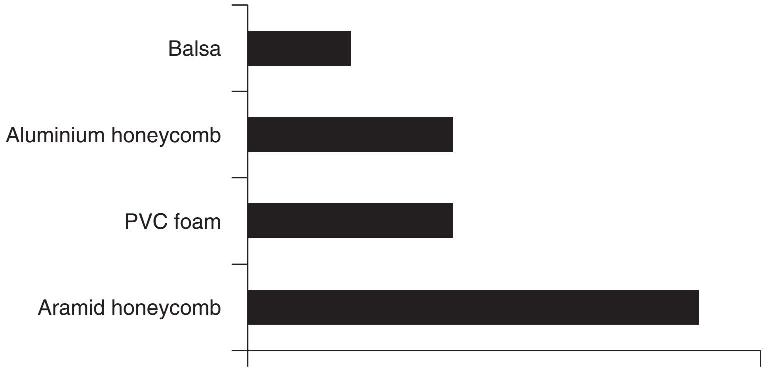


Figure 2.15. Relative costs of various cores for sandwich composites

2.11.4 Processing costs

The following figures for processing costs are some examples of the orders of magnitude for specific cases; a different context can lead to a very different cost.

Worldwide plastics consumption is of the order of 170 million tonnes annually in round figures, with a turnover of $560 billion – that is to say, an average cost of €3.3 per kg.

European costs and consumption are of the same order.

For a given processing technology, the processing costs are highly dependent on:

- the annual production
- the size and shape of the parts
- the precision level
- the material cost
- the processing difficulties
- the recycling possibilities.

For extruded goods such as films, sheets and tubes, the costs are of the order of:

- €2.5–3/kg for commodities
- €5/kg for high-performance films.

Each different design with a profile requiring the machining of a specific tool is charged with the tool cost.

The average cost for packaging is of the order of €4–5/kg.

The injection moulding cost of a part roughly represents the price of the raw polymer. The average selling prices are of the order of:

- €6/kg for building purposes
- €9/kg for consumer goods
- €11/kg for technical parts.

Each different design of parts requires the machining of a specific mould whose cost (for example, €50 000 or much more) is charged to the series of parts manufactured.

The composites, even those that are mass-produced, always have a high added value, for example:

- €4–6/kg for mass-produced parts
- €10/kg up to €40/kg for advanced composites.

Table 2.16 displays some approximate average selling prices of thermoplastics per kg.

Table 2.16 Average selling prices versus market

Market	Average prices (€ per kg)
Miscellaneous	4
Building & civil engineering	4
Electricity & electronics	4
Mechanics & industry	5
Automotive & transportation	6
Shipbuilding	6
Sports & leisure	9
Medical	15
Aerospace	38

Table 2.17 analyses some examples of the relative processing cost versus the annual production in units. The various technologies listed are not suitable for all materials or parts:

- machining is used with numerous materials
- rotational moulding uses liquid resins
- vacuum forming uses thermoplastic sheets
- blow moulding uses special grades of thermoplastics
- injection moulding is used with numerous thermoplastics, with a very few exceptions such as PTFE.

Table 2.17 Examples of processing methods and relative costs per unit*

	Prototypes
Units per annum	Machining
1	150
10	125

Processing methods for small and medium annual production

Units per annum	Hand lay-up	Machining	Rotational moulding, simple tooling	Rotational moulding, sophisticated	Vacuum forming	Blow moulding	Injection
100	25	110	35		60		
1000	15	100	10	40	15	80	200
10 000			7	7	7	10	20

Processing methods for high annual production

Units per annum	Rotational moulding, sophisticated tooling	Blow moulding	Injection
100 000	3	2.5	2.5
1 000 000	2.5	1.5	1

* Relative to the part cost for injection moulding 1 million parts per year.

The costs shown in this table are index-linked and do not have intrinsic value. The reference (base 1) is the part cost for injection moulding 1 million parts per year. The comparison is only valid for this table.

2.11.5 Some good reasons to use plastics and a few examples of success stories

The cost of a plastic part is generally higher than that of its metal counterpart and the 'overspend' must be compensated for by:

- the redesign of the parts, the integration of several functions
- the choice of new assembly technologies that save costs

- the decrease of operating costs. The automotive, aerospace and railway sectors are excellent examples of the compensation of material overspend by operating cost savings. The weight savings from the use of polymers and composites offer higher performances, increased payload and/or speeds and/or allow decreased fuel consumption. Consequently, the operating costs are reduced. The overspending allowed for a traditional solution compared with a polymer solution is roughly:
  - €300 per kg gained for a helicopter
  - €1200 per kg gained for a satellite
- maintenance cost savings, mainly due to corrosion resistance (but beware of ageing).

A few examples illustrate these features:

- For surgical parts, the replacement of stainless steel by liquid crystal polymer (LCP) leads to a material cost of the same order, but the ease of LCP processing compared to metal results in a lower final cost. The cost savings are about 50% for some standard parts and up to 90% for high-tech parts.
- Material for endoscopic surgery: two thermoplastics can replace a metal part. A 40% carbon fibre reinforced polyamide was initially used, which satisfied the mechanical and economic requirements but led to some processing troubles. A glass fibre reinforced LCP, of very similar properties, was then selected for its great fluidity, which made it possible to mould long parts with thin walls in much shorter cycle times (16 s instead of 26 s). The low thermal dilation coefficient in the direction of the flow is also an advantage. The matrix is more expensive but reinforcement is cheaper and, with a 38% shorter cycle time, the overall cost saving is 42%.
- Framework of load compensator on plane wings: injection moulding of carbon fibre reinforced PEEK replaces the aluminium alloy previously used. This part plays a critical role in plane safety and must resist the static and dynamic stresses and hydraulic fluids. The grade selected after many tests has a high fluidity allowing the manufacture of parts with dimensions of 200 mm by 400 mm. With 30% carbon fibre reinforcement, this PEEK grade:
  - saves weight
  - saves finishing costs because the part is ready for use when it exits the press without finishing operations, in contrast to the metal part
  - improves the behaviour with the hydraulic fluids.
- Thermostat casing for automotive cooling system: a new design with PPS (polyphenylene sulfide) makes it possible to integrate eight of the 12 components of the previous device. The 40% glass fibre reinforced grade has a medium fluidity that allows injection of complex shapes and resists hot glycols well. Benefits are:
  - weight saving
  - processing, finishing and assembling cost savings thanks to the integration of 67% of overall components and the ability to use the plastic part directly at the exit of the press without finishing operations, in contrast to the metal part.
- Replacement of metal bearings by a self-lubricating polymer. Metal bearings must be lubricated and are damaged by accidental breaks in lubrication or by aqueous lubricants. Special self-lubricating grades of PAI (polyamide imide) perform well and modifying the graphite, PTFE or other lubricating filler levels can optimize the performances. If there is any overspending versus metal, it can be compensated for by a lighter weight, the possibility to use almost all types of lubricants, and the maintenance cost savings in the case of a lubrication break.

- For the electricity & electronics markets, Table 2.18 displays the performances and costs of six engineering thermoplastics reinforced with glass fibres and UL94 V0 rated. The designer can choose between four levels of costs, five levels of water absorption and several levels of mechanical and thermal properties according to the requirements.

Table 2.18 Examples of UL94 V0 glass fibre reinforced engineering thermoplastics

	PBT	PA66	PET	PPA	PPS	LCP
Density (g/cm^3)	1.65	1.45	1.67	1.68	1.65	1.65
Cost/litre (€/l)	6	6	8	11	11	34
Water absorption (%)	0.1	1	0.2	0.2	0.05	0.02
HDT (°C)	204	250	224	293	260	265
CUT (°C)	120	130	120	180	210	220
Modulus/cost	1.6	1.5	1.2	1.2	1.3	0.3
Impact/cost	13	51	10	6	8	3
HDT/cost	34	39	26	28	24	8

2.12 Survey of main markets

The main markets and market shares for thermoplastics from the breakdown in statistics from different countries are roughly:

- packaging, 33–48%
- building & civil engineering, 19%
- automotive & transportation, 5–13%
- electricity & electronics, 3–8%
- household appliances, 3–6%
- miscellaneous appliances, 2–4%
- sports and leisure, 2–5%
- furniture & bedding, 1–4%
- agricultural, 2%
- medical, 2%.

2.12.1 Packaging

Packaging, the primary outlet for thermoplastics, consumes between 33% and 48% of all thermoplastics, depending on the country.

Several exceptional features explain the high level of thermoplastic use for packaging:

- Technical properties: thermoplastics offer an exceptional set of well-balanced properties, comprising low density, mechanical performances, physical characteristics, ease of processing, aesthetics and cost.
- Economical interest: thermoplastics are suitable for economical processing, from mass production down to low output specific packaging or even household uses.
- Aesthetic properties: thermoplastics allow much more design freedom than paper, cardboard, wood, glass, metals and other conventional materials.
- Environmental requirements: the light weight, the high waterproofing and damping properties compared to paper and cardboard make thermoplastics environment-friendly.

According to a report from the Packaging Science Department of Clemson University in the USA, packaging is essential for some basic reasons:

- Containment is the primary purpose of packaging – to carry food and water; industrial, agricultural and domestic chemicals . . .
- Protection:
  - of the contents from the environment: despoiling, breakages, contamination, pollution or leakage, protection of food from bacteria . . .
  - of the environment from the contents: leakage of pollutants, poisons, toxic and aggressive products . . .
  - of people, thanks to the shatter resistance that avoids the cutting shreds of broken glass
  - of the enclosed atmosphere: oxygen barriers keep organic produces fresh . . .
  - against inopportune uses: safety caps, child-resistant caps . . .
- Information: thermoplastics can be directly printed to inform the prospective user, without the possibility to falsify use-by dates and other information.
- Aesthetics: thermoplastics can be transparent or opaque, coloured, decorated, mimicking metal, wood . . . to appeal to prospective users and customers.
- Ease-of-use: extrusion and injection moulding are mass-production processes. Thermoforming and welding are convenient for high, medium and low outputs, welding even being possible with household devices. Use of thermoplastics allows original applications and continuous innovation for the best-known application, resealable packaging; flexible, shrinkable, tear-proof, barrier films; inviolable packaging . . .

The commodity thermoplastics are the most-used plastics in this sector, accounting for 95% of all thermoplastic packaging. Polyolefins are the most important, accounting for more than 65% of the total plastic weight. Polyethylene terephthalate, polystyrene and PVC are also commonly used.

Engineering thermoplastics such as acrylics (PMMA), polyamides and polycarbonates are only used for specific properties.

Thermoplastic composites are not listed in packaging statistics. There are only specific applications in the transport of fragile and expensive goods.

TPEs are not listed in packaging statistics: there are only specific uses for thermoplastic styrenics (TPS), copolyester TPEs (COPE) and polyether bloc amides (PEBA) in tear-proof films, and for TPOs and TPVs in seals, etc.

Figure 2.16 shows the estimated shares of the most-used thermoplastics. Very different figures can be found elsewhere according to the estimations, countries, types of packaging etc. that are taken into account.

Environmental regulations and trends are leading to a decay in the consumption of PVC.

Plastics comprise 17% of all materials used in packaging and package over 50% of consumer goods. The future is promising for many reasons:

- Some sets of thermoplastic properties are unattainable for the other materials, for example:
  - the flexibility and resistance of thermoplastic films versus paper and cardboard
  - impact behaviour compared to glass
  - chemical behaviour compared to metals
  - weldability of films with industrial systems or household devices
  - damping properties of foams of polystyrene, polyethylene, PVC, polypropylene
  - water- and gas-proofing versus paper and cardboard

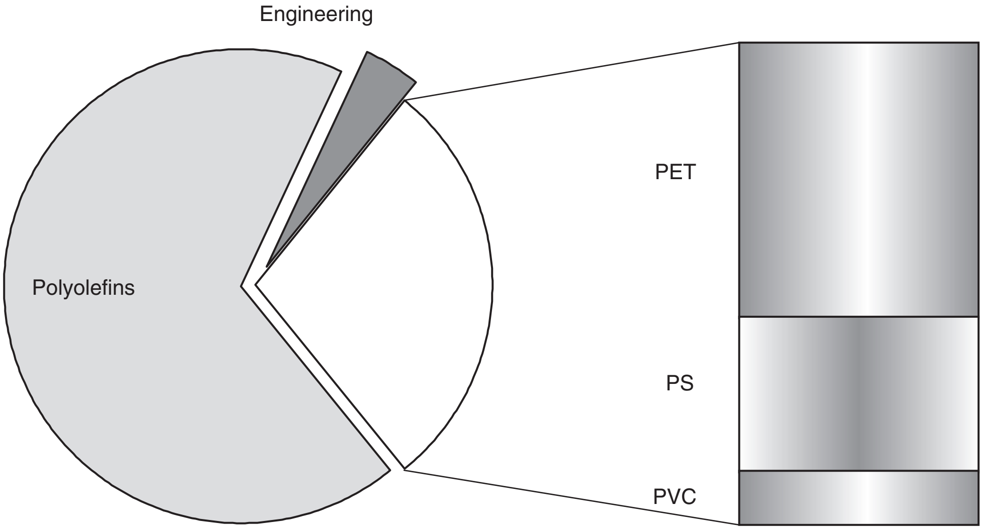


Figure 2.16. Thermoplastic shares in the packaging market

  - ○ elasticity and sealing properties of TPEs
  - ○ low modulus, soft touch . . . of TPEs, and some soft thermoplastics.

Without plastic packaging:

- the weight of packaging would increase several times
- production costs and energy consumption would be doubled
- waste volume would be increased by 150%
- packaging failures during storage, handling and transport would be generally increased
- injuries and economic losses would also be increased.

Moreover, over a ten-year period, plastic weight per unit of packaging has decreased at the rate of 2% per annum.

Thermoplastics can also lead to composites and hybrids including other conventional materials – such as paper, cardboard, metals and glass – to integrate several functionalities thanks to the exceptional combination of properties: for example, multilayers of polyethylene (a water barrier) and PVA (an oil barrier), shatterproofing of glass containers . . .

Polymers also have some general handicaps:

- the environmental constraints and public image
- raw material costs (see Figure 2.17) considered as a function of volume (€/litre)
- the low modulus and strength
- the propensity to creep.

Figure 2.17 shows that the cost per volume of the commodity thermoplastics is intermediate between steel and aluminium, which explains their development in packaging and the poor penetration of the much more expensive engineering thermoplastics.

When they cannot directly compete with conventional materials, the versatility of thermoplastics easily allows a partnership with them. Examples are numerous:

- multilayer films with paper
- spread papers and cardboards
- multilayer films with metal foils
- protective coatings for metals.

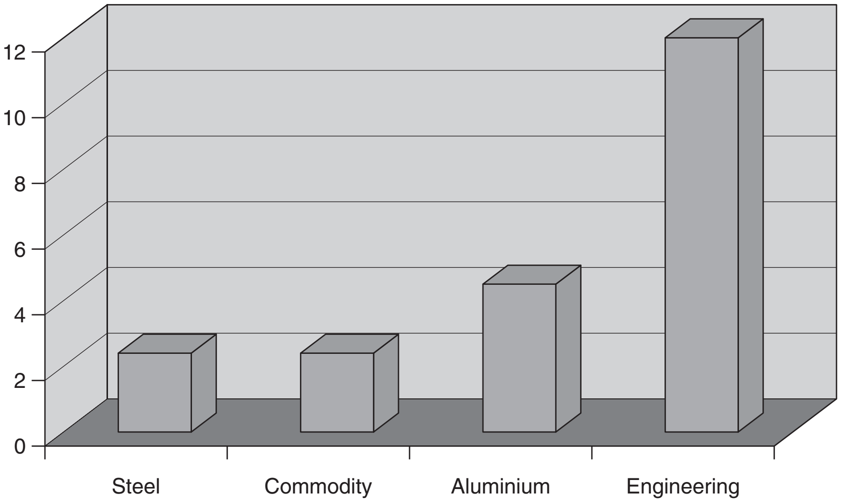


Figure 2.17. Cost per volume (€/l) of materials most used for packaging

The versatility of plastics allows the industrialization of innovative solutions combining several functions such as, for example:

- packaging and display units for toys, knick-knacks . . .
- packaging and support of fitting for fans, taps . . .
- aesthetics and insulating housing for champagne bottles . . .

Let us quote some application examples for some thermoplastics. These examples may be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade in the real conditions of service life.

Polyethylene

- Films for packaging: food, non-food, shrink, stretch, retail bags . . .
- Liquid food bottles, household chemical bottles . . .
- Drugs, cosmetics and toiletries containers . . .
- Crates and totes.
- Food and beverage containers.
- Housewares.
- Industrial and shipping pails.
- Basins, bottles, stoppers, hollow parts, pallets . . .
- Large-sized objects: cisterns, tanks, septic tanks, industrial drums . . .

PE foams

- Flakes, chips, sheets, blocks used for impact protection and damping in the packaging of various products such as cameras, electronic devices . . .
- Antistatic, conductive foams for electronics packaging . . .
- Isothermal packaging.
- Cool bags.

Polypropylene

- Blow moulded and sheet thermoformed products for food, personal care, health, medical and lab ware applications, household chemicals and beauty aid products . . .

- Clear or drop impact resistant containers, boxes, hot filled bottles, dessert pots, horticultural pots, integrated hinge boxes, bottles and other cans up to several litres, caps and closures for beverage and cosmetic applications, medical disposable trays, containers for irrigation, parenteral, haemodialysis solutions . . .
- High clarity parts for medical and food packaging . . .
- Oriented, bi-oriented and cast films and foils for food, non-food and medical packaging, confectionery, tobacco, clothing packaging, medical pouches, monoblister packaging, film tapes, straps . . .
- Talc-filled reinforced polypropylene films and foils are beginning to replace PVC for corrugated board, labels . . .

Polypropylene foam

- Reusable packaging or shuttle packaging for heavy parts such as doors, windscreens, rear mirrors . . .
- Packaging of fragile parts: electronics, office automation devices, electric motors . . .
- Damping blocks, intermediate layers . . .
- Functional packaging useful for shipping and installation on site.

Polymethylpentene

- Films, caps, containers and bottles for cosmetics . . .

COC

- Pharmaceutical containers and packages, primary packaging of pharmaceuticals . . .
- Films and packaging with barrier properties, blister packaging, shrink caps, sleeves and stand-up pouches, co-extruded films . . .

EVA

- Films and sheets with high clarity, puncture resistance, impact strength, low heat-seal temperature used for shrink-wrap, heavy-duty shipping sacks, produce bags, bag-in-box food and technical packaging films . . .

EVOH

- Films for flexible food packaging . . .
- Lids for thermoformed food packages . . .
- Pouches for sauces, coffee, tea, soup . . .
- Free-standing pouches . . .
- Packaging for organic solvents, agricultural pesticides and all kinds of oils . . .

EMA

- Packaging films and sealants, puncture-resistant films for pouches and blister packs, glass coatings . . .
- Packaging, food and non-food, perfume bottle caps, shampoo bottles, various bottles and containers, glass product coatings . . .

PVC

- Films and sheets for packaging and thermoforming consume 7% of all PVC . . .
- Clear and opaque bottles consume 1% of the PVC total . . .
- Food and non-food packaging, various containers for chemicals, clear blisters . . .
- Jar lid gasketing . . .

- Blisters and dosage packs for pharmaceuticals and medicines, single dose medication packaging, shatterproof bottles and jars . . .
- Foam for packaging of fragile goods, warm or cold foods . . .

PVDC

- Barrier films for food, pharmaceuticals, chemicals . . .

PS, ABS

- Transparent packaging . . .
- Containers, trays . . .
- Food packaging, cups and dairy containers from thermoformed sheets, vacuum-formed packages . . .
- Refrigeration packaging . . .
- Cosmetics packaging . . .

EPS

- Boxes, crates, cases for cooled foodstuffs: fish, ice creams . . .
- Packaging of electrical household and business appliances, TV, radio, office automation, printers, computers, electric tools . . .
- Structural industrial packaging: engines of cars . . .
- Packaging & display units . . .
- Flakes, chips, sheets . . .

Thermoplastic polyester

- Beverage bottles . . .
- Trays for food . . .
- Packaging for tablets, pills, capsules, suppositories; urine containers, sterilizable equipment . . .
- Films, shrink films . . .
- Packaging of cosmetics and health care products . . .

Polyamide

- Films, sheets and plates for packaging and thermoforming, barrier layers of multilayer films . . .

Polycarbonate

- Baby bottles, water dispensers, water bottles . . .

PPE

- Microwaveable food packaging . . .

ETFE

- Food packaging, pharmaceutical packaging, industrial packaging . . .

PCTFE

- Food, pharmaceutical, health care, medical, industry and chemical packaging . . .
- Moisture-proof film packaging . . .

ECTFE

- Sterilizable, pharmaceutical and industrial packaging . . .
- Technical packaging, pouches for gas sampling . . .

Cellulosics

- Aesthetic packaging . . .
- Films, transparent wrapping, blister packaging . . .
- Containers, bottles, boxes and tubing . . .
- Healthcare, cosmetics, perfumery and personal care supply containers and packaging . . .

PEEK

- Integrated circuit packaging (hard disk drive; HDD) trays . . .

TPE

- Seals and closures for cosmetics and toiletries . . .
- Food and beverage: capping for dairy products, fruit juices, sports drinks, beers, wines and food . . .
- Pharmaceutical packaging closures, seals and liners . . .
- Kitchen and household food storage, lids and seals, cookware, housewares and closures . . .
- Airtight boxes with integrated TPV seal (bi-injection moulding of PP and PP/EPDM-V) . . .

Biodegradable polymers

Packaging is the primary application of biodegradable plastics for several reasons:

- Plastic bags have been restricted or taxed in Ireland, Germany, South Africa, Taiwan and elsewhere due to concerns about disposal.
- Packaging often has a short lifetime.
- Packaging produces pronounced visible pollution.

Consequently there is new interest in degradable polymers despite a general overspend.

The natural and biodegradable thermoplastics are, for example:

- starch and other natural derivates of uncertain formula . . .
- polylactic acid (PLA)
- polyglycolic acid (PGA)
- polycaprolactone (PCL)
- polyhydroxyalkanoate (PHA)
- polyhydroxybutyrate (PHB).

These materials are of interest for packaging as shown by some examples:

- UK supermarket chains Co-op, Kwik Save and Somerfield use degradable carrier bags. In Italy, the large supermarket chain IPER is using Cargill Dow's NatureWorks-brand resin in film to wrap fresh food and pasta at its 21 locations.
- Major UK supermarket Tesco will use PE carrier bags containing a degradable additive supplied by Canadian firm EPI following a six-month trial.
- Cellulose hydrate is used with sweets and as artificial skin for sausages.
- Cellulose acetate has been used for dry food without fat.
- At the Olympic Winter Games in Lillehammer, biodegradable products were used for catering.
- Investigations for yoghurt cups are ongoing.
- Foil bags for the collection of biological waste and biodegradable loose-fill packaging materials are already in use.

- Cargill Dow has some commercial applications in Europe and Asia. A major market has been blister packaging used to wrap such products as Sony Walkman radios and digital versatile discs (DVDs).
- Milk bottles are now available in Europe.
- Transparent containers for olive oil and other cooking oils will be soon available.
- Cadbury will use a cornstarch polymer for the chocolate tray in its Milk Tray range.

For the packaging market, the sector with the highest consumption of thermoplastics, recycling is of course of crucial importance. Unfortunately, plastic recycling presents technical and economic difficulties and is less advanced, industrially, than that of metals or glass.

Apart from consumption, packaging is also a crucial sector because:

- the products are of short lifetime
- polymers are very resistant to degradation, their natural elimination is often impossible and the environment is polluted for a long time
- a high percentage of the packaging wastes, such as films, bags and bottles, are very lightweight and lead to evident pollution:
  - ○ visual: films, polyethylene bags; PVC or polyester bottles . . .
  - ○ physical: obstruction to water flow . . .
- end-of-life wastes are often domestic and the sources are very diffuse
- the wastes are often soiled with food, oils, chemicals . . .

The main methods for the recycling of polymer-based packaging wastes are:

- energy recovery by combustion. Table 2.19 (after Neste) displays some calorific properties of plastic wastes showing the excellent properties of polyethylenes compared to coal
- mechanical recycling and re-use with virgin material in the same or another application.

Table 2.19 Calorific properties of coal and plastic waste fuels

	Coal	Polyethylene	Mixed plastics
Low heat value	25	40	32
Carbon	64	81	65
Ash	16	3	18

Conversion into basic chemicals by chemolysis or thermolysis is a secondary method.

The situation varies significantly according to the country. Table 2.20 shows the contrasting approaches to the problem of packaging waste in Europe with:

- the total of treated wastes ranging from 15% to 85% according to country
- opposite methods of treatment chosen by Germany, with 51% of packaging waste handled by mechanical recycling, and Denmark, with 9%
- energy recovery (20%) is slightly higher than mechanical recycling (18%).

Table 2.20 Treatment of the packaging wastes in various European countries

	Total (%)	Energy recovery (%)	Recycling (%)
Denmark	85	76	9
Germany	70	19	51
France	49	37	12
Italy	22	10	12
United Kingdom	17	6	11
Spain	15	6	9
European Union	38	20	18

To ease recycling, some general rules, which of course suffer from exceptions, can be stated:

- mark parts to make the later identification of the materials easier
- avoid the use of incompatible polymers in the same part or subset
- standardize the polymers used
- preferably choose a material that can be recycled in the same fabrication.

The use of thermoplastics, TPEs and composites is growing in the various segments of packaging:

- films: polyethylene, polyester, PVC
- bottles, cans and other containers: PET, polyethylene, PVC (declining)
- foams for damping and protective packaging: polystyrene, polyethylene and others . . .
- rigid and transparent sheets of PVC, polycarbonate, PMMA for blisters and boxes . . .
- sealing against gas, liquids, dust, moisture and air: TPEs and some soft thermoplastics
- structural packaging.

To forge ahead in the packaging sector, thermoplastics must enhance their performance in terms of their characteristics, ease of processing, productivity and recycling. For example:

- better thermal behaviour: to handle temperature rises in packaging processes:
  - ○ hot food filling of bottles, containers . . .
  - ○ quick re-heating of food containers
- better low-temperature behaviour: freezing and deep-freezing
- ease of processing: the aptitude for processing leads to lighter and cheaper packaging, shorter cycles, factors of productivity
- low finishing costs: easier printability, bulk colouring, in-mould decoration, in-mould assembly and adapted design cut the finishing and assembling costs
- recycling: it is necessary to ease recycling and to find industrial outlets by:
  - ○ choosing compatible materials
  - ○ using the mono-material concept.

2.12.1.1 Films for packaging

Figure 2.18 schematizes some aspects of the versatility of films.

Economic statistics mix all films and sheets, sometimes including or excluding bags, sacks and so on. Consequently, the following data are not specifically related to packaging films only and are somewhat 'fuzzy'. Very different figures can be found elsewhere.

Table 2.21 displays the consumption of thermoplastics for films in Europe:

- around 70% of film is made out of polyethylene
- 77% of LDPE and LLDPE is transformed into films.

Figure 2.19 displays the supremacy of the polyethylene family with roughly 70% of the film market.

Typically, film usages can be divided into:

- packaging
  - ○ food
  - ○ non-food
  - ○ stretch and shrink wraps
- non-packaging.

Food packaging film is used as, for example:

- in-store bags for produce such as vegetables, breads and other bakery goods
- tray covers for institutional deliveries

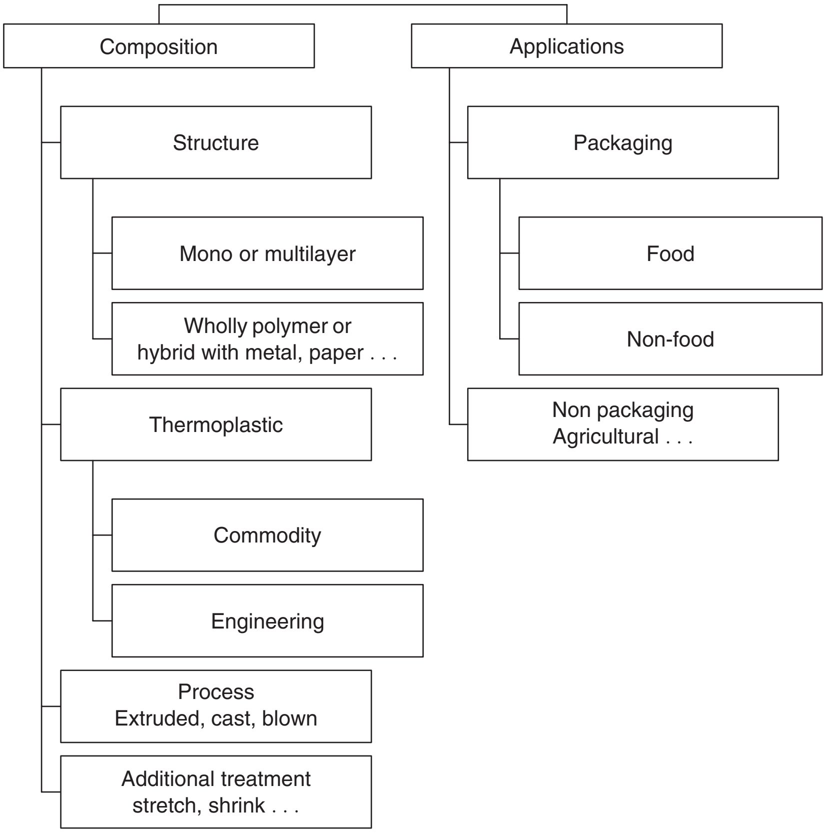


Figure 2.18. Versatility of films

Table 2.21 Resin sold into common film applications in Europe (2001)

	Share of the plastic family in the film market	Share of film applications in the total for the plastic family
Unit	1000 tonnes	Percent
LLDPE+LDPE	60	77
PP	17	28
PVC	12	18
HDPE	9	19
Nylon	1	14
PET (excluding recording films)	1	4
Total	100	33

- bags-in-a-box (for wine, for example)
- edible bags containing food directly reheated in boiling water
- candy and confection bags and wrappers
- carton liners
- poultry and seafood wraps . . .

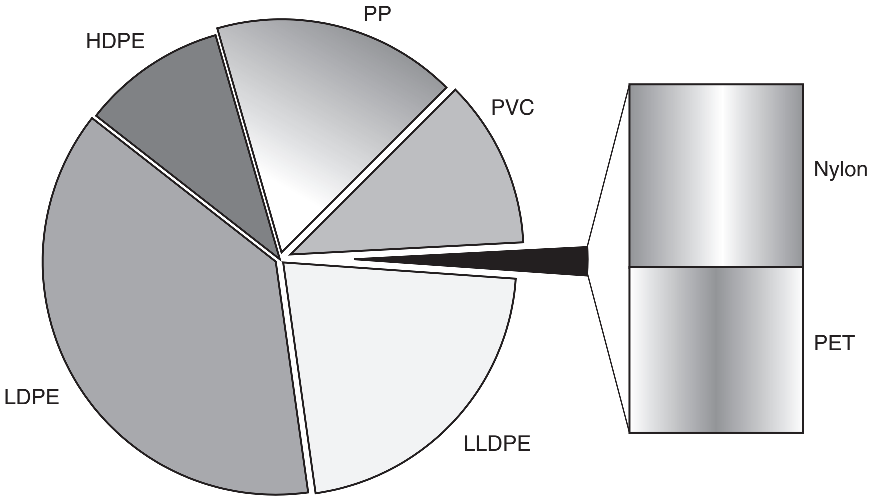


Figure 2.19. Thermoplastic shares in the film market

Non-food packaging film is used as, for example:

- industrial liners for shipments, shipping sacks, multiwall sack liners . . .
- bubble packing
- overwrap
- rack and counter bags
- envelopes.

Stretch wrap is a strong, flexible film that can be stretched to take the shape of the contained goods. It is used at home to over-wrap fresh meat and other leftovers or industrially to secure shipping cartons to pallets. It is usually made of LLDPE, LDPE or PVC.

Shrink wrap is a film that is applied loosely around products, then sealed and shrunk by heating to take the shape of the contained products. It can be used to bind multiple packages, or to secure an entire pallet of packages, to bundle magazines and papers, to protect and display albums, CDs and so on. It is usually made of LLDPE, LDPE or polypropylene.

Let us remember that non-packaging applications are numerous, for example:

- agricultural films
- construction films such as vapour and moisture barriers in walls, foundation, roofing
- protective cloths and drapes
- medical and health care films
- garment bags, self-service bags, household wraps
- disposable diapers
- recording tapes
- dielectric films . . .

Table 2.22 displays the main properties and film applications of some thermoplastics.

2.12.1.2 Bottles and other containers

Thermoplastic bottles and other containers are growing fast by replacing glass principally but also metals in the packaging of food, beverage, household and industrial chemicals, oils, drugs, cosmetics, toiletries . . .

Table 2.22 Properties and film applications of the main thermoplastics

	Applications	Properties
	Commodity thermoplastics	
LDPE/LLDPE	Stretch wrap, shrink wrap Bags, textile bags, mattress bags, boiling bags, bags-in-a-box, garment bags, shipping sacks Carton liners, industrial liners, bin liners Bubble packaging, envelope films Overwrap	Good clarity Good moisture barriers Fair gas barriers Heat sealing Strong and highly flexible
EVA	Typically used in combination with PE for bag-in-box applications Packaging of meat, poultry and ice	Excellent adhesion Good flex crack resistance Good heat sealing properties
HDPE	Bags, retail bags Carton and box liners, industrial liners Shipping sacks Envelope material such as DuPont's Tyvek®	Good moisture barrier Fair gas barrier Resistant to grease and oils Stiffer than other polyethylene films Strong and puncture resistant
PP	Packaging for cigarettes, foods, sanitary goods Shrink wrap Diapers Sterile wrap	Good clarity, high gloss Excellent moisture barrier Average gas barrier improvable by combination with PVDC coating or acrylic Good tensile strength Higher melting point than PE
PVC	Some stretch and shrink wraps for industrial and pallet wrap Some bags and liners Blood bags, IV bags Packaging for fresh red meats Adhesive tapes, labels	Excellent clarity Semi-permeable to oxygen Good barrier to oil and grease Puncture resistant Good cling
PET	Metallized packages Microwave packaging Brick packs, cigarette wrap Medical packaging, sterile wrap Labels	Clear Good mechanical properties Good thermal properties
	Engineering and speciality thermoplastics	
PVDC	Household wrap (Saran™) Layer barrier onto other materials such as PP	Excellent moisture and gas barrier Resistant to grease and oil
EVOH	Multilayer, co-extruded with PE, that has good moisture barrier properties Modified atmosphere packaging	Excellent gas barrier but it loses those properties when moistened
Nylon	Conventional and microwave cooking applications Coating for other materials that are permeable Cheese packaging	Good oxygen barrier Semi-permeable to carbon dioxide Relatively high melting point

Now, plastics are the third most common material used in packaging, very nearly equivalent to glass, some way behind paper and cardboard but ahead of metals, as we can see in Figure 2.20.

Thermoplastics offer an exciting set of diversified characteristics:

- Technical: dramatic weight reduction versus glass leads to many energy savings, such as less energy and fuel used in packaging production, handling, transport of the

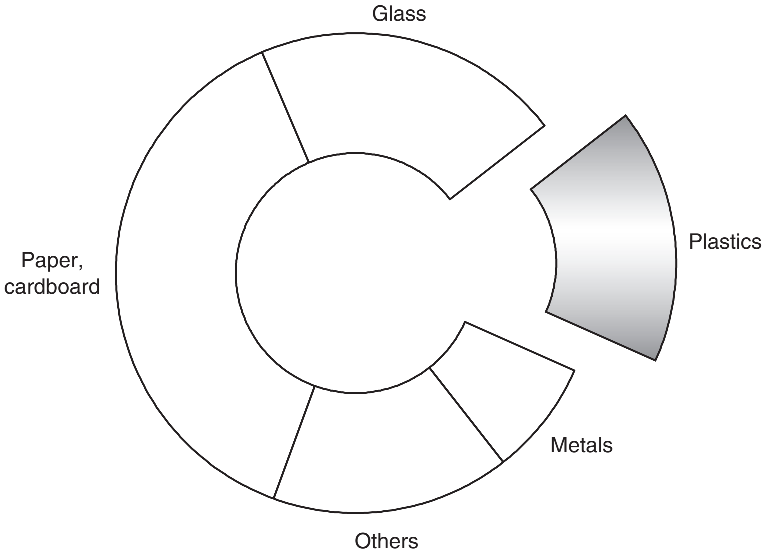


Figure 2.20. Material shares in the packaging market in Western Europe

product and of the end-of-use wastes. Figure 2.21 shows examples of bottle weights according to the material used – glass or PET – and capacity.

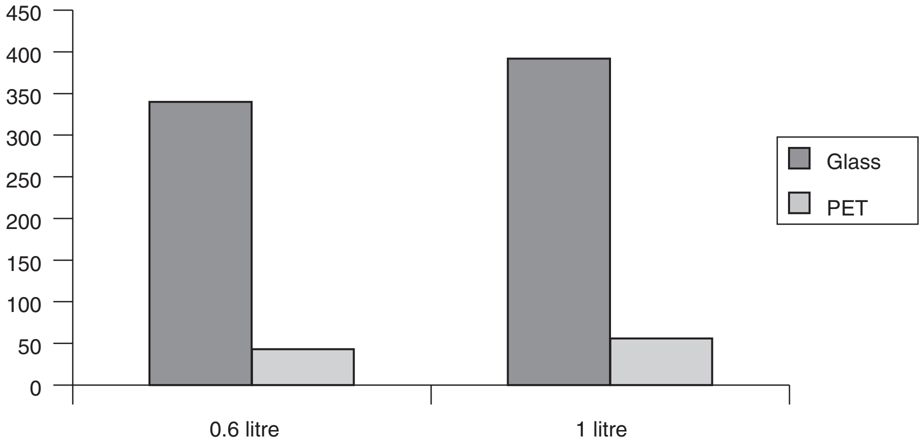


Figure 2.21. Bottle weights (g) according to the material used and capacity

- Economical: plastics are the economical answer for mass production as well as for specific packaging.
- Aesthetics: plastics allow much more design freedom than glass or metals.
- Environmental: the reduction of weight compared to glass makes plastics environment friendly.

Table 2.23 displays identified Western European and North American consumption for bottles, containers and other blow-moulded items, and average annual growth rates (AAGR).

Table 2.23 Identified consumption for bottles, containers and other blow-moulded items, and average annual growth rate (AAGR)

	Consumption (1000 tonnes)			AAGR (%)	
	1995	2000	2001	2001/2000	2001/1995
Western Europe & North America					
PE	2915	3741	3768	0.7	4
PVC	498	238	205	−14	−14
PET	1872	3010	3326	10.5	10
Total	5285	6989	7299	4.4	5.5

Polyethylene use is growing slowly while PVC use drops by 14–16% each year, to the benefit of PET.

Figure 2.22 shows the supremacy of polyethylene and thermoplastic polyester (PET) in the European bottle and other blow-moulded container market.

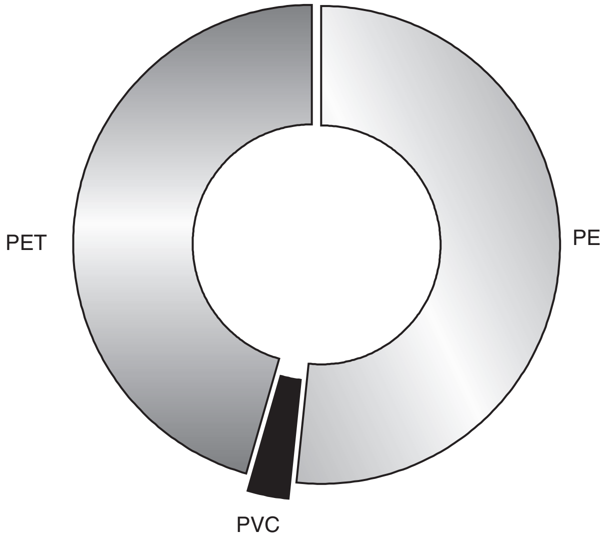


Figure 2.22. Material shares in the bottle market in Western Europe

Blow-moulded containers have various and diversified applications from small bottles to drums for packaging of foods and beverages, chemicals, motor oils, cosmetics, toiletries, drugs and pharmaceuticals. Table 2.24 displays some examples for industrialized countries.

The use of bottles and other containers depends on several growing markets, for example:

- water bottles are increasing dramatically at the highest AAGR of 11.7%
- juice and non-carbonated beverage bottles are growing at an average of 7.1% per year in spite of a slowing compared to recent years
- PET salad dressing and condiment containers are replacing glass with a 6.7% average annual growth
- dry food containers are growing at a similar rate of 6.7% per year
- milk, the slowest growing beverage packaging, increases at an AAGR of 3.5%

Table 2.24 Identified consumption of PE, PVC and PET for bottles, containers and others according to the end use

	1000 t	Share (%)
HDPE (USA)		
Blow-moulded chemicals bottles	656	34
Blow-moulded food bottles	602	31
Blow-moulded drugs, cosmetics & toiletries packaging	129	7
Drums	118	5
Blow-moulded motor-oil bottles	91	5
Blow-moulded other items	349	18
Subtotal PE	1945	100
PET (Western Europe)		
Beverage bottles	1541	84
Food packaging	211	11
Cosmetics & pharmaceutical packaging	94	5
Subtotal PET	1846	100
PVC bottles (Western Europe)	130	

- beer packaging is an enormously promising sector for PET with an estimated international consumption of more than 300 billion containers a year and a worldwide growth rate of 4% per year. Plastic bottles are not much used and could develop well.

The rapid growth of PET can be explained by:

- environmental pressure on PVC
- the suitability of PET for hot-filling
- possibility to carry PET packaging directly from freezers to ovens, including microwaves
- superiority of PET clarity versus that of PE
- better balance of gas permeabilities, combining the moisture impermeability of PE with a better oxygen and CO_2 impermeability than PVC. Table 2.25 compares the permeabilities of the main three thermoplastics under roughly the same conditions. Results are expressed in the same units for a given gas.

Table 2.25 Gas permeability of PET, PE and PVC

	PET	PE	PVC
Moisture	<1	1	7
Air	10	700	28
N_2	8	500	12
Oxygen	60	1500	87
CO_2	150	6500	200

To improve their development in packaging, thermoplastics must innovate and enhance their performances in terms of characteristics, ease of processing, productivity and recycling. Such improvements include:

- better gas impermeability
- better thermal behaviour: temperatures are rising in packaging processes because of:
  - hot food filling of bottles, containers . . .
  - quick re-heating of food containers.

- better low-temperature behaviour: freezing and deep-freezing
- ease of processing: the aptitude for processing leads to lighter and cheaper packaging, and shorter cycles, factors of productivity
- innovative processes to improve shelf life of products
- innovative materials to improve shelf life of products
- recycling: it is necessary to make recycling easier and to find industrial outlets.

The bottle and container sector stimulates manufacturers and researchers who study and innovate in several directions:

- New PET grades and blends targeting packaging:
  - new PET grades that can be used in beer bottles for heat-pasteurization after bottling
  - new alloy of PET with polytrimethylene naphthalate which improves the CO_2 and O_2 barrier by several times compared with PET
  - PET/PEN blends or copolymers with aesthetic and performance characteristics similar to glass and the durability and convenience of cans
  - use of oxygen-scavenging resins blended with PET for smaller single-serve carbonated soft-drink bottles.
- New coatings to improve impermeability:
  - PET coating with an epoxy-amine barrier
  - Plastipak's Actis plasma coating is being used to extend shelf life while preserving flavour.
- Multilayers:
  - multilayer PET with a barrier polymer such as EVOH, polyamide or proprietary materials
  - multilayer structures with oxygen scavengers for flavour protection
  - incorporation of a central layer including post-consumer recycled material from the post consumer bottles with barrier layers on each side and a virgin layer of PET on the internal and external surfaces. The bottle is designed to keep the beer as fresh as glass bottles or aluminium cans over a four-month period.
- Innovation:
  - Amcor PET Packaging is developing 'smart packaging' that incorporates special features that enable it to be tracked through the supply chain. Indicators can be built in to provide information on the freshness of the packaged product.
  - Heat-set technology and use of nitrogen gas to increase the ability to hot-fill PET containers and extend the content's shelf life.

2.12.1.3 Foams

Foams are efficient as:

- damping materials, providing an economic protection against vibrations and moderate impacts
- insulating materials, providing an economic protection against heat for fish, ice cream and other refrigerated products.

Thermoplastic foams – mainly polystyrene, PVC, polyethylene and polypropylene – account for roughly 50% of all plastic foams, the other 50% being polyurethane, a thermoset material. For all uses added together, EPS accounts for more than 90% of all thermoplastic foams, followed by PVC with a few percent, and polyethylene and polypropylene.

Packaging is not the main market for foams and statistics distinguish this sector only for EPS, where it accounts for roughly 30% of all EPS applications for a typical industrialized country. The annual growth rate varies according to the country but is, more or less, in line with the average for plastics growth.

Let us quote some examples of applications without claiming to be exhaustive:

- EPS: heat insulation, damping, structural functions:
  - boxes, crates, cases for cooled foodstuffs: fish, ice creams . . .
  - packaging of electrical household appliances, TVs, radios, office automation, electric tools . . .
  - structural industrial packaging: car engines . . .
  - packaging & display units.
  - flakes, chips, sheets . . .
- Polyethylene: heat insulation, damping functions:
  - flakes, chips, sheets, blocks are used for impact protection and damping in the packaging of various products such as cameras, electronic devices . . .
  - antistatic, conductive foams for electronics packaging
  - isothermal packaging
  - cool bags . . .
- Polypropylene: damping and protection, thermal insulation, structural functions:
  - reusable packaging or shuttle packaging for heavy parts such as doors, windscreens, rear mirrors . . .
  - packaging of fragile parts: electronics, office automation devices, electric motors . . .
  - damping blocks, intermediate layers . . .
  - functional packaging useful for shipping and installation on site . . .
- PVC: packaging of fragile goods, warm or cold foods . . .

2.12.2 Building & civil engineering

With a consumption of 19% of all thermoplastics, the building & civil engineering market is the second largest outlet for thermoplastics.

Several exceptional features explain the high level of thermoplastic use for this engineering sector:

- Technical motivations: using thermoplastics is favoured by:
  - design freedom, allowing a high level of function integration
  - ease of use: low density and attractive performance/weight ratio lead to weight reduction, providing easier handling and setting up
  - good thermal insulation . . .
  - ease of maintenance, but beware of the mar resistance
  - resistance to moisture, but beware of ageing.
- Economical features: thermoplastics provide:
  - a favourable economical solution for mass production as well as ‘niche’ production
  - higher productivity due to ease of handling and setting up . . .
- Aesthetics: thermoplastics allow:
  - much more design freedom than steel, concrete and other conventional materials
  - decoration possibilities to mimic stone, marble, wood, metal . . .
  - pleasant finish.

- Environmental features: thermoplastics save energy throughout their lifetime because of their high thermal insulation properties . . .

Statistics differ according to the source and the country considered. For example, window frames can be mainly made of PVC in one country and of a composite in another. Figure 2.23(a) displays an example of plastic shares in the building market, showing the supremacy of thermoplastics, but different data can be found.

Thermoplastics are matching cheap conventional materials and, consequently, commodities are the most used with a pre-eminence of rigid and soft PVCs (Figure 2.23(b)). However, some engineering plastics are used for specific applications such as glazing, for example.

Thermoplastics and TPEs are commonly used in elements and fittings that are not highly loaded. They allow innovative techniques, such as the rehabilitation of old mains without

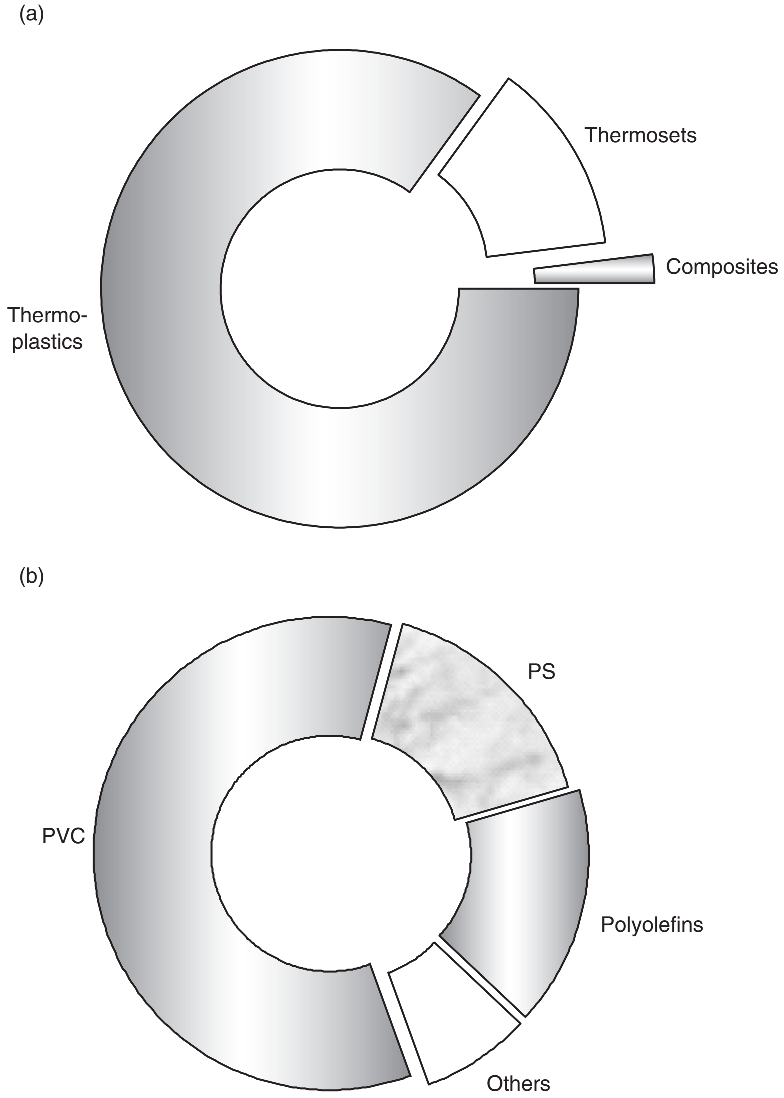


Figure 2.23. (a) Plastic shares in the building market; (b) thermoplastic shares in the building market

the opening of trenches that would be expensive, time consuming and disturbing for road traffic. Some examples are listed below without claiming to be exhaustive:

- Use of a polyethylene liner folded into a 'C' shape and held by taping (Subcoil by Wavin). After insertion into the existing mains to be rehabilitated, pressure is applied to tear up the tape and lay the liner onto the main inner wall. This wall ensures the structural function and the polyethylene liner ensures watertightness and corrosion protection.
- Use of a PET liner (Neofit by Wavin) that is inserted into the pipe to be rehabilitated to form a close-fit liner.

Let us quote some application examples for some thermoplastics. These examples may be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade in the real conditions of service life.

Polyethylene

- Films . . .
- Pipes and conduits . . .
- Large-sized objects: cisterns, tanks, septic tanks . . .
- Gas, water or sewer pipes, sheaths . . .

Polyethylene foams

- Thermal insulation of roofs, walls, ceilings, floors . . .
- Thermal insulation of sandwich panels for industrial construction . . .
- Insulation of pipes, pipelines; half-shells for insulating heating piping and air-conditioning . . .
- Panels and sandwich structures for protection of oil wellheads . . .
- Phonic insulation of floors . . .

PE fibres

- Removable protective panels . . .

Polypropylene

- Filaments, fibres and fabrics for indoor and outdoor carpeting, carpet backing, outdoor carpets around swimming pools or miniature golf courses . . .
- Frameworks for ventilation, fan blades, air filters . . .

Polybutylene

- Pipes for cold and hot pressurized water . . .

EVOH

- Wallpaper . . .
- Multilayer pipes with polyethylene or polypropylene for under-floor heating systems in domestic and commercial buildings, preventing oxygen from dissolving in the hot water and avoiding metal corrosion of other parts in the heating device . . .

EMA

- Film sandwich for bulletproof glazing . . .

CPE

- Coated fabrics: extrusion of coated scrim for tarpaulins . . .

PVC

- 47% of the PVC total is consumed by pipes & fittings for potable water, sewers, irrigation, drain, rainwater, soil and waste systems, venting, ducting, fire sprinkler piping, chemical and food processing . . .
- Monolayer tubes, corrugated or multilayer pipes, spiral wound, small or large diameter . . .
- Siding consumes 15% of the PVC total, with gutters, downspouts, boardings . . .
- Windows and doors consume 4% of the PVC total in shutters, architectural glazing systems, conservatory devices . . .
- Fencing, barriers, decking . . .
- Docking, landfill liners, membranes, swimming pool liners . . .
- Internal and external cladding, roofing and ceiling systems . . .
- Flooring and wall coverings . . .
- Anticorrosion components for cooling towers, laboratory sinks . . .
- Pipes for paper and surface treatment sectors, electroplating plants, photographic, semiconductor and chemical industries . . .
- 'Synthetic wood' or wood-plastic composites (WPC) made from rigid PVC heavily filled with wood flour, extruded in wood-like profiles that can be sawn, nailed and screwed just like natural wood . . .

PVC foam

- Thermal insulation of roofs, walls, ceilings, floors . . .
- Thermal insulation of sandwich panels for industrial construction.

PVC-C

- Pipes and fittings for hot and corrosive environments . . .
- Window profiles . . .
- Anticorrosion components for cooling towers, laboratory sinks . . .
- Pipes for paper and surface treatment sectors, electroplating plants, photographic, semiconductor and chemical industries . . .

EPS

- Heat insulation of roofs, walls (insulation from the interior or exterior), floors of buildings and hangars including heavy handling (aeronautical) and under-floor heating . . .
- Breeze blocks, prefabricated components, coatings, mortars and light concretes containing expanded beads . . .
- Insulated panels for refrigerated warehouses and other cold storage . . .
- Structural insulated panels . . .
- External panels of house or building with glass fibre reinforced plastic (GFRP) skins . . .
- Disposable formworks . . .
- Conduits of cooling agents . . .
- Soundproofing of buildings . . .
- Floating floors, reducing particularly the noise of impact . . .
- Public works: antifreeze bases of roads or railways . . .

PA11 or 12

- Anticorrosion protection: lined pipes; buried gas pipelines; pipes co-extruded with MDPE and HDPE to increase their performance; dirty water and effluent pipes used in aggressive environments . . .

- Potable water transportation equipment and water treatment plants: powder-coated metal parts . . .

PMMA

- Glazing applications, shatter-resistant glazing, architectural and protective glazing, windows and skylights, sight glasses (e.g. observation windows), transparent thermoformed products . . .
- Lighting, lights, lighting diffusers, light-control lenses in lighting fixtures . . .
- Signs: internally illuminated outdoor signs, indoor and outdoor signs, diffusers, side-lit signs, very thin illuminated displays, fluorescent signs . . .
- Civil engineering: acoustic screens . . .
- Cast and extruded sheets, cell-cast sheets, stretched sheets, films down to 50 microns; laminated protective surfaces on ABS, PVC or other plastic sheets that are thermoformed into parts requiring resistance to outdoor weathering for residential siding and transformer housings . . .

Polycarbonate

- Glazing, architectural glazing, roofs of verandas, stations, stadiums, sheeting applications . . .
- Protective glazing, vandal-proof windows, shatter-resistant glazing, windows and skylights . . .
- Lighting, light globes, lighting diffusers, outdoor lighting fixtures, traffic lights . . .

Acetal

- Plumbing and installation sector; small pressure vessels, sound-damping mountings for WCs and bathrooms, toilet cistern valves . . .
- Ballcocks, faucets (taps), faucet cartridges, faucet underbodies, valve stems . . .
- Irrigation equipment and valves . . .
- Pump and filter housings, impellers, plumbing systems . . .
- Fittings, hinges, shower heads . . .

PPE

- Plumbing and installation sector, pump and filter housings, impellers, plumbing systems . . .

Perfluorinated thermoplastics (PTFE or TFE, PFA, FEP)

- Films, knitted, woven, braided or sewn fibres for architectural fabrics . . .

PVDF

- Linings and liquid surface coating systems for architectural fabrics . . .

PVF

- Weather-resistant films, UV screening films for glazing panels, surface covering for PVC films, surface protection for sign industry . . .

Cellulosics

- Lighting, signs, diffusers, lighting devices and accessories, profiles . . .

Polysulfone

- Plumbing fixtures, faucet (tap) components . . .
- Potable water fittings . . .

Polyimide

- Non-flammable scenery, coloured filter holders for studio and theatre spotlights . . .
- Fire-resistant wallpaper . . .

Thermoplastic elastomers

TPS

- Window seals . . .
- Gasketing, tap washers, toilet buffers . . .
- Bitumen modification, roads, roofing, paving, impact-resistant shingles . . .

TPO

- Soft-touch overmoulding . . .
- Roofing . . .

TPV

- Roofing . . .
- Geomembranes . . .
- Residential and non-residential glazing, window and door weather seals . . .
- Expansion joints, water-stops . . .
- Pipe seals . . .

TPV PP/NBR-V

- Seals, tubes, pipes, profiles for oil contact . . .

TPE/PVC

- Residential and non-residential glazing, window and door weather seals . . .
- Roofing . . .
- Flooring . . .

TPU

- Architectural glass lamination . . .
- Mining screens . . .

MPR (melt processable rubber)

- Damping mounts for noise and vibration . . .
- Window and door weather stripping . . .

COPE

- Breathable films for construction . . .
- Railway pads . . .

PEBA

- Breathable films for construction . . .

Wood thermoplastic composites

The reinforcement of thermoplastics with wood fibres is relatively recent because of the weak compatibility of the two types of materials.

About 20 years ago, the first industrial development was launched with a polypropylene filled with 50% wood flour.

Other developments followed a few years later:

- a polyethylene filled with approximately 50% wood fibre for deck boards, landscape timbers, picnic tables and industrial flooring
- a PVC filled with 40% wood for French doors and windows
- a composite with 70% wood.

More recently, about ten years ago, the first wood composite was marketed in pellets.

The market is fast-growing in the USA where there is a considerable amount of wood residues of low prices comparable with those of inorganic fillers such as talc and calcium carbonate.

The highest growth area for the wood-plastic composite industry is in decking and other elements for construction such as industrial flooring, window and door profiles, hot tub siding, office accessories, landscape timbers, railings, moulding, fencing and others.

Currently marketed wood composites are based on 30% to 70% natural-fibre-filled polypropylene, polyethylene, polystyrene and PVC. Formulations have high performances and are more expensive than the virgin material.

It is necessary to divide the building & civil engineering market into several sub-markets with differing functions, environmental stresses and requirements.

In building we can consider two broad subdivisions:

- exterior applications subjected to direct sunlight, rain, temperature variations . . .
- interior applications subjected to less harsh constraints: sunlight irradiation for example is less severe, but aesthetics requirements are more stringent.

Figure 2.24 shows some applications.

Civil engineering applications can be divided into two broad families:

- piping for water, gas and sewers
- installations using geomembranes, seals and anticorrosion materials.

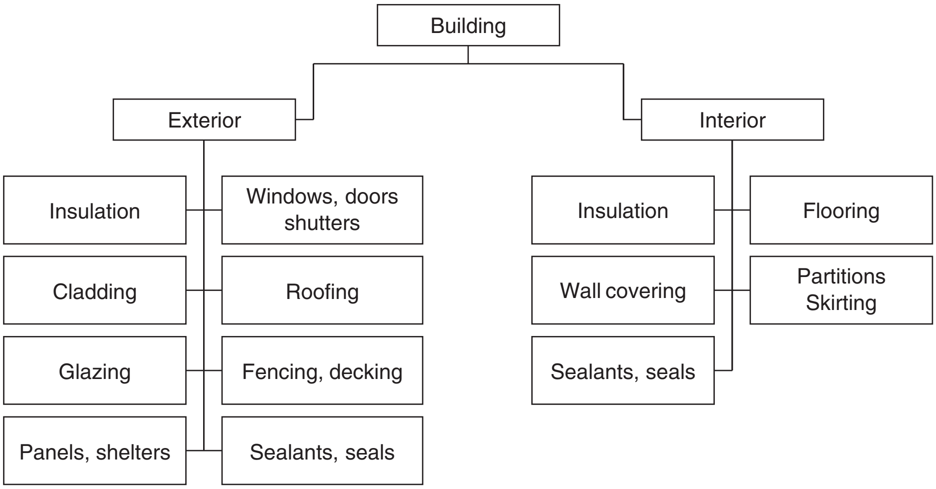


Figure 2.24. Thermoplastic applications in building

Figure 2.25 shows some applications.

Recycling is particularly important for the building & civil engineering market, the sector with the second-largest consumption of thermoplastics. Unfortunately, plastics recycling presents technical and economic difficulties and is less advanced, industrially, than that of metals or glass.

The main polymer recycling method for building and construction wastes is mechanical recycling, which accounts for around 10% of the collected wastes. Landfill and incineration are used far too much, representing 90% of the total wastes.

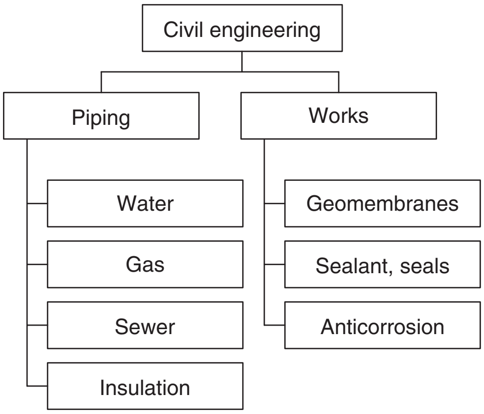


Figure 2.25. Thermoplastic applications in Civil engineering

From Table 2.26, the building and civil engineering sector is:

- the second-largest industrial generator of wastes
- the fourth-largest industrial generator of collectable plastic wastes; plastic wastes are only 0.1% of the total wastes of the sector
- produces roughly 3% of overall post-user collectable plastics.

Table 2.26 Wastes from the main industrial sectors, agriculture and municipal solid wastes

	Post-user collectable plastics		Total wastes		Collectable plastics/ total wastes
	(1000 t)	(%)	(1000 t)	(%)	(%)
Distribution & Industry	4130	21	353 000	13.3	1
Electrical & Electronic	854	4	7000	0.2	12
Automotive	851	4	15 000	0.6	6
Building & Construction	530	3	449 000	17.0	0.1
Agriculture	286	1	1 041 000	39.3	<0.1
Others (mines, sludges, energy production)			557 000	21.8	
Municipal solid waste	13 329	67	205 000	7.8	6.5
	19 980	100	2 627 000	100	

Concerning recycling, Table 2.27 shows that the building & civil engineering sector leads to:

- a very high 90% of landfill and incineration versus 63% for plastics wastes in total
- a 10.9% total recovery by mechanical recycling (as a proportion of end-use waste) compared with 12.6% for plastics wastes in total
- too little energy recovery and feedstock recycling to be noticed in statistics.

Table 2.27 Breakdown by recovery route of collectable plastics waste in Western Europe, 2001 (1000 tonnes)

	Building & Construction	Total
Total available plastics waste collectable	530	19 980
Landfill and incineration	472	12 578
Energy recovery	0	4583
Feedstock recycling	0	298
Mechanical recycling	58	2521
% total recovery as a proportion of end-use wastes	11	37¨

From an environmental point of view, this poor recycling situation is compensated for by the improvement of energy efficiency in the home.

Thermal insulation made from expanded polystyrene or other foams, thermoplastic window frames, etc. help to reduce heat loss. This is very important in cold countries because domestic heating can represent almost one quarter of the total energy consumption. Consequently:

- fuel consumption is reduced
- natural resources are preserved
- CO_2 emission is highly reduced (by two to five times) even taking into account the CO_2 emissions from plastic production.

2.12.2.1 Building exteriors

The main applications of thermoplastics are related to the following.

- Insulation
  - thermal insulation can be from the interior or the exterior of the building
  - acoustic insulation is developing
  - polystyrene foam dominates the thermoplastic foams but is competing with polyurethane foam (thermoset).
- Windows are made of PVC or composites according to the country.
- Glazing can be:
  - sheets and plaques for domes, skylights . . .
  - glazing films.
- Cladding, fascias, shuttering and panels can be interior/exterior items.
- Sealing can be ensured by:
  - seals and gaskets for windows, doors . . .
  - sealants for masonry . . .

Table 2.28 displays some recent thermoplastic market shares for Western Europe. Note the supremacy of PVC followed by PS with thermoset competition for insulation.

Table 2.28 Recent market shares for some exterior building applications in Western Europe (%)

	PVC	PS	PE	Thermosets	Total
Insulation	<1	56	<1	43	100
Windows	100				100
Profiles	100				100

Let us cite some application examples for some thermoplastics. These examples may be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the cited thermoplastic family for their specific problem and test the right grade under real service life conditions.

Insulation

Polystyrene and polyurethane (thermoset) foams dominate the market, with PVC and polyethylene foams accounting for less than 1%.

EPS used in building represents 18% of total polystyrene consumption.

Light structural functions

- Framework: pultruded long glass fibre reinforced plastics.
- Load-bearing panels for individual construction, Azurel by Dow made of wood and expanded polystyrene hybrid.

- Windows and doors: extruded PVC is used for doors and windows for houses, buildings, factories. Though the window and door market is fast growing (7.3% per year in the USA), the market share of plastics is only a few percent of the total US demand for windows and doors.
- Decking made out of PVC, wood-plastic composite.
- Deck plank: vinyl profiles or composite boards are used to form the base of the walking surfaces or stairs.
- Railings including rail posts, cap rails, head rails and balusters can be made out of PVC.
- Garden portals of plastic panels screwed on metal structures.
- Frontages in sandwich made of PVC foam core and skins of fire-resistant glass fibre reinforced polyester. The panels are attached onto a steel framework.
- Panels in sandwich of expanded polystyrene core with composite skins.

Transparency

Glazing, domes, skylights . . . consume 20% of all polycarbonate. Acrylic sheets account for 66% of total acrylics.

The main thermoplastic solutions for transparency in building are:

- PVC, the cheapest but it is necessary to study the construction carefully to avoid high temperatures exceeding the polymer's continuous use temperature
- PMMA, the most naturally weather resistant
- polycarbonate, the best from the point of view of impact resistance.

The applications are, for example, skylights, domes, veranda roofs in simple or double-wall sheets of polycarbonate, exterior spotlights, waterproofed lights, globes.

Decoration

- Architectural panels made of PVC . . .
- Caps, end covers, fascias, fascia cover plugs, post caps, snap caps: vinyl parts or profiles placed along the tops of fences, open ends of planks, stairs and framing, screw heads . . . to conceal hardware, provide a finished look and prevent water penetration.
- Fill strips: vinyl strips fitted into the channels of deck planks to cover exposed hardware.
- Post base trim covers: vinyl trim pieces used to cover post-to-floor connections.
- Rail covers: vinyl trim that covers rail-to-post connections.

Waterproofing

Polymers provide several solutions for roofing and weatherboarding: flexible membranes, rigid sheets or plates, or tiles.

Roofing membranes can differ by:

- raw material: PVC and alloys, TPO
- formulation and reinforcement with fibres, fabrics . . .
- seam type: solvent, welding, gluing, self adhesive.

All these parameters influence the durability of the membrane. Durability also depends on the area of application.

For rigid roofing, it should also be remembered that PVC is the main thermoplastic for gutters.

Seals and sealing

Prefabricated seals for windows, doors, etc. are made out of TPEs and TPVs competing with rubbers.

Flexible structures

Canvas and other fabrics and films are used to realize structures. According to the usage, the materials are standard, such as PVC-coated fabrics, or sophisticated, such as PTFE-coated glass fabrics . . .

Canvas coated with a polymer is used as a roofing material for applications such as industrial or storage buildings, garden canopies, exhibition halls, and so on.

Various stadiums and other large structures have an inflatable roof made of a volume of a coated fabric inflated by pneumatic pressure and attached to a concrete or concrete and steel building.

Portable temporary inflatable structures are designed for a huge variety of usages: emergency shelters, leisure marquees, decontamination or rescue units, urban rescue, personal protection, exhibitions, temporary warehousing, receptions, weddings and so on. A reception structure 43 m long, 30 m wide and 15 m high can be installed in two days and dismantled in one day.

2.12.2.2 Building interiors

Figure 2.26 shows the versatility of thermoplastic applications by some examples for interior building use.

Apart from PVC and other commodity plastics, engineering plastics and wood-plastic composites are used for specific advantages corresponding to specific applications.

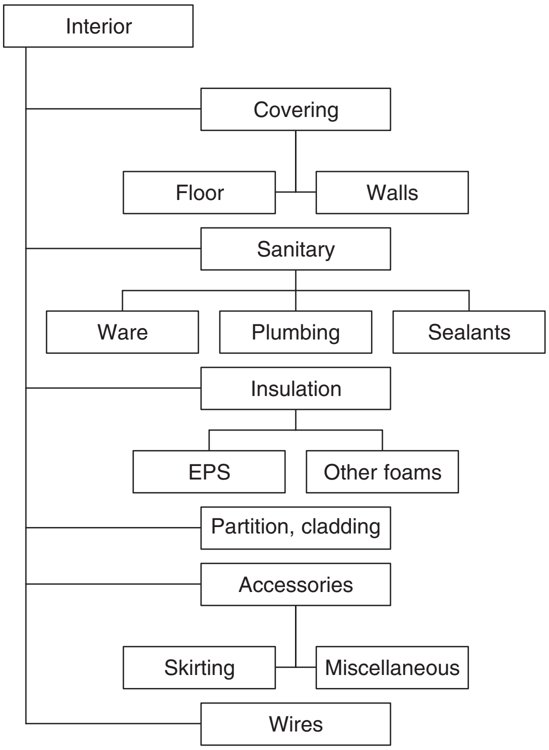


Figure 2.26. Building: interior elements

Styrenics, possibly foamed

Styrenics, approximately 18% of which (mainly EPS) are consumed in the Building & Construction sector, are used in building interiors for:

- interior heat insulation of buildings, prefabricated elements and partitions, window frames, expansion joints, conduits for air-conditioning, cases for travelling shutters. EPS is the most important application of styrenics. The low thermal conductivity, compressive strength and mechanical resistance of extruded foams and low moisture absorption properties provide excellent heat insulation, fair support and long-term performance
- elements for decoration and furniture
- polystyrene mirrors for interior decoration are composed of a flat sheet with a thin and flexible reflective top layer.

Soft and U-PVC, possibly foamed

Table 2.29 displays some applications of PVCs in the construction industry.

PVCs are used in building interiors for:

- Pipes for plumbing and other applications consume 43% of all PVC (including civil engineering)

Table 2.29 Consumption of PVC by the Western European construction industry

	2001 consumption (million tonnes)	Share (%)
Pipes and fittings	1.6	43
Profiles	1.3	35
Cables	0.5	14
Flooring	0.3	8
	3.7	100

- profiles for decoration, proofing, cladding and other interior and exterior applications are the second outlet for PVC. Interior cladding made from U-PVC hollow panels improves insulation, and reduces condensation and mildew growth. For bathrooms, living rooms, bedrooms and hobby rooms they can lead to high cost savings on conventional tiling
- floor covering, wallpapers: PVC is appreciated for its hygienic, easy to use, and economical properties
- insulation of electric wires
- heat insulation of buildings, but consumption is far below that of EPS.

Polyethylene

Polyethylene is used in building interiors for:

- pipes, tubes and protective conduits
- vapour and moisture barrier films
- foams for insulation against heat, moisture, water, air and noise: insulation of piping, walls, underlay for flooring, interior insulation of garage doors . . .
- insulation of electric wires.
- furniture fittings.

Engineering plastics

- Because of their pleasant aspect, light weight, ease of working, and insensitivity to greasy fingers in sanded finishing, cast acrylic sheets are often used in building interiors.

Sawing, milling, drilling, bending, thermoforming, welding, metallization, decoration mimicking stones and marble, graining, fire retardancy, impact-resistant grades, and alloys with PVC allow a multitude of applications, such as:

  - ○ washing tubs and washstands, worktops in kitchens and bathroom fittings in residential and private home applications
  - ○ door coverings, furniture parts and wall cladding for shops, hospitals, post offices, homes for the elderly, elevators, staircases; profiles such as handrails, angle protectors . . .
  - ○ flat and convex acrylic mirrors are 15 times more impact resistant than glass for only one-third the weight.

- Acrylics and polycarbonates are used in glazing (doors and windows, fanlights, dormers, skylights . . .) and in lighting devices.
- Polyacetals are used for sanitary, plumbing and furniture fittings.
- Polyamides are used for flooring (woven carpets and rugs) and furniture fittings.

Composites with wood

- Decorative laminates made of particleboards with outer decorative plastic layers such as PVC and so on.
- Wood-plastic composites based on 30% to 70% natural fibre-filled polypropylene, polyethylene, polystyrene and PVC.

2.12.2.3 Pipes and tubing

Table 2.30 shows for Western Europe:

- The recent annual consumption of major plastics for tubes, pipes, conduits and fitting for all applications. Other polymers are used but are not listed in economic statistics.

Table 2.30 European consumption of major thermoplastics for tubes, pipes, conduits and fittings

	Consumption in tubes, pipes, conduits and fittings (1000 tonnes)	Total consumption for each thermoplastic family (1000 tonnes)	Shares of tubes & pipes versus total for polymer family (%)	Polymer shares versus total for pipes & tubes (%)
		All applications		
U-PVC	1654	4026	41	57
HDPE	740	4775	15	26
Soft PVC*	188	1849	10	6
PP**	170	7360	2	6
LDPE	93	4636	2	3
LLDPE	39	2384	2	1
ABS	24	633	4	1
Total of identified thermoplastics	2908	25 663	11	100
		Pressure pipes alone		
	(1000 tonnes)		(%)	
PE water pipes	337		59	
PE gas pipes	140		24	
(Subtotal PE)	(477)		(83)	
PVC pipes	100		17	
Total of pressure pipes	577		100	

* Including other profiles
** Not listed in economic statistics, estimated

Nearly 3 million tonnes of plastics are consumed by this sector, accounting for 7.4% of all plastics. The pipes and tube sector is roughly ranked like the automotive and transportation or electricity and electronics sectors for the consumption of plastics.

- The consumption of PE and PVC for pressure pipes alone: the shares of these polymers are very different from the above data.

Pipes and tubes can be classified in several ways. Figure 2.27 displays two examples.

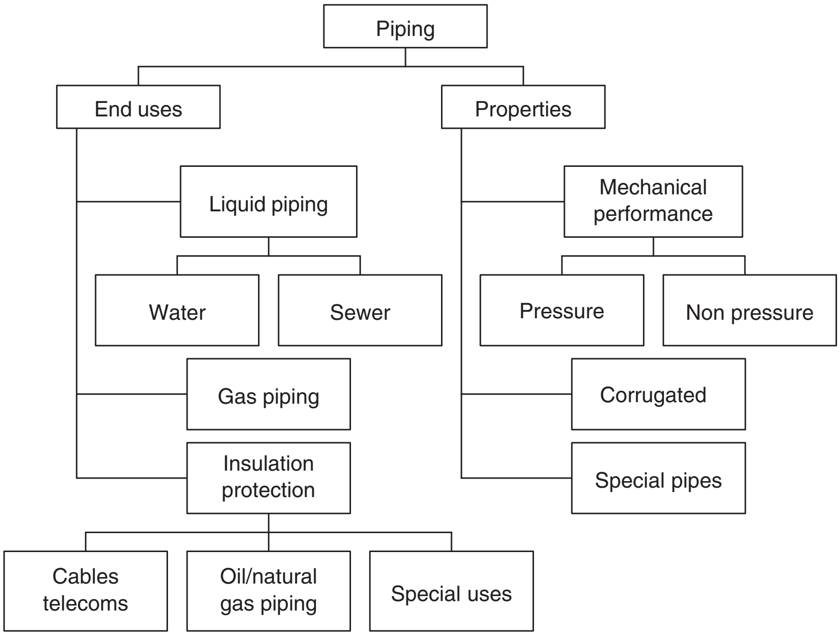


Figure 2.27. Thermoplastic pipes & tubes

Thermoplastics are matching cheap conventional materials (see Figure 2.28) such as:

- metals: iron and steel, aluminium, copper, lead
- minerals: clays and concrete.

Consequently, commodity thermoplastics are the most used, with rigid and soft PVCs dominating. However, some engineering thermoplastics are used for specific applications that justify their cost.

Typical materials are:

- commodity plastics: PVC, PE, PP and their derivatives: crosslinked polyethylene (PEX), cellular PVC
- engineering plastics: chlorinated polyvinyl chloride (CPVC), ABS, PET for special purposes
- hybrids: metal/plastic, PEX-Al-PEX.

Let us quote some application examples for some thermoplastics. These examples may be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade in real service life conditions.

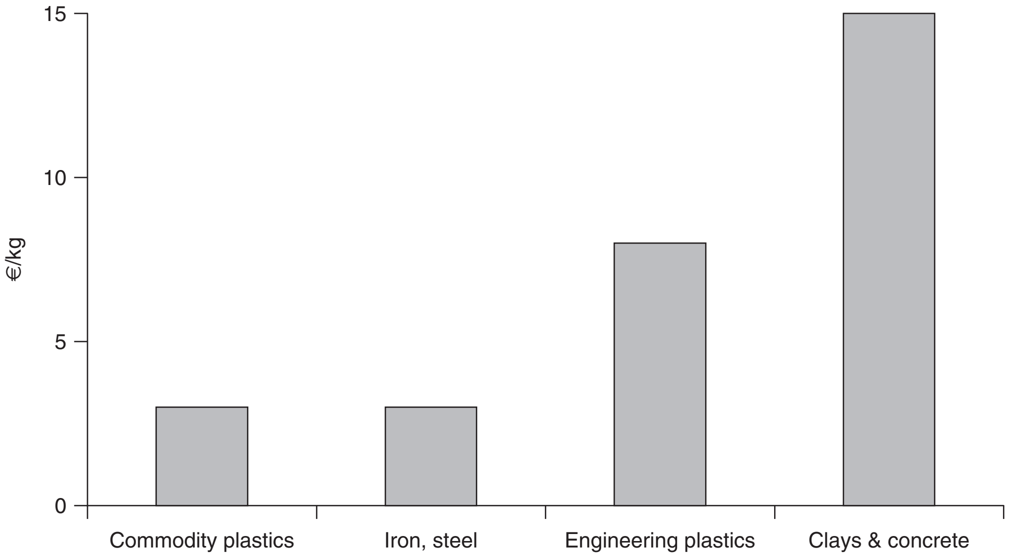


Figure 2.28. *Typical approximate costs of pipes*

Rigid PVC

- General-purpose ducting systems.
- Drain-and-waste and vent lines for carrying cold water.
- Rainwater systems, channel drainage systems, land drainage systems (corrugated pipes).
- Water transportation (molecular orientated PVC).

Modified PVC

- Pressure pipes with higher impact resistance and greater ductility.
- Hot- or cold-water lines.

Polyethylene

- High density PE (HDPE) is normally used for high-pressure pipes up to 20 bar for water and up to 7 bar for gas. Low density PE is used for lower pressure applications mainly in agriculture. Examples of applications are potable water up to 20 bar, gas up to 7 bar, surface water drainage systems, storm water drainage, cable ducting.

Flexible polybutylene (PB)

- Hot- and cold-water lines.
- Under-floor heating.

Polypropylene

- Higher temperature pipes.
- Surface water drainage systems.

ABS

- Food industry piping.
- Drain-and-waste and vent lines.

PET

- Liner into pipes to be rehabilitated.

2.12.2.4 Geomembranes, geotextiles, geogrids

Geomembranes are giant impermeable membranes made of (un)reinforced polymeric materials and used to stabilize earth and to secure landfills ensuring containment of hazardous or municipal wastes and their leachates. Functionalities are varied:

- basal liners
- capping systems
- cushioning layers
- strengthening layers for soil reinforcement
- containment liners
- waterproofing membranes.

In many of these applications, geomembranes are associated with a geotextile or geogrid underliner that protects the geomembrane from direct contact with stones, gravel and other damaging materials. In the case of landfills and other waste storage, the geotextile or geogrid can also drain gases and leachates generated by certain wastes.

Geomembranes and associated geotextiles are also used for the rehabilitation of channels, tunnels, reservoirs and so on, economically providing complete reliability for waterproofing, and avoiding liquid losses.

Geotextiles are fabrics used to:

- stabilize or reinforce soil for roads, railroads, airfields, embankments, retaining structures, reservoirs, canals, dams, bank protection and coastal engineering
- protect geomembranes from direct contact with stones, gravel and other damaging materials
- separate different layers of soil in civil engineering applications
- filter or drain soil in civil engineering applications, landfills and so on.

Geomembranes must be resistant to:

- puncture, compression, tensile stress, tear, creep . . .
- long-term ageing: oxidation, temperature, thermal cycling, UV, chemical attacks by the environment, contact with industrial pollutants or waste by-products, wet and dry cycles, stress cracking
- exchanges with the environment:
  - ○ loss of additives to the environment through migration: plasticizers, antioxidants, UV stabilizers, low molecular weight components . . .
  - ○ absorption of elements from the environment: water, chemicals . . .

Let us quote some application examples for some thermoplastics. These examples may be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the cited thermoplastic family for their specific problem and test the right grade under real service life conditions:

- channels and irrigation channels . . .
- dam, baffle and levee covers . . .
- floating covers for canals, etc., fly ash covers, manure storage, coal-pile liners and covers, liners and caps . . .
- heap leach pads, filter beds, sludge drying beds . . .
- landfill lining & caps . . .

- reservoirs, tailing ponds, golf course ponds, decorative ponds and lakes, cooling ponds, fire ponds, farm ponds, aquaculture ponds, tanks for whales . . .
- stormwater run-off . . .
- municipal swimming pools, ice rinks . . .
- secondary containment, paper waste containment, industrial ponds for mining, brine, tank liners . . .
- solar evaporation ponds . . .
- tunnel waterproofing . . .
- waste treatment: waste water, black liquor, wastewater treatment station, oxidation ponds, sewage lagoons . . .

The thermoplastics used – mainly polyethylene (slightly more than 50%) and PVC (slightly less than 50%) – are necessarily flexible to allow their positioning, easy to seam and repair, puncture- and impact-resistant, long lasting, and cheap. For example, let us quote some applications without claiming to be exhaustive:

- Polyethylene and VAE or EBA copolymers such as LLDPE geomembrane pond liners, HDPE alloy geomembrane liners, lightweight tarps and containment liners. Beware of low elongations at yield and the stress cracking sensitivity of certain polyethylenes.
- Soft PVC, PVC-NBR such as containment liners, fish-safe grade pond liners, coated fabrics or laminates for tarps and shelters, landfills and canal linings (since the 1950s), decorative ponds and lakes. Unfortunately, soft PVCs are subject to plasticizer desorption and extraction, becoming harder and brittle.
- Polypropylene is a material of choice for sewage lagoons. Long service lives (20 years) are claimed by certain processors.
- Ethylene interpolymer alloys are used for fuel, fertilizer or transformer oil containment.

2.12.3 Automotive & transportation

The automotive & transportation market, with a consumption estimated variously from 5% up to 13% of the thermoplastics total according to the region considered, is the third outlet for thermoplastics. It is also an important sector for thermoplastic composites and TPEs.

The car industry is subject to many constraints:

- economic competition, worsened by production overcapacities
- margin reductions
- shortening of the development cycles especially for the small ‘niche’ series
- strengthening of pollution, recycling and energy regulations.

All these reasons persuade carmakers to lighten vehicles, improve their quality and performances, extend guarantees, reduce development and manufacturing times, reduce costs and support materials that can be recycled.

Several exceptional features explain the high level of thermoplastics and thermoplastic composites used for the automotive & transportation market:

- Technical motivations: using thermoplastics is favoured by:
  - ease and freedom of design (realization of forms impossible with metals)
  - integration of functionalities
  - ease of construction and assembly
  - reduction of design and manufacturing times. The vehicle models are refreshed and renewed more and more often. All these modifications require replacements and modifications of tools that are easier with plastics than with metals

  - low density and remarkable performance/weight ratios, leading to weight reduction and consequently better car performances and/or decreased fuel consumption and pollution
  - ease of maintenance, but beware of the mar resistance
  - non-rusting (but beware of ageing)
  - acoustic damping (i.e. noise reduction).
- Aesthetics: thermoplastics allow:
  - much more design freedom than steel
  - decoration possibilities: bulk colouring, in mould decoration . . .
  - pleasing finish.
- Economic features: thermoplastics provide:
  - a favourable economic solution for mass production as well as 'niche' production
  - reduction of design and manufacturing times
  - reduction of finishing costs: plastics allow the integration of functions and, consequently, lead to the reduction of assembly costs
  - higher productivity due to adapted processes, integration of functions, fewer processing steps . . .
- Environmental features: thermoplastics save energy throughout their lifetime because of their light weight . . .

On the other hand, recycling brings some particular problems due to economic conditions, the polymer modifications and reinforcements.

To progress in the automotive industry, plastics must improve their performance characteristics, ease of processing, productivity and recycling, for example:

- Better thermal resistance: under-the-hood applications are undergoing an increase in the service temperature. In the cockpit interior, temperatures are tending to increase due to increased use of glazed surfaces. The rise in lamp power and headlight miniaturization is leading to a temperature increase in the optical system and reflector. For the body, painting on line requires sufficient thermal resistance to tolerate the cooking temperature. Consequently, it is necessary to use new polymer grades or new, more thermally resistant families.
- Better low-temperature behaviour: regulations tend towards an increase in low-temperature impact resistances and a more ductile behaviour.
- Ease of processing: improved flow properties and processability lead to cycle time reductions and productivity gains.
- Low finishing costs: bulk colouring, in-mould decoration, an intelligent design and an effective maintenance of the moulds reduces or avoids painting and other finishing operations, cutting the finishing costs.
- Recycling: more effective solutions are sought. The development of the mono-material concept is favourable to thermoplastics and self-reinforcing thermoplastic composites such as self-reinforced polypropylene (Curv™ from BP).

The use of thermoplastics and composites is growing in various segments of vehicles:

- bumpers
- body, external elements
- passenger compartment
- under-the-hood and other mechanical elements.

Figure 2.29 displays the market shares of the most used commodity and engineering thermoplastics in the automotive industry.

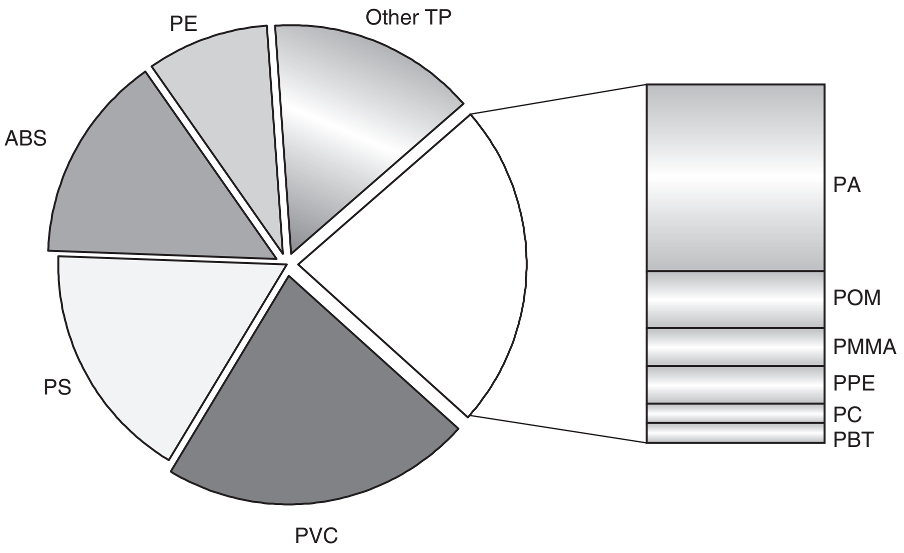


Figure 2.29. Thermoplastic shares in the automotive market

Only the PVC consumption is decreasing because of environmental regulations.

Let us mention some automotive & transportation application examples for some thermoplastics. These examples may be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade under real service life conditions.

Polyethylene

- Fuel tanks for the automotive industry.
- Fluid containers.

PE foam

- Safety padding of instrument panels, door panels or sun visors.
- Energy-absorbing bumpers.
- Door fillings.
- Carpet underlays.

PE fibres

- Removable protective panels for armoured cars.

Polypropylene

- Bumpers, bumper fascias, exterior trims, headlight casings and rear light bases, spoilers, step pads, body side mouldings, wheel trims . . .
- Interior trims, dashboards, instrument panel inserts, pillar trims, consoles, airbag system parts, door and quarter-panel trims, lift-gate trims . . .
- Under-the-hood parts, ventilation and air conditioning units, battery boxes, air ducts, air vents, ventilation nozzles, fan blades, fan bases, fan shrouds, heating device housings, belt covers, corrugated sheaths for wires and cables, windscreen washer parts . . .
- Fender liners . . .
- Polypropylene filaments, fibres, fabrics for carpeting, carpet backing.

PP foam

Damping and protection: air, water and dust proofing, thermal insulation, soundproofing:

- Energy-absorbing bumpers.
- Door fillings, door panels.
- Safety padding . . .
- Floor filling.
- Toolboxes . . .

EVOH

- Barrier layer in automotive plastic fuel tanks.

EMA

- Automotive paint-free applications.
- Moulded-in-colour film laminate technology for bumper fascias.
- All-plastic deck lid for the 2005 Ford Mustang convertible.
- Tailgate cap for the 2004 Hummer.
- Decorative automotive trims . . .

PVC

The automotive & transportation sector consumes 2% of the total for PVC in:

- Instrument panels and associated mouldings, dashboards, interior door panels and pockets, sun visors, security covers, headlining, floor coverings, floor mats, arm rests, seat coverings . . .
- Exterior side mouldings, protective strips, window trims, body side mouldings . . .
- Underbody anti-abrasion coating, mud flaps, anti-stone damage protection . . .
- Body seam sealing, seals, foamed gaskets . . .

PVC foam

- Cores for sandwich panels for body structures of refrigerated lorries and similar vehicles; roofs of coaches; containers for maritime, road, railway and air transport; wagons to carry and store food on board aircraft; shelters, bodies of military light machines.

ABS

- Interior and exterior trims . . .
- Radiator grilles.
- Instrument panels.
- Glove box doors.
- Consoles.
- Housing of heating systems.
- Steering column trim . . .

SAN

- Tail lights.
- Reflectors . . .

Polyamide

- Wheel trims, grilles, trap doors for gasoline (petrol) tanks, engine covers, clutch pedals, intake manifolds, headlight parabolas, spoilers, radiator tank fittings, door handles, window winders, interconnection boxes, decorative parts, air and water filter elements, airbag canisters . . .

PA 11 or 12

- Hydraulic, fuel and water hoses; truck air brake hoses; monolayer and multilayer plastic fuel lines . . .

Aromatic PA

- Bearing retainers in engine compartments, gears, pivots . . .
- Bobbins for electronically controlled automatic transmissions for trucks, solenoid coils in control modules for five-speed automatic truck transmissions.
- Fuel pumps, cam covers, clutch parts, oil filter bodies . . .
- Vandal-proof seats, seat adjustment parts . . .
- Mechanisms of rear-view mirror, housings . . .
- Wiper controls, headlamp controls and surrounds . . .

Thermoplastic polyester

- Under-the-bonnet parts . . .
- Exterior parts such as wiper arms, wiper blades, window wiper holders, exterior mirror housing, door handles . . .
- Headlamp bezels, lighting, fog lamp reflector bodies and brackets . . .
- Airflow mass meter housings and sensors . . .
- Vacuum nozzles . . .
- Valve bodies . . .
- Brake and clutch system components . . .
- Connectors, sensors, gear housings, brake booster valve bodies, tandem brake boosters . . .
- Electronics, electronics boxes (E-boxes), fuse boxes, flex connectors, child lock motor gear housings, ignition modules, ignition caps . . .

PMMA

- Transparent and decorative parts for automotive and transport applications . . .
- Lenses for taillights and parking lights, rear lights . . .
- Instrument panels, dials, indicators, tachometer covers . . .
- Nameplates, medallions . . .
- Warning triangles . . .
- Glazing applications, shatter-resistant glazing: aircraft, boats, mass transit . . .
- Films, laminated protective surfaces on ABS, PVC or other plastic sheets that are thermoformed into parts requiring resistance to outdoor weathering: motorcycle shrouds, recreational vehicle panels . . .
- Polymethacrylimide (PMI) rigid foams as the core material for composites used in buses, aerospace launch vehicles, commercial and military aeroplanes, unmanned aerial vehicles, helicopters, ships, high-speed trains, Formula One racing cars, high-performance bicycles, cross-country skis . . .

Polycarbonate

- Automotive lighting: head and fog lamp lenses, interior lighting covers and exterior lighting applications . . .
- Glazing for automotive, aircraft, boats, mass transit . . .
- Exterior parts, large parts, bumpers, body panels . . .
- Structural foamed polycarbonate for roof of 4WD.
- Films for instrument panels, in mould decoration . . .

- Interior cladding, dashboards, instrument panel retainers, knee bolsters, glove box doors, steering column covers, defroster/demister grilles, speaker grilles . . .
- Card guides . . .
- Nameplates and bezels . . .

Acetals

- Heater and air conditioner control system components, functional parts in the heating, ventilation and coolant sectors . . .
- Snap fittings and fixing parts for interior linings . . .
- Door handles, styling strips, housings and seat belt components, steering columns, window-support brackets, window cranks . . .
- Automotive under-the-hood components, fuel pumps and other fuel system components, ball cocks and caps for gasoline systems, gears, cams, bushings, clips, lugs . . .
- Windscreen washer parts, windscreen wipers . . .

PPE

- Heater and air conditioner control system components, functional parts in the heating, ventilation and coolant sectors . . .
- Instrument panels, interior mirror housings . . .
- Seat backs . . .
- Grilles, spoilers, exterior mirror housings, wheel trims . . .
- Large parts such as body panels, fenders . . .
- Under-the-hood components, impellers for water pumps in engine cooling . . .
- PA/PPE for motorcycle fairings, bumpers and static structural components – Nissan X Trail front guards and Renault, Toyota side kit panels . . .
- Foamed PPE: automotive door padding, knee bolsters, pillar trims, sun visors, instrument panel retainers, top covers, centre-stacks . . .

Perfluorinated thermoplastics (PTFE or TFE, PFA, FEP)

- Seals, rings . . .

PVDF

- Weathering protection for other thermoplastics . . .

PVF

- Film covering in aircraft interiors to reduce flammability . . .

Cellulosics

- Furniture trims . . .
- Sun visors . . .
- Face shields . . .

Polysulfone

- Under-the-hood parts, fasteners . . .
- Connectors, fuses . . .
- Plane interior parts . . .
- Visor of astronaut helmets . . .

PPS

- Exhaust gas return valves . . .
- Carburettor parts, fuel lines . . .

- Ignition plates . . .
- Pump rotors . . .
- Flow control valves for heating systems, heat exchange elements . . .
- Under-the-hood parts, cases . . .
- Reflectors . . .

PEEK

Automotive

- Piston components, seals, washers . . .
- Bearings . . .
- Transmission components, transmission thrust washers, braking and air-conditioning systems, ABS brake systems . . .
- Engine control systems . . .
- Truck oil screens . . .
- Starting discs in bus gears . . .
- Linings . . .

Aircraft

- Airbus interior components, bow-shaped luggage compartment retainers . . .
- Cable conduits, cable clips, ventilation wheels inside aviation fans, suction manifold of aviation pumps . . .
- Electrical wire harnesses isolated by monofilaments, sleeves . . .
- Convoluted tubing . . .
- Wire insulation . . .
- Pump casings and impellers . . .

PEI

Automotive

- Transmission components . . .
- Throttle bodies . . .
- Ignition components, sensors and thermostat housings . . .
- Automotive lighting, headlight reflectors, fog-light reflectors . . .
- Bezels and light bulb sockets . . .

Aircraft

- Air and fuel valves . . .
- Steering wheels . . .
- Food tray containers, cooking utensils and re-usable airline casseroles . . .
- Interior cladding parts, structural components, semi-structural components . . .

PAI

- Non-lubricated bearings, seals, bearing cages, rotating and sliding components.
- Hook joints for transmission seal rings . . .
- Tag axle assembly of cement trucks and heavy vehicles . . .
- Ceramic coated pistons for 5-HP engine . . .

Polyimide

Aeronautical and space

- Bearings, grooved couplings in self-lubricating polyimide.
- Jet engine cones, hydraulic fluid tanks for jet engines, stiffeners of acoustic panels, spacers for engine acoustic panels, protection hoods, empennages, supports for satellite antennas.

- Honeycombs.
- Parts intended to function in space vacuum.
- Soundproofing and thermal insulation of missiles, planes and helicopters; cryogenic protection on satellites, piping insulation, protection for embarked equipment in polyimide foams.

Automotive

- Self-lubricated discs for windscreen wipers, synchronization rings of heavy lorry gearboxes.
- Base plates of cigar-lighters, bases of car lamps.
- Heat shields, insulation shields for sparkplug heads in polyimide sheet.

LCP

- Components for ignition systems . . .
- Components for fuel handling, fuel or gas barrier structures . . .
- Transmission system components, pump components . . .
- Sensors . . .
- Lamp sockets . . .

Thermoplastic composites

- Bumper beams.
- Front-ends.
- Protection shields beneath the engine.
- Hatchback doors, noise shields.
- Frames of front and back seats, seat slides.
- Instrument panels, consoles, package trays, parcel shelves and trays, glove compartments.
- Pedal supports.
- Venture Industries is patenting Sandwiform™ glass-reinforced polypropylene structural sandwich material. Panels with decorative skins are formed in a one-step, thermo-compression process for trunk elements.
- Thermoplastic composites for the vertical body panels of General Motors' Saturne (1000 vehicles per day).
- Thermoplastic panels for the Smart ForFour.
- Underbody parts in self-reinforced polypropylene (Curv) for the Audi A4.
- Trunk lid of the Mercedes-Benz CL500 made out of polyamide blend allowing the integration of GPS and telephone antennae.
- Fascia of the Dodge Neon made out of supergloss Surlyn alloy (DuPont).
- PC/PBT alloys for the Smart car.
- Polyethylene rotomoulded panels for the Think produced in Norway.
- Thermoplastic nanocomposites for the step-assist on the 2002 GMC Safari and Chevrolet Astro Van.
- Hatchback doors in GMT.
- Noise shields in GMT

TPS

- Airbag covers, armrests, upholstery . . .
- Rack and pinion boots . . .
- Automotive weather-stripping . . .

- Air-duct covers and hoses . . .
- Insulation of electric wires . . .
- Window seals . . .

TPO

- Automotive soft skins for interior and instrument panels, claddings, lower B pillar skins, soft-touch overmoulding . . .
- Interior door panels, scuff plates . . .
- Airbag covers, armrests, upholstery . . .
- Automotive fascias, front-ends, mudguards . . .
- TPO skins for low-pressure injection moulding . . .

TPV

- Under the hood: tubes and connectors, plugs, bumpers, grommets for steering, air induction systems, fuel line systems . . .
- Interior: grips, knobs, mats, plugs, bumpers, grommets . . .
- Under the chassis: suspension parts, belly pans, plugs, bumpers, grommets . . .
- Control cable sheathing . . .
- Exterior: spoilers, trims, lighting seals, mirror gaskets, dynamic and static weather seals . . .

TPV PP/NBR-V

- Under-the-hood components.
- Tubes and connectors for air induction systems . . .
- Bellows . . .
- Seals for gas oil filters, carburettors, brake fluid tanks . . .
- Mounts for damping noise and vibrations, shock absorbers . . .

TPE/PVC

- Interior: skins, grips, knobs, mats, plugs, bumpers . . .
- Steering wheels, gear lever knobs . . .
- Gear lever boots . . .
- Console box lids . . .
- Window encapsulations . . .
- Wire harness grommets . . .
- Exterior: trims, seals, weather seals . . .
- Tubes for windscreen washers . . .
- Pipe covering . . .

TPU

- Side mouldings . . .
- Constant velocity boots . . .
- Lumbar supports . . .
- Mounts . . .

COPE

Automotive

- Constant velocity joint (CVJ) boots, rack and pinion bellows . . .
- Air ducts . . .
- Air bag covers, steering wheels . . .

- Airbrake tubing . . .
- Damping mounts for engine hoods . . .

Railway

- Railway pads . . .

PEBA

- Air bag covers . . .
- Airbrake hose and tubing . . .
- Damping mounts . . .
- Screenwash tubes . . .

The automotive market must be segmented into several sub-markets with differing functions, environmental stresses and requirements.

We can consider three major subdivisions (see Figure 2.30):

- Exterior applications subjected to direct sunlight, rain, temperature variations, mechanical aggression (gravel splashing, scratches . . .), and increasing requirements related to styling, low cost, weight saving, ease of processing, safety, respect for the environment and recycling.

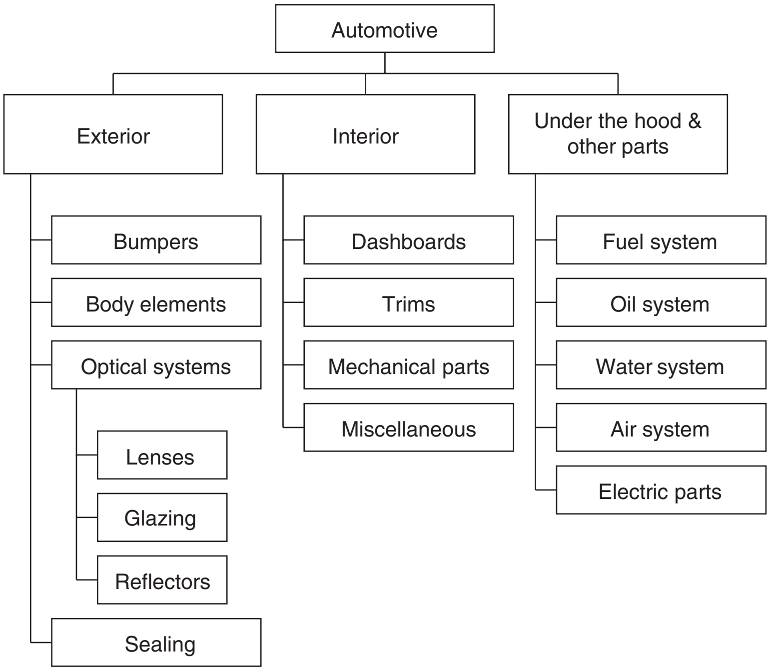


Figure 2.30. Market segmentation of the automotive sector

- Interior applications subjected to temperature, sunlight irradiation through glazing and increasing requirements related to styling, comfort, low cost, ergonomics, weight saving, ease of processing, safety, respect for the environment and recycling.
- Under-the-hood and other mechanical parts subjected to a harsh environment characterized by high temperatures, aggressive fluids (fuel, oils, coolant fluids, brake fluids, ozone . . .). On the other hand, there is no exposure to UV or light.

The penetration of thermoplastics and thermoplastic composites ranges from the totality of the considered parts – for example, bumpers or fuel tanks where metals are nearly ousted – down to applications that are widespread but with only a few consuming part types, such as wire supports, and promising outlets, for example glazing or structural parts.

Well-established applications are, for example:

- bumpers
- fuel tanks
- lights: headlights, rear and side lights
- ancillary equipment such as rear-view mirror housings, wheel trims, luggage boxes, bases for roof racks . . .

Developing applications

- Sealing: weatherstrips, light seals made of TPEs
- Thermoplastic fenders
- Body elements such as panels, doors, spoilers . . .

Emerging applications

- Glazing . . .

To favour the penetration of thermoplastics in the automotive industry, several concepts are being developed to ease assembly, stock control and purchasing. The passenger compartment is a good example of two of these concepts:

- the mono-material concept, and
- ready-to-install modules.

Mono-material concept

Some parts such as dashboards are an inextricable combination of various subparts of different materials making it impossible to dismantle. The choice of compatible materials is advised to allow recycling. For example, a part can be made out of several olefin subparts:

- long fibre reinforced polypropylene (LFRT) for a structural subpart
- polypropylene foam for a damping subpart
- thermoplastic polyolefin elastomer for the skin.

Ready-to-install modules

The automotive industry favours sets of parts assembled by the plastic furnisher and including non-plastic elements such as metal components, electronics . . . This simplifies purchasing and on-line operations. For example, a seat module includes the frame, cushioning, slide system, position control device . . .

Let us quote some application examples for some thermoplastics. These examples may be commercialized, in development, potential or related to very specific uses. As always, the designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade under real service life conditions.

Fuel tanks

The first polyethylene fuel tanks were used 40 years ago on Porsche rally cars and a few years later on special series of the VW Beetle. Weight savings were of the order of 30–50% versus the replaced metal tank. There are also other advantages such as:

- greater design freedom allowing optimization of free-space use and consequently of capacity

- better impact behaviour
- better corrosion resistance
- lower cost due to the ease of manufacturing.

There is also a significant drawback: the inherently higher fuel permeability of polymers. The strengthening of environmental regulations (PZEV; Partial Zero Emission Vehicle) leads to severe requirements concerning fuel impermeability, needing modification of the techniques now in use. Moreover, some carmakers such as Ford and GM require higher mechanical and thermal resistance, and conductive materials.

Here are a number of possibilities for improving fuel impermeability, including:

- thermoforming of six-layer HDPE/EVOH
- combination of PA/PO alloys and EVOH multilayer (Permblok by Atofina)
- fluorination of HDPE
- internal or/and external organic or organo-mineral coatings
- nanosilicate coatings, for example, SMA and silica nanoparticles with epoxy derivates forming a crosslinked network
- re-design of the fuel line with capless fuel tanks (Velsatis and other Renault models).

Dashboards

A dashboard is a complex part with several subparts of very different functionalities:

- structural beam or substrate
- instrument panel with various dials and glazing
- cushioning
- skin
- grilles for heating and demisting
- glove boxes
- racks . . .

Polyolefins are well adapted to the mono-material concept: talc-filled polypropylene and LFRT for structural parts, foamed polyethylene and polypropylene for damping, polypropylene/EPDM alloys or copolymers for skins. Some other functions need incompatible polymers with specific characteristics such as optical properties. Without claiming to be exhaustive, the other thermoplastic materials are:

- PVC and PVC/ABS, PVC/ASA alloys
- ABS, ASA, SMA
- polycarbonate and alloys with ABS
- PMMA
- polyamides, polyphthalamides
- acetal
- polyphenylene oxide (PPO) or polyphenylene ether (PPE)
- GMTs . . .

Bumpers

There are many solutions according to the materials, output and processing methods, for example: rigid beam, damping foam and skin with various thermoplastic versions such as:

- glass fibre reinforced polypropylene beam, polypropylene foam and TPO (polypropylene/EPDM) skin: a big advantage is the mono-material solution, which eases recycling
- beam and foam with polycarbonate skin.

Interior trims

Interior trim applications are decorative coverings with mechanical, safety and aesthetic functions. They include:

- interior panels, doors, pillars . . .
- steering wheels, steering wheel covers and airbag doors . . .
- glove box doors, consoles, package shelves . . .
- defroster/demister and loudspeaker grilles . . .

In these cases, polyolefins are also well adapted to the mono-material concept: talc-filled polypropylene and LFRT for structural parts; foamed polyethylene and polypropylene for damping; polypropylene/EPDM alloys or copolymers for skins. Some other functions need incompatible polymers with specific characteristics such as metallization possibilities. Without claiming to be exhaustive, the other thermoplastic materials used for these applications are:

- PVC and PVC/ABS, PVC/ASA alloys
- polystyrene, ABS, ASA, AES
- polycarbonate and alloys with ABS
- polyamides, polyphthalamides
- acetal
- double-wall panels made out of polycarbonate and polyphenylene oxide (PPO) or polyphenylene ether (PPE) that can be shaped by thermoforming
- GMTs.

Airbag systems

Cars are now equipped with several airbags to ensure safety when a crash occurs but there are some drawbacks such as the cost, the volume, which dictates the steering wheel design and limits the capacity of other storage boxes, and the weight.

The airbag system includes an ignition device that quickly generates a large volume of gas that inflates the airbag itself. The latter is a bag of synthetic textile possibly coated with silicone. Its properties are:

- controlled gas impermeability
- high tensile and tear strengths
- high pliability
- good durability.

To reduce weight, improve pliability and low-volume storage, and save costs, there are trends to reduce the fabric weight while preserving the properties.

Lenses

Lenses of headlights are often in polycarbonate and rear lights in co-moulded acrylics.

Ancillary equipment

There are multiple parts with multiple functions as varied as:

- housing of rear-view mirrors
- grilles, back ventilation grids
- luggage boxes, in composites or thermoplastics
- wheel trims
- door handles
- accelerator pedals
- bases of cigar lighters

- seals
- safety transparent sandwich composites for glazing: polyvinyl butyrate or ionoplast core and two glass skins
- electrical wiring channels and pockets
- assembly aids, integral fasteners
- adhesive films . . .

All thermoplastics – commodity, engineering or speciality – are used but in very small quantities for each specific function.

Under-the-hood

The thermoplastics used are as diversified as the functionalities served. Table 2.31 displays examples of the choice of thermoplastics for different part types.

Table 2.31 Examples of choices of thermoplastics versus types of parts

Predominant environment	Part examples	Thermoplastic selection examples
Oil	Valve covers	PA 6
	Thrust washer for automatic transmission	PPA
	Oil supply components	PA 6
	Oil filter and oil filter casing	PA 66
	Pump paddle	Polyimide
Fuel	Fuel tank	PE
	Fuel pump	PBT
	Fuel supply component	PA 6, PBT
	Fuel manifold	Polyamide
	Gauge support, cap	POM
	Fuel line coupling	PPS
	Carburettor parts	PEI
	Fuel level sensor	POM
Water	Water tank	PE
	Water inlet and outlet housings	Composites
	Water supply components	PA 6, PPA
	Thermostat housing	PA 6
	Cooling system	PPO
Air	Air vent systems, air conditioning and climate control parts	PP, ABS, PA 6, PP/talc, rotomoulded PE
	Air supply components	ABS, PA 6, PBT
	Air intake manifold	PA, PA 66, PA 4.6
	Fans	PA 6
	Air sensors	PBT
	Filters	PBT
Electric parts	Electric or electronics components	PC, PC-HT, PA 6, PBT
	Bobbin frame	Polyimides
	Collector	Polyimides
	Ignition distributor	PBT
	Fuse, connector	PBT
	Wire support	PA 66/PPE, PA 6/PP
	Wire and cable coating	PVC, CPE, EVA, XLPE, TPE, PA 66/PPE, PA 6/PP
Miscellaneous	Silencer of turbocharger	PA, possibly semi-aromatic
	Tension pulleys	PA 6
	Gear, stabilizer arm	POM

Engine covers: example of competition between nylon and BMC

Engine covers are generally made out of:

- glass-reinforced nylon by European carmakers
- BMCs and SMCs by American carmakers.

Certain groups manufacturing cars in both the USA and Europe use BMC in the USA and PA in Europe. Thermal behaviour favours BMC but, on the other hand, nylon is advantageous for recycling. However, the situation is changing in the USA, where the Chrysler Group is adopting a mineral-reinforced nylon (Minlon by DuPont) for the rocker covers on the 2004 Chrysler Town & Country, Dodge Caravan and Grand Caravan with 3.3 and 3.8-litre V-6 engines. The weight gain is of the order of 30% versus aluminium.

Intake manifold: PA overview

Many automakers use reinforced nylon for air intake manifolds because of direct advantages, for example:

- weight saving because of the performance/weight ratios, which lead to fuel economy without sacrificing performances
- cost saving due to the ease of manufacturing
- design freedom allowing an improvement of the air-flow boosting performances
- virtually unlimited possibilities of part integration
- rusting resistance compared to metals
- aesthetics . . .
- reduction of space used . . .

Plastic manifolds are not only used on mass production cars but also on sports cars such as Porsche models, the Chevrolet Camaro and so on. For the intake manifolds used on the Camaro and Firebird, PPA is replacing PA because of several advantages:

- high-temperature resistance
- better moisture behaviour
- higher resistance to tensile creep reducing leakage risks

On the other hand, the price is higher but there are also some running advantages:

- a significant weight reduction with a PPA part weighing 5 kg versus 12 kg for the aluminium counterpart, that is, a 58% weight saving
- 25% higher air-flow and 20 HP extra power.

Radiator fan: PA instead of steel

The first plastic automotive fan blades were made with glass-reinforced PA instead of steel for direct advantages such as:

- weight savings of 60% due to the low density and good mechanical performances
- a 50% cut in vertical stress on the water pump bearing at 5200 rpm because of the light weight
- a higher flexibility.

Moreover there are indirect benefits, such as:

- improvement of the pump bearing durability because of the lower vertical loading
- fuel economy without sacrificing performances
- boosted performances
- improvement of worker and customer safety because of the flexibility and rusting resistance.

Body elements

There are a multitude of solutions according to the material and processing methods. Without claiming to be exhaustive, thermoplastic solutions include:

- Structural foamed polycarbonate for roof of 4WD.
- Nanocomposites: General Motors and Basell Polyolefins continue the development of nanocomposites for high-volume applications in external trim parts such as body panels. Three grades of TPO-based nanocomposites reinforced with 2.5% nanoclay have been commercialized by Basell Polyolefins. The first application of these nanocomposites was a low-volume minivan step option.
- Thermoplastic composites, GMT. According to The European Alliance for SMC, the production of glass mat reinforced thermoplastics (GMT) and long fibre reinforced thermoplastics (LFT) was up about 9% in 2002, demonstrating bright future prospects. Some examples are:
- ○ thermoplastic composites for the vertical body panels of General Motors' Saturne (1000 vehicles per day)
- ○ thermoplastic panels for the Smart ForFour
- ○ PC/PBT alloys for the Smart car
- ○ trunk lid of the Mercedes-Benz CL500 made out of polyamide blend allowing the integration of GPS and telephone antennae
- ○ fascia of the Dodge Neon made out of supergloss Surlyn alloy (DuPont)
- ○ polyethylene rotomoulded panels for the Think produced in Norway
- ○ hatchback doors in GMT
- ○ noise shields in GMT
- ○ underbody parts in self-reinforced polypropylene (Curv) for the Audi A4
- ○ monocoque frames of special vehicles in composites.

Fenders

According to Bayer's forecasts, the demand for plastic fenders will double from its current 8000 tonne annual level by 2010. Some current solutions are, for example:

- PPO/PA blend for passenger cars. A new conductive version of the on-line paintable Triax PA/ABS blend is proposed by Bayer. Heat deflection temperature is in the 180–200°C range ensuring resistance to the temperatures encountered in the drying ovens during cathodic dip coating.
- Thermoplastic composites for the fenders of the Class A from Mercedes, and the Scenic and Laguna from Renault.

Sealing

Sealing is evolving from thermoset rubbers towards TPEs, particularly TPVs.

Glazing

Glazing applications are a significant prospect for polycarbonate but currently regulations do not authorize its use.

Exatec (Bayer and GE) and Battenfeld are developing a 5 kg roof part that requires a subsequent anti-scratch and UV protective coating.

Seating

- Frames and seat slides of front and back seats can be made out of GMTs. Long glass fibre reinforced polyamides are used for very light seats intended for sports cars.
- Polyamide is used for the swing arm of the seat-reclining mechanism.

Shields and barriers: damping, sound and heat absorbing materials

There are myriad such applications, for example:

- under-carpet heat and acoustic shields
- cabin-side barriers between the engine and the passenger compartment, made of sound-absorbing material, to prevent engine noise
- under-layers for interior trim panels, door panels, headliner or package shelves
- cushioning and soundproofing of the dashboards, sun visors . . .

Foams and mats:

- Foams of PE are used for: insulation against moisture, water, temperature and noise; for interior sealing of the doors; heat and phonic insulation of headliners; seals of air conditioning systems; loudspeakers; cushioning of vanity mirrors; cushioning and soundproofing of dashboards; panels of doors; sun visors; under carpet doubling; supports for adhesive tapes to smooth out unevenness.
- Foams of PP are used for: side protection of doors, armrests with integrated baby seat, floor insulation, heat and phonic insulation of transmission tunnels, trunks, cushioning of sun visors, steering columns, knee bolsters, armrests, tool boxes and racks . . .
- Lightweight mats of fibres, which can be die-cut and thermally moulded, can be applied behind any interior trim panel, door panels, headliners or package shelves as superior sound absorbers.

2.12.4 Electrical & electronics

The electrical & electronics market, with consumption estimated from 3% up to 8% of the thermoplastics total according to the region, is the fourth outlet for thermoplastics. It is also an important sector for thermoplastic composites and TPEs.

The electrical & electronics industry is subject to many constraints:

- economic competition, worsened by production overcapacities
- margin reductions
- strengthening of safety, pollution, recycling and energy regulations.

All these reasons persuade manufacturers to save costs, improve quality and performances, and to support materials that can be recycled.

Several exceptional features explain the high level of thermoplastics and thermoplastic composites used for this sector:

- Technical motivations: the use of thermoplastics is favoured by:
  - insulating properties with the possibility to make polymers conductive when necessary
  - choice between flexibility and rigidity
  - ease and freedom of design allowing a broad integration of functionalities
  - ease of processing and assembly
  - high impact resistance versus glass and ceramics allowing miniaturization
  - low density and attractive performance/weight ratio leading to weight reduction
  - low or zero maintenance
  - non-rusting (but beware of ageing)
  - acoustic damping (noise reduction)
  - elasticity and sealing properties of TPEs and TPVs
  - the replacement of conventional materials because of an exceptional combination of properties unattainable for ceramics and glass

  - adaptation to mass production and small series
  - cost cutting
  - the possibility to associate several polymers to integrate several functionalities thanks to the exceptional combination of properties. For example, co-moulding of hard plastic and soft TPE.
- Aesthetics: thermoplastics allow:
  - much more design freedom than conventional insulating materials
  - decoration possibilities: transparency, bulk colouring, printability, paintability, in-mould decoration
  - pleasing finish.
- Economic features: thermoplastics provide:
  - a favourable economic solution for mass production
  - reduction of manufacturing times
  - reduction of the finishing costs: plastics allow the integration of functions and, consequently, lead to reduced assembly costs
  - higher productivity due to adapted processes, integration of functions, fewer processing steps . . .

Polymers also have some general handicaps:

- high raw material cost (but attractive final cost)
- recycling brings some particular problems due to economic conditions, polymer modifications and reinforcements.

The electrical & electronics market dictates some specific regulations. Among them a typical example is the UL (Underwriters Laboratories) requirements related to the long-term service temperature and the fire rating.

2.12.4.1 The UL Temperature Index

The temperature index is the maximum temperature that causes a 50% decay of the studied characteristics in the very long term. It is derived from long-term oven-ageing test runs. The UL Temperature Index depends on:

- The targeted characteristics. There are three categories in the UL Temperature Indices according to the properties considered:
  - electrical only
  - electrical and mechanical, impact excluded
  - electrical and mechanical, impact included.

  For the same grade with the same thickness, the three indices can be identical (for example, a polyethylene grade with a 50°C UL index temperature) or different (for example, a polyamide grade with a temperature index varying from 75°C for the electrical and mechanical properties, impact included, up to 105°C for the electrical properties only).
- The thickness of the tested samples. The UL temperature indices increase with the thickness of the samples. For example, for a defined polyamide grade, the UL Temperature Indices for the same category are:
  - 75°C for a 0.7 mm thickness
  - 95°C for a 1.5 mm thickness
  - 105°C for a 3 mm thickness.
- The formulation of the grade used.

Like all laboratory methods, the temperature index is an arbitrary measurement that must be interpreted and must constitute only one of the elements by which judgement is made.

2.12.4.2 The UL Fire Rating

The UL94 Fire Rating provides basic information on the material's ability to extinguish a flame, once ignited. The samples can be tested horizontally (H) or vertically (V) and the burning rate, the extinguishing time and dripping are considered. The main categories are:

- V0: the most difficult to burn, extinguished after 10 s, neither dripping nor flaming particles.
- V1: extinguished after 30 s, neither dripping nor flaming particles.
- V2: extinguished after 30 s, flaming particles or drips permitted.
- 5V: extinguished after 60 s, flaming particles or drips permitted.
- HB: burning horizontally at a 76 mm/min maximum rate.

The UL rating depends on:

- The grade. An inherently flammable polymer can be V0 classified for a special fire-retardant grade or, vice versa, an inherently fire-resistant polymer can be HB classified for a special grade containing too high a level of flammable plasticizer.
- The sample thickness. For the same grade of polyethylene, the UL ratings are:
  - V2 for a 1.6 mm thickness
  - V0 for a 6 mm thickness.

Smoke opacity is another increasingly important characteristic measured by optical density.

Fire-retardant additives can be halogenated or halogen-free, which reduces the corrosivity, toxicity and pollution risks.

To progress in the electrical & electronics industry, plastics must improve their performance characteristics, ease of processing, productivity and recycling, for example:

- Better thermal resistance in the long term and better durability to favour long-term service without maintenance, and miniaturization.
- Better fire behaviour, lower smoke emission and more widespread use of halogen-free grades.
- Ease of processing: improved flow properties and processability lead to cycle time reductions and productivity gains.
- Low finishing costs: bulk colouring, an intelligent design and an effective maintenance of the moulds, dies and other tools reduce or avoid finishing operations, cutting the finishing costs.
- Recycling: more-effective solutions are sought.
- Development of highly conductive thermoplastics, cheaper and easy to process.
- Development of cheap thermoplastics with specific properties for solar cells, displays and other high potential applications.

Thermoplastics are predominant among the plastics used in the electrical & electronics industry with a market share greater than 75%, versus 16% for thermosets and 8% for all composites.

Figure 2.31 displays the market shares of the most commonly used commodity and engineering thermoplastics in the electrical & electronics industry. Only polyamides are identified among the engineering thermoplastics.

Let us quote some application examples for some thermoplastics. These examples may be commercialized, in development, potential or related to very specific uses. The designer

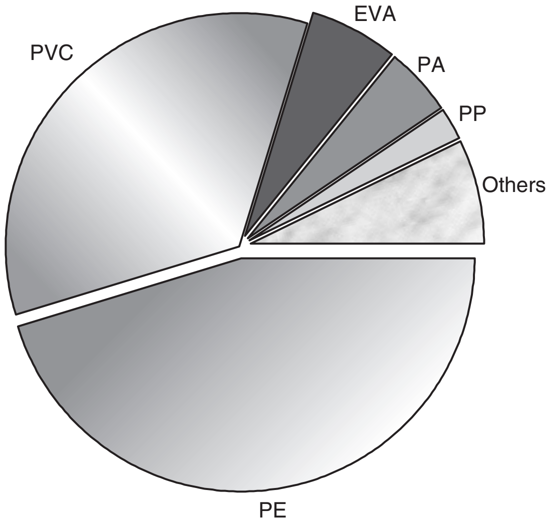


Figure 2.31. Thermoplastic shares in the electrical & electronics market

must verify the possibility of using the quoted thermoplastic family for their specific problem and test the right grade under real service life conditions.

Polyethylene

- Wire and cable insulation . . .
- Moulded electrical accessories, electrical connectors . . .

Polypropylene

- Film capacitors for military and industrial AC applications . . .
- Moulded electrical accessories . . .

PMP

- Wire and cable insulation . . .
- Printed circuits, bobbins, connectors, ink-cartridges for printers . . .

COC

- Electronics: bi-oriented films, metallized films, light guides and diffusion plates for LCDs, semiconductor containers . . .

EVA

- Electric wire and cable sheathing . . .

CPE

- Wire and cable jacketing . . .

PVC

- Wire and cable insulation consumes 4% of all PVC with construction and automotive wires, electrical cord jacketing, fibre optic sheathing, heat-shrinkable sleeves . . .
- Components in phone systems, power tools, refrigerators, washing machines, air conditioners, computers, keyboards, housings . . .
- Floppy Disk jackets . . .

Styrenics

- Knobs, buttons . . .
- Lighting diffusers . . .

ABS

- Telecommunication equipment . . .
- Consumer electronic equipment . . .
- Power tool housings . . .
- Computer housings, transparent and translucent covers for PCs and copiers, keyboards, business machine equipment . . .

SAN

- Outer covers of printers, calculators, instruments, transparent covers for PCs and copiers, business machine equipment . . .
- Telecommunication equipment . . .
- Consumer electronic equipment . . .

PA

- Electricity, electrical household appliances: cases and fuse holders, junction boxes, miniature junction boxes, inlet and outlet cable channels . . .
- Housings of power tools, casing of projectors . . .
- Switches, contactors, socket-outlets, connectors, air resonators, washing machine pulleys . . .

PA 11, 12

- Electricity, electrical household appliances: electrical cables, optical fibres, flexible telephone cables, inlet and outlet cable channels . . .
- Housings of microscopes, connectors . . .

Aromatic PA

- Connectors for electronic and electrical devices such as personal computers, digital cameras and mobile telephones; safety switches, telecommunication parts . . .
- Used with lead-free solder especially in card connector applications for mobile telephones, personal computers and smart media . . .
- Chassis and housings for electrical and electronic equipment, sliding parts in video recorders, disk supports in CD players . . .
- Induction motor supports . . .

Thermoplastic polyester

- Miniaturized electronic components . . .
- Telecom & IT connectors, mobile phone casings, bobbins . . .
- Low voltage switch gears, electric-motor parts . . .
- Lighting and lamp fittings, lamp bases of energy saving lamps . . .
- Connectors, circuit breakers, switches . . .
- Power distribution and circuit protection . . .
- Wire and cable or fibre optic applications, optical fibre tubing . . .

PMMA

- Lighting, lights, lighting diffusers, light-control lenses in lighting fixtures . . .
- Signs: internally illuminated outdoor signs, diffusers, side-lit signs, very thin illuminated displays, fluorescent signs . . .

- Electrical engineering: lamp covers, switch parts, dials, control buttons, embedment of components . . .
- Optoelectronics: covering of displays, from small LCDs in cellular phones to large rear-projection television sets or screens designed for audio-visual presentations . . .
- Transparent technical parts: indicators, dials, inspection holes, caps, casings, hoods and other electrical parts . . .
- Knobs, small furniture . . .

PC

- Internal components and current carrying devices, brush holders, coil bobbins & forms . . .
- Power distribution, connectors, insulators, relay components, meter housings and covers, casket hardware . . .
- Light globes, lighting diffusers, light-control lenses . . .
- Outdoor lighting fixtures . . .
- Traffic lights . . .
- Optical media, computer and audio compact discs . . .

POM

- Control dials.
- TV tuner arms.
- Heating appliance insulation . . .
- Telephone components . . .

PPE

- Electrical terminal housings, distributor cabinets and large capacitor cases . . .
- Relay sockets, cable connectors, bulb sockets, coil formers . . .
- High tolerance electrical switch boxes and connectors . . .
- Sensors and circuits . . .

Perfluorinated thermoplastics (PTFE or TFE, PFA, FEP)

- Coaxial cable connectors, terminal and high voltage insulators; transformers, relays, antennae, power amplifier components . . .
- Laminates for critical microwave components, antennae and subassemblies, RF/microwave materials, hybrid RF multilayers, digital/microwave hybrid multilayer PCB assemblies, cellular base station antennae . . .
- Dual-band hi-power passive circuits . . .
- Millimetre wave components . . .
- PTFE/woven-glass composites . . .
- Lowest loss applications . . .
- Telecommunications . . .
- Wireless communications . . .

ETFE

- Electrical sleeving, wire and cable insulation and jacketing, appliance wires, motor lead wires, compact wire and cables, airframe wiring, extruded coatings . . .
- Battery components . . .
- Coil forms . . .
- Electrical components: sockets, connectors, switches, insulators, cable clamps . . .

PCTFE

- Electroluminescent display panels . . .

ECTFE

- Electrical wire and cable insulation and jacketing, wire wraps, motor lead wires, compact wire and cables, airframe wiring, extruded coatings . . .
- Coil forms . . .
- Electrical components: sockets, connectors, switches, insulators, cable clamps . . .

PVDF

- Wire and cable insulation and jacketing, telecommunication wires and cables, optical fibre coating, extruded coatings . . .
- Semiconductors . . .
- Electrical components: sockets, connectors, switches, insulators, cable clamps . . .
- Piezoelectric films . . .

PVF

- Printing circuit lamination, release film in the manufacture of PCBs . . .
- Sign industry: surface protection . . .
- Electrical and wire marking applications . . .

Cellulosics

- Lighting, diffusers, lighting devices and accessories . . .
- Displays and profiles . . .

Polysulfone

- Frames of integrated circuits . . .
- Connectors, switches, insulators, sockets . . .
- Reels . . .
- Plates on terminals . . .
- TV components . . .
- Films for capacitors . . .
- Parts of alkaline batteries . . .
- Cartridges of printers . . .

PPS

- Connectors, terminal blocks, relay components, switch components . . .
- Coil formers, bobbins . . .
- Moulded bulb sockets for electrical power stations, thermostat parts, halogen lamp housings . . .
- Control panels, plates on terminals . . .
- Brush holders . . .
- Motor housings . . .
- Electrical appliance and PC brackets, components for floppy disk drives . . .
- Parts for heaters, grids of hair dryers, parts of domestic irons, coffee machines, microwave ovens, cooking appliances . . .

PEEK

- Wire insulation for extremely high temperature applications, cable couplings and connectors, sub-sea connectors, coaxial connector jacks, sub-sea controlled environment connectors . . .

- Wafer wands, wafer transport carriers . . .
- Surface-mounted trimming potentiometers . . .
- Appliances: handles, cooking equipment . . .
- Integrated circuit packaging (hard disk drive) trays . . .

PEI

- Electrical control units . . .
- Wire insulation . . .
- Reels . . .
- Integrated circuits . . .
- Connectors, high-heat connectors . . .
- Computer components, mobile phone internal antennae . . .
- RF-duplexers or micro-filters, EMI shielding . . .
- Fibre-optic connectors, optical transceivers . . .
- Lighting applications, reflectors, reflectors with dichroic coating without primer . . .

PAI

- Insulators . . .
- ESD (electrostatic discharge) for integrated circuits, hard disk drives, circuit boards . . .
- Parts for high-speed electronic printing and reproduction equipment . . .
- Burn-in sockets . . .

PI

- Insulating elements and spacers for electron accelerators and cathode-ray tubes.
- Overmoulding of motor collectors, bodies of generator coils, overmoulding of coils, coil frames, insulation of rotor axes.
- Printed circuit boards usable up to 300°C.
- Terminal plates and terminals, lamp bases, connectors, parts of circuit breakers.
- Insulating collars for chain saws, insulating elements and crossings for electric blowtorches.
- Drive wheels for microwave ovens, handles for electric ovens and other household appliances, parts for spit-roasters, air vents for slide projectors.
- Syntactic foams for microwave and RF applications.

LCP

- Bobbins, coils . . .
- Sockets, switches, relays, electrical and electronic connectors, fuse holders, closures . . .
- Chip carriers . . .
- Sensors, LED housings . . .
- Surface-mount devices, surface-mount interconnection devices, PCMCIA card frames . . .
- High-performance motor components . . .
- Imaging devices . . .
- Guides . . .
- Hard disk drive components . . .

PBI

- Semiconductor industry, vacuum chamber applications, clamp rings for gas plasma etching equipment, wafer retaining rings for gas plasma etching, vacuum tips . . .

- Wafer carriers . . .
- Connectors, connectors for aircraft engines . . .
- Vacuum cups, fingers and holders for incandescent and fluorescent light bulbs . . .

TPS

- Insulation of electric wires . . .
- Grips, buttons, seals, feet, gaskets . . .

TPO

- Insulation of electric wires . . .
- Grips, buttons, seals, feet, gaskets . . .

TPV

- Grips, buttons, bumpers, seals, feet, gaskets, spacers for electrical machines . . .
- Moulded electrical accessories, electrical connectors, shields, electrical connections . . .
- Power transmission and distribution systems . . .
- Wire and cable jacketing (halogen-free flame retardant; HFFR) . . .
- Microphone boom on headset . . .
- Scroll wheel on Logitech mouse . . .
- Telecommunication splice seals . . .

TPE/PVC

- Moulded electrical accessories, electrical connectors . . .
- Wire and cable jacketing . . .
- Grips, handles, feet, pads for small electrical machines . . .
- Seals, integrated seals . . .
- Motor and vibration mounts . . .

TPU

- Moulded electrical accessories, electrical connectors . . .
- Wire and cable jacketing . . .
- Grips, handles, feet, pads for small electrical machines . . .
- Seals, integrated seals . . .
- Motor and vibration mounts . . .

MPR

- Wire and electric cables for industry and robotics . . .
- Damping mounts for noises and vibrations . . .
- Soft handles and grips . . .

COPE

- Low noise gears . . .
- Plugs, pads, feet, damping mounts . . .
- Moulded electrical accessories, electrical connectors . . .
- Wire and cable jacketing . . .
- Antenna covers . . .
- Keypads . . .

PEBA

- Wire and cable jacketing, electrical and communication cable jacketing, coil cables . . .
- Low-noise gears . . .
- Plugs, pads, feet, damping mounts . . .

The electrical & electronics market can be divided into several sub-markets differentiated by their functions and requirements.

We can consider three large subdivisions (see Figure 2.32):

- wire and cable coating
- electrical components
- electronics components.

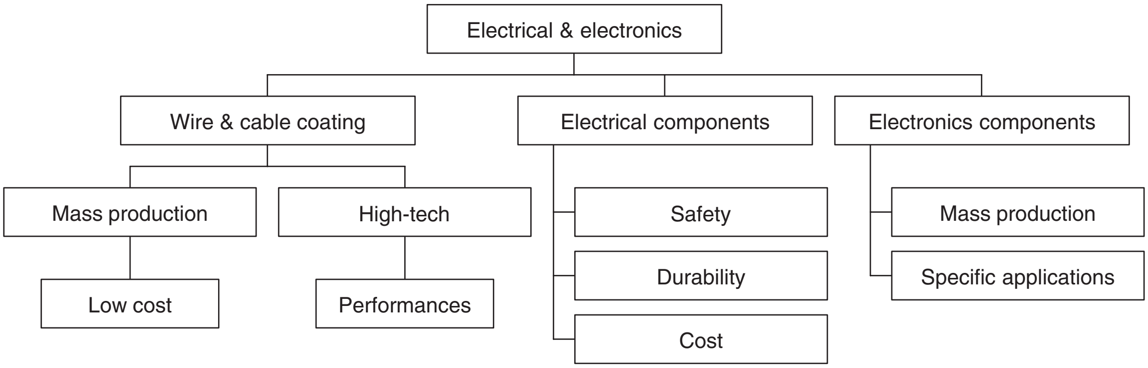


Figure 2.32. Market segmentation of the electrical & electronics sector

Each category comprises both mass-production and high-tech products, with stringent economic requirements for the former and specific performances for the latter.

The penetration of thermoplastics and thermoplastic composites ranges from the totality of the considered parts, for example housings and casings where metals are nearly ousted, down to areas where there are only a few applications, such as for highly conductive polymers.

Let us quote some application examples for some thermoplastics. These examples may be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade under real service life conditions.

Wire and cable coating

Wires and cables are universal and essential components of the electrical & electronics industry. Well known from simple building and automotive wiring, their complexity for energy cables is generally unsuspected.

The properties are as diverse as the targeted functions:

- Building and automotive wiring is lightweight, mass-produced and cheap with fair electrical and mechanical performances and long-term durability.
- Industrial wiring must have customized properties.
- Energy cables are high-tech goods.

General-purpose wires and cables are, for example:

- power transport and distribution networks: dry-insulated, armoured or unarmoured cables for medium, high and very high voltages
- low-voltage cables, aerial or underground for distribution networks and connection
- domestic wires and cables and appliance cords for mobile apparatus with a 750 V maximum rated voltage
- industrial cables, maximum rated voltage 1000 V, for industrial equipment and power supply to mobile apparatus.

Special cables and wires for specific purposes:

- wires and cables intended for electrical equipment fitted in automobiles; aircraft; lifts; ships; machine tools; railway equipment, coaches, wagons, etc.; mines; handling equipment for transporting goods, conveyors, pumps, etc.; petrochemical industry; oil equipment; iron and steel industry; welding, etc.
- precision and data cables for computer equipment, electronics, automatic control instruments
- heating cables.

Telecommunications wires and cables:

- cables for aerial and underground medium- and long-distance lines
- cables for exchange area networks' underground and aerial junctions, subscribers' cables
- telephone cords
- cables for private installations.

Submarine and underwater cables:

- cables for power transport
- cables for telecommunications.

Connection accessories for power cables:

- low voltage: connections, branching
- medium voltage terminations
- medium voltage plug-in terminations: separable connectors, bushings . . .
- medium voltage connections and branching for dry or paper insulated cable, lapped, injected, heat-shrinkable . . .
- prefabricated medium voltage connections for dry-insulated cable
- high and very high voltage: terminations, connections.

Market shares are roughly estimated at:

- 65% for power cables (50% for low voltage and 15% for medium and high voltage)
- 25% for telecommunications
- 10% for other cables.

For Western Europe, the wire and cable market is estimated at roughly €18 billion.

As shown in Figure 2.33, polyethylene has the highest consumption (nearly 60%) in both thermoplastic and thermoset (PEX) forms, and also foamed PE (2%). PVC is second (roughly 30%) and the others are polypropylene, TPEs, polyamide, fluoropolymers . . .

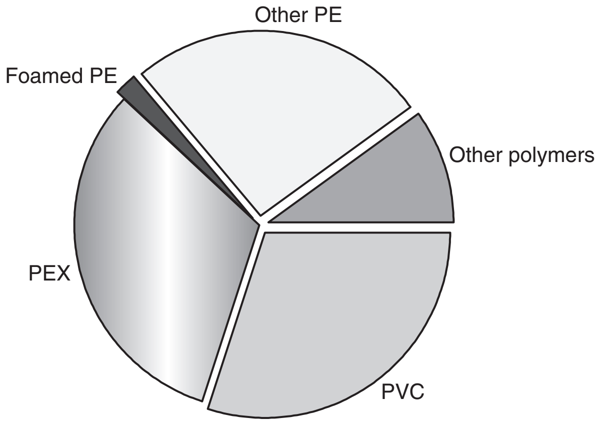


Figure 2.33. Thermoplastic shares in the wire & cable coating market

Table 2.32 displays the share of the wire & cable sector in the total consumption of each polymer family.

Table 2.32 Share of the wires & cables sector in the total consumption of each thermoplastic family

	%
LDPE	5
HDPE	2
LLDPE	2
PVC	8*
PA	2

* More than 25% of flexible PVC

Apart from PVC, polyethylene and its copolymers, other thermoplastics are used for special applications that justify their higher cost. They are, for example:

- fluoropolymers for high temperature and/or chemical resistance
- PA 11 or 12
- PEEK, PEI for high-temperature service
- TPEs: special grades are marketed, possibly crosslinked after extrusion.

Electric components

Wires and cables just carry the electric current and the electric network needs a multitude of other electric equipment including:

- connectors, switches . . .
- electric power equipment
- motors and controls
- measuring and control equipment
- lighting and wiring equipment
- current-carrying equipment
- non-current-carrying wire devices
- pole line hardware.

These very dissimilar parts used for very different functions, from small parts without any special features up to electrical generators, consume significant shares of engineering plastics and composites, as we can see in Table 2.33.

Connectors, switches, electric distributors, fuse boxes and other electric fittings need a subtle balance of electrical and mechanical properties, durability, cost and aesthetics. This broad field creates fierce competition not only between engineering thermoplastics and SMC/BMC for the main applications but also with polypropylene and polyethylene or PVC for the lower performance parts and, at the opposite end of the scale, with high-tech plastics such as polyetherketone, polyetherimide, liquid crystal polymers . . . For example, without claiming to be exhaustive:

- polycarbonates and polyphenylene ethers are used when chemical resistance is not necessary
- polyamide is commonly used but its applications are limited by sensitivity to moisture

Table 2.33 Share of the electrical & electronics sector, excluding wires & cables, in the total consumption of certain polymer families

	%
ABS	19–28*
PA	8–19*
POM	9–12*
PBT	21
PC, excluding optical media	7
PC/ABS	20–25*
Thermosets	7
Composites	13

*According to country, year and source

- the aptitude for metallization of semicrystalline syndiotactic polystyrene (SPS) filled with 30% glass fibre should open uses in the connector industry but, unfortunately, its marketing is uncertain in the near future
- thermoplastic polyesters PET and PBT are commonly used, but polyethylene naphthalate, which offers higher performance in certain characteristics, is still too expensive
- PEEK, PEI . . . are used for special purposes that justify their cost
- polyimides: terminal plates and terminals, connectors, parts of circuit breakers.

Photovoltaic solar cells

Apart from plastic frames for solar cells, there is intensive development work to use polymer films as cheap and flexible photovoltaic materials.

At present, photovoltaic cells are made of thin, rigid sheets of silicon with other semiconducting materials. Standard commercial panels convert about one tenth of the sunlight into electricity, that is, an efficiency of about 10%. The highest performance panels have an efficiency of roughly 20%.

The goal of polymers in photovoltaic cells is to make very cheap active materials even if their efficiency is very low. So, a cheap mass-production process could lead to domestic and industrial applications. Some research dates back 20 years and today several techniques are competing, with either hybrid or all-polymer systems. Among the various methods we can quote as examples:

- Deposition of a merocyanine-dye layer on a transparent electro-conducting film of polyester coated with indium-tin oxide (ITO). Two layered structures were studied:
  - ○ aluminium/merocyanine/ITO
  - ○ silver/merocyanine/ZnO/ITO – the most efficient.
- Production of a two-layer film made out of copper phthalocyanine and a perylene tetracarboxylic derivative. A power conversion efficiency of about 1% has been achieved.
- The Grätzel technology, consisting of a junction between a polymer and a liquid electrolyte, has a conversion efficiency higher than 10%. The photovoltaic generation is located in the polymer and the electrolyte ensures charge transfer. However, the liquid electrolyte evaporates over time as the operating temperature increases.
- Amorphous silicon can replace the expensive and more-efficient rigid monocrystalline and polycrystalline silicon sheets used in most common solar panels. Less efficient than crystalline silicon, it can be applied to a flexible plastic foil by Plasma Enhanced

Chemical Vapour Deposition (PECVD). It is expected that these amorphous silicon foils could be processed at low costs using the processing methods adopted for films.
- A hybrid, made of tiny nanorods dispersed in an organic polymer, can be easily sandwiched between electrodes and can produce, at present, about 0.7 V.
- An Austrian team boosts the performance of plastic cells by mixing a conducting polymer, MDMO-PPV (an asymmetrically substituted polyphenylenevinylene), with a molecule made from carbon fullerene . . .

Today the best all-polymer solution achieves a conversion efficiency of a few percent.

Fuel cells

There are many types of fuel cells, for example:
- proton exchange membrane fuel cells (PEM)
- phosphoric acid fuel cells (PAFC)
- direct methanol fuel cells (DMFC)
- alkaline fuel cells (AFC)
- solid oxide fuel cells (SOFC)
- molten carbonate fuel cells (MCFC)
- regenerative fuel cells (RFC).

For cells working at low and moderate temperatures, thermoplastics could have openings for components such as membranes and plates. Polybenzimidazole (PBI), LCPs and PPS could be suitable for these applications.

For cells working at high temperatures, plastics are candidates for:
- membranes: a sulfonated fluoropolymer manufactured by DuPont (Nafion®) is available, but at high temperatures its conductivity is greatly reduced
- binders for solid fuel (MCFC) such as polyethylene, polypropylene and polybutylene.

Measuring and control equipment

Thermoplastics are used for insulation and housings, allowing a broad choice according to the technical and economic requirements, for example:
- ABS: housing of testers
- polypropylene: housing of testers
- polycarbonate: transparent housing, magnifying windows
- PMMA: transparent housing, magnifying windows.

Lighting

Lighting consumes transparent thermoplastics for light diffusion, and composites and other thermoplastics for boxes and housing. For example:
- polycarbonate: the lighting sector consumes roughly 3% of the polycarbonate total
- acrylics: transparent housing
- polyimides: lamp bases.

Wiring equipment

PE, PVC and composites are broadly consumed:
- PVC for cable shelves . . .
- polyethylene for tubing . . .

Substrates for electronic equipment

For insulating substrates for electronic equipment, thermoplastic laminates are used:
- Commodity thermoplastics
  - PVC
  - polypropylene

- Engineering thermoplastics
    - polycarbonate
    - polyamide
    - polyester
- Speciality thermoplastics
    - polyimide
    - PTFE.

2.12.5 Household, entertainment & office appliances

Technically the household, entertainment & office appliance market appears heterogeneous, including a variety of functionalities, shapes, forms and properties. Table 2.34 proposes a classification method based on the lifetime and the main function but many other classifications are possible.

Most household and entertainment appliances are mass-production goods that are sold by the million. Production of business or office appliances varies from small series (shredders, for example) to medium or high series (PCs and other computers). Prices are very varied from a few tens of euros up to thousands of euros and more. Table 2.35 provides an idea of the economic importance of some typical devices.

Despite their apparent heterogeneity, these various appliances have several points of similarity:

- electrical properties
- aesthetics and mar resistance
- impact resistance
- dimensional stability
- durability
- fire-resistant behaviour for the large parts
- high performance/price ratio leading to a material choice according to the cost of the end product.

But there are also some differences between technical parts with specific functionalities and, consequently, specific material families and properties are utilized.

The household, entertainment & office appliance market consumes an estimated 3% up to 6% of the thermoplastics total, according to the region, making it the fifth outlet for these materials.

The household, entertainment & office appliance industry is subject to many constraints:

- economic competition, worsened by production overcapacities and market saturation for several products
- margin reductions
- strengthening of safety, recycling, environmental and energy regulations

All these reasons persuade manufacturers to save costs, improve quality and performances, and to support materials that can be recycled.

Several exceptional features explain the high level of thermoplastics and thermoplastic elastomers used for the household, entertainment & office appliance market:

- Technical motivations: use of thermoplastics is favoured by:
    - insulating properties
    - ease and freedom of design allowing a broad integration of functionalities
    - ease of processing and assembly

Table 2.34 Examples of functionalities and properties of appliances

Estimated average lifetime (years)	Primary functionality	Item examples	Main properties
Very long lifetime			
10+	Cooling	Refrigerators Freezers	Thermal insulation Cold impact Aesthetics Airtightness Ease of cleaning Microbial resistance Durability Cost
Long lifetime			
10	Washing	Dishwashers Washing machines Dryers	Hydrolysis resistance Chemical behaviour Heat resistance Durability Cost
10	Cooking	Ovens: Electric Gas Microwave	High temperature resistance Fat, grease, oven-cleaner resistance Electrical insulation Durability Microwave transparency
10	Business or office appliances	PCs and other computers, printers, photocopiers, shredders . . .	Aesthetics Mar and scratch resistance Heat resistance Electrical insulation Durability Ease of cleaning Cost
10	Miscellaneous household appliances	Safety, alarm devices Waste compactors	Mechanical performance Aesthetics Durability
Medium lifetime			
5–10	Entertainment appliances	Radios, televisions, audio systems, video systems, VCRs, electronic video games . . .	Aesthetics Mar and scratch resistance Heat resistance Electrical insulation Durability Ease of cleaning Cost
5–10	Medium-sized household appliances	Vacuum cleaners Floor care devices	Aesthetics Impact resistance Electrical insulation Antistatic behaviour Cost Resistance to floor care products
5–10	Small household appliances	Kitchen Personal care	Aesthetics Food and chemical resistance Impact resistance Heat resistance Ease of cleaning Microbial resistance Cost

Table 2.35 Examples of some economic parameters concerning household appliances

	No. of households with equipment (%)	Sales (units per year per capita)	Average unit price (€)	Sales (€ per year per capita)
High cost appliances				
Dishwashers	45	0.02	580	12
Washing machines	95	0.04	490	20
Refrigerators	96	0.04	465	19
Medium cost appliances				
Microwave ovens	72	0.03	130	4
Vacuum cleaners	86	0.05	125	6
Low cost appliances				
Food mixers	49	0.02	86	1.5
Electric shavers	29	0.02	85	1.5
Steam irons	71	0.04	45	2
Coffee makers	68	0.07	33	2
Hairdryers	72	0.04	25	1

- impact resistance
- low density and attractive performance/weight ratio leading to weight reduction
- low or zero maintenance
- non-rusting (but beware of ageing)
- acoustic damping (noise reduction)
- elasticity and sealing properties of TPEs and particularly TPVs
- the replacement of conventional materials because of an exceptional combination of properties unattainable for metals, ceramics and glass
- adaptation to mass production and small series
- cost cutting
- the possibility to associate several thermoplastics to integrate several functionalities thanks to the exceptional combination of properties, for example, co-moulding of a hard thermoplastic and a soft TPE.

- Aesthetics: thermoplastics allow:
- much more design freedom than conventional insulating materials
- decoration possibilities: transparency, bulk colouring, printability, paintability, in-mould decoration
- pleasing finish.
- Economical features: thermoplastics provide:
- an economical response to mass production
- reduction of manufacturing times
- reduction of the finishing costs: plastics allow the integration of functions and, consequently, lead to the reduction of assembly costs
- higher productivity due to adapted processes, integration of functions, fewer processing steps . . .

Thermoplastics also have some general handicaps:

- high raw material cost (but attractive final cost)
- recycling bringing some particular problems due to economic conditions, polymer modifications and reinforcements . . .

The household, entertainment & office appliance market is subjected to some specific regulations for specific parts, notably large ones. Moreover, standards and regulations depend on the country. Among them a typical example is the UL requirements related to the long-term service temperature and the fire rating.

The UL Temperature Index

Described in detail in Section 2.12.4.1, the UL temperature index is the maximum temperature that causes a 50% decay of the studied characteristics in the very long term.

Like all the laboratory methods, the temperature index is an arbitrary measurement that must be interpreted and must constitute only one of the elements of judgement.

The UL Fire Rating

Described in detail in Section 2.12.4.2, the UL94 Fire Rating provides basic information on the material's ability to extinguish a flame, once ignited.

Smoke opacity is another increasingly important characteristic measured by optical density. Fire-retardant additives can be halogenated or halogen-free, which reduces the corrosivity, toxicity and pollution risks.

To progress in the household, entertainment & office appliance industry, thermoplastics must improve their performance characteristics, ease of processing, productivity and recycling, for example:

- better thermal resistance in the long term and better durability to favour miniaturization and long-term service without maintenance
- ease of processing: improved flow properties and processability leading to cycle time reductions and productivity gains
- better fire behaviour, lower smoke emission and more widespread use of halogen free grades
- low finishing costs: bulk colouring, an intelligent design and an effective maintenance of the moulds, dies and other tools reduce or avoid finishing operations, cutting the finishing costs
- recycling: more-effective solutions are sought.

Thermoplastics are predominant among the plastics used for the household, entertainment & office appliance industry with styrenics pre-eminent, including polystyrene, high-impact polystyrene, EPS, ABS, SAN, ASA . . . followed by PP. Several engineering thermoplastics such as PA, PC, PBT, PPO and POM are also used.

Figure 2.34 displays the market shares of the most commonly used commodity and engineering thermoplastics in the household, entertainment & office appliance industry. Among the engineering thermoplastics, PA, PC, PBT and POM are identified in statistics.

These average data hide dissimilarities according to different products (and countries), as we can see in Table 2.36.

The penetration of thermoplastics and thermoplastic composites ranges from the totality of the considered parts – for example, small household appliance housings and casings where metals are nearly ousted – down to areas where there are only a few applications, such as highly conductive polymers.

Let us quote some application examples for some thermoplastics. These examples can be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for a specific problem and test the right grade under real service life conditions.

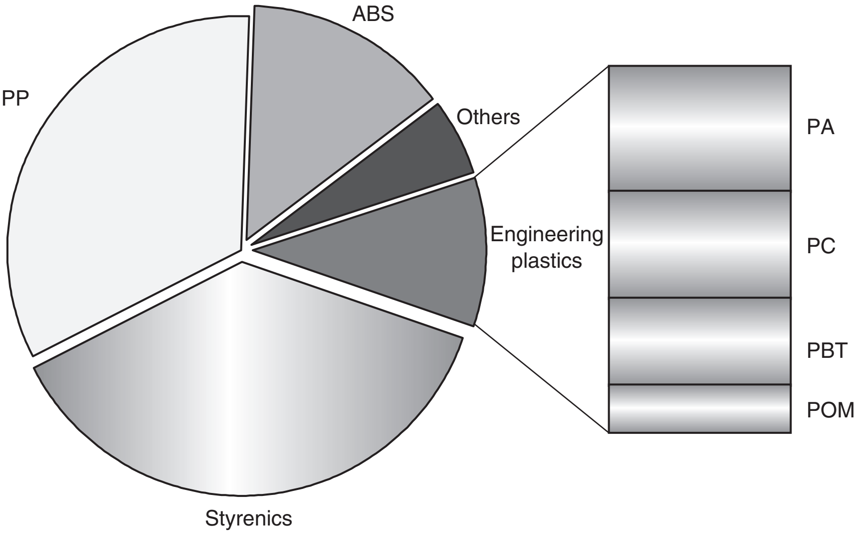


Figure 2.34. Thermoplastic shares in the household, entertainment & office appliance market

Table 2.36 Thermoplastic shares (%) for three different types of appliances

	Computers	TVs	Stereos
ABS	34	14	6
HIPS	10	73	28
PC/ABS alloys	29		
PPO	12	5	19
PC	5	8	12
Others	10		35
Total	100	100	100

Polyethylene

- General-purpose parts . . .

Polypropylene

- White goods, components for the 'wet side' of domestic washing machines, dryers and dishwashers; refrigerator parts, floor care and small appliances, house wares, kitchenware, good clarity parts, jug kettles; toaster and iron parts . . .

Polybutylene

- Blow-moulded tanks for electric domestic heaters . . .

PMP

- Small appliances, ovenware, kitchenware, microwave ovenware, tableware, cooking utensils, water tanks for coffee makers or electric irons . . .

COC

- Optical applications: storage media, CD, CD-ROM, DVD, SACD (super audio compact disc); lenses for cameras on mobile phones, digital cameras, compact cameras, CD-players, video recorders . . .

- Office automation equipment such as photocopiers, prisms, mirrors, polygon mirrors, optical films . . .

PVC

- Trims . . .
- Components in phone systems, power tools, refrigerators, washing machines, air conditioners, computers, keyboards, housings . . .
- Floppy Disk jackets . . .

Styrenics

- Air conditioners . . .
- Video and audio tape cassettes . . .
- TV components . . .
- Microfloppy diskettes . . .
- Refrigerator door linings . . .
- Small appliances, service ware, cutlery, tumblers and thin-wall multicavity parts . . .
- Splash shields . . .
- Knobs, buttons . . .
- Lighting diffusers . . .

EPS

- Insulation of refrigerators . . .

ABS

- Refrigerator door linings, refrigerator inner liners, trays . . .
- Domestic appliance housings, vacuum cleaners, small appliances, food mixers, electric shavers, electric toothbrushes . . .
- Electroplated parts, handles . . .
- Air conditioner housings . . .
- TV components and housings, video and audio tape cassettes . . .
- Telephone handsets . . .
- Lighting diffusers . . .
- Telecommunication equipment . . .
- Consumer electronic equipment . . .
- Power tool housings . . .
- Computer housings, transparent and translucent covers for PCs and copiers, keyboards, business machine equipment . . .

SAN

- Kitchenware such as mixing bowls and basins; small appliances, food mixers, coffee filters, outer casings of thermally insulated jugs . . .
- Tableware, drinking tumblers, cutlery, jars and beakers, storage containers for foods . . .
- Bathroom fittings, electric toothbrushes, toothbrush handles, sanitary ware, soap dispensers, shower cubicle, shelves . . .
- Dishwasher parts, washing machine trims . . .
- Radio dials, TV set screens, hi-fi covers . . .
- Refrigerator parts: trays, fittings, shelves . . .
- Cylindrical impellers for air conditioners . . .
- Outer covers of printers, calculators, instruments, transparent covers for PCs and copiers, business machine equipment . . .

- Telecommunication equipment . . .
- Consumer electronic equipment . . .

PA

- Electric household appliances: inlet and outlet cable channels, housings of power tools, projector casings, air resonators, washing machine pulleys . . .
- Antifriction parts: bearings, rods . . .
- Technical parts: gears, screws and bolts, pulleys, collars, valve casings, rings, clips, ventilators, cooling fans . . .

PA 11 or 12

- Electric household appliances: electrical cables, flexible telephone cables, inlet and outlet cable channels, connectors . . .
- Optical fibres . . .
- Housings of microscopes . . .

Aromatic PA

- Connectors for electronic and electrical devices such as personal computers, digital cameras and mobile telephones; safety switches, telecommunications parts . . .
- Use with lead-free solder especially in card connector applications for mobile telephones, PCs and smart media . . .
- Sliding parts in video recorders, disk supports in CD players . . .
- Domestic appliances . . .
- Electric razor heads, electric iron parts, vacuum cleaner motor supports, sewing machine parts . . .

Thermoplastic polyester

- Telecom & IT connectors, mobile phone casings, bobbins . . .
- Low voltage switch gear, electric-motor parts . . .
- Lighting and lamp fittings, lamp bases of energy saving lamps . . .
- Housings for the home appliance market . . .
- White goods connectors . . .
- Small appliances . . .

PMMA

- Transparent thermoformed products . . .
- Electrical engineering: lamp covers, switch parts, dials, control buttons, embedment of components . . .
- Optoelectronics: covering of displays from small LCDs in cellular phones up to large rear-projection television sets or screens designed for audio-visual presentations . . .
- Office equipment: writing and drawing instruments, telephone dials . . .
- Transparent technical parts: indicators, dials, inspection holes, caps, casings, hoods and electrical parts . . .

PC

- Optical media, computer and audio compact discs . . .
- Telecommunications, mobile phones, housings for GSM phones . . .
- Electrical chargers, battery boxes . . .
- Electric portable tool housings; computer and business machine parts . . .
- Transparent and decorative parts for vending machines, appliance panels, knobs and housings, housewares . . .

- Equipment housings . . .
- Power tools . . .

POM

- Control dials, pump and timer parts, valves, gears . . .
- TV tuner arms . . .
- Vapour pumps and distributors for domestic irons, shock-proof kettles . . .
- Parts of timers and slide projectors, housings of portable tools . . .
- General business machine parts, spring and screen parts . . .
- Coils, rewind rollers for radio and videocassettes, stereo cassette parts, tape decks . . .
- Precision parts for measurement and control technology . . .
- Heating appliance insulation . . .
- Telephone components . . .
- Housing parts, handles and knobs . . .
- Gears, sprocket wheels, gearwheels, cams, springs, clips . . .

PPE

- General business machine parts, brackets and structural components of office products, business machine chassis, frames & housings; large computer and printer housings (painted, foamed) . . .
- Internal appliance components, heating appliance insulation, insulators . . .
- Power tools, portable mixers, hairdryer housings . . .
- Coffee pots, drink vending machines and washing machine parts . . .
- Microwave components . . .
- Telecommunications frames and chassis, cell phone battery covers . . .
- TV backplates and deflection yokes . . .
- Structural and interior components . . .
- Foamed PPE: computers, business equipment, electrical/electronic appliances, telecommunications . . .
- Housing parts, handles and knobs . . .
- Frames, ventilating parts . . .
- Water purification equipment parts . . .
- Gears . . .

Perfluorinated thermoplastics (PTFE or TFE, PFA, FEP)

- Self-lubricating components . . .
- Bearings, bushings . . .
- Telecommunications . . .
- Wireless communications . . .

ETFE

- Battery components . . .

PCTFE

- Electroluminescent display panels . . .

Cellulosics

- Household appliance items . . .
- Door handles, curtain rings . . .
- Hairdressing items . . .

Polysulfone

- Frames of integrated circuits . . .
- TV components . . .
- Parts of alkaline batteries . . .
- Cartridges of printers . . .
- Parts for coffee machines, drinks dispensers, tubes, water tanks . . .
- Components for humidifiers, cookers . . .
- Port-holes . . .
- Components for cameras, projectors . . .

PPS

- Electrical appliance and PC brackets, components for floppy disk drives . . .
- Parts for heaters, parts of domestic irons, coffee machines, microwave ovens, cooking appliances . . .
- Hairdryer grilles and components, cutting head for electric shavers . . .
- Air outlet grilles for microscopes . . .

PEEK

- Laundry system wheels . . .
- Automatic espresso machines, high-tech coffee machines . . .

PEI

- Hot water reservoirs, heat exchange systems . . .
- Microwavable bowls, utensils . . .
- Computer components, mobile phone internal antennae . . .
- RF-duplexers or micro-filters, EMI shieldings . . .
- Lighting applications, reflectors, reflectors with dichroic coatings without primer . . .

PAI

- ESD for integrated circuits, hard disk drives, circuit boards . . .
- Parts for high-speed electronic printing and reproduction equipment . . .

PI

- Office automation components . . .
- Plate bearings for printers, cable guides for printer heads; bearings and sockets for photocopiers; sliding parts and guiding rollers for high-speed printers and photocopiers . . .
- Paper/print drum separation arms, drive wheels for photocopiers, drive rollers . . .
- Drive wheels for microwave ovens, handles for electric ovens and other household appliances, parts for spit-roasters, air vents for slide projectors . . .

LCP

- Sensors, LED housings . . .
- Imaging devices . . .
- Hard-disk drive components . . .
- Optical devices, optical lens components . . .
- Fibre optics components, fibre optics connectors . . .
- Dual oven cookware, ovenware . . .

TPS

- Gasketing . . .
- Workbench feet, end caps, appliance feet and pads . . .
- Handles, soft-touch overmoulding . . .

TPO

- Workbench feet, appliance feet, supports and pads . . .
- Handles, soft-touch overmoulding . . .

TPV

- Grips, handles for irons, flatware, vacuum cleaners, steam extractors, handheld vacuums and other floor care items, coloured utensil grips . . .
- Feet, pads for small appliances, dishwasher sump boots . . .
- Foamed seals for coolers, integrated seals . . .
- Bumpers or edge accessories for vacuum cleaners, steam extractors, handheld vacuum cleaners . . .
- Cord holders . . .
- Motor and vibration mounts . . .
- Wheel treads . . .
- Grips, handles, feet and pads for office supply, personal care, sports and leisure, tool and garden devices . . .
- Grips, buttons, bumpers, seals, feet, gaskets and spacers for computers, printers, copiers, scanners and fax machines, telecommunications, audio & video . . .
- Microphone boom on headset . . .
- Scroll wheel on Logitech mouse . . .
- Printer rollers . . .
- Scanner lids . . .
- Shockproof, water-resistant shields and other parts of webcams, cameras, personal digital assistants . . .

TPE/PVC

- Grips, handles, feet, pads for small appliances . . .
- Seals, integrated seals . . .
- Motor and vibration mounts . . .

TPU

- Moulded electrical accessories, electrical connectors . . .
- Gaskets and seals, hydraulic seals . . .
- Hoses and tubing, flexible tubing . . .
- Motor and vibration mounts . . .
- Drive belts . . .

COPE

- Moulded electrical accessories, electrical connectors . . .
- Low-noise gears, sprockets, caster wheels . . .
- Antenna covers . . .
- Keypads . . .
- Head phones . . .
- Liquid dispensers . . .

- Hoses and tubing, flexible tubing, hose jackets, convoluted tubing . . .
- Tool handles and grips for pliers, screwdrivers . . .
- Bearings, plugs, pads, feet, damping mounts . . .
- Roller coverings . . .
- Belting . . .
- Shock-proofing casings . . .

PEBA

- Wire & cable jacketing, electrical and communication cable jacketing, coil cables . . .
- Low-noise gears, sprockets, caster wheels . . .
- Liquid dispensers . . .
- Grips, pencil grips . . .
- Bearings, plugs, pads, feet, damping mounts . . .
- Photocopier, printer and telephone parts . . .
- Shock-proofing casings . . .

2.12.6 Mechanical engineering

The mechanical engineering sector is often omitted in statistics and its content is very unclear, overlapping other sectors such as electricity, appliances and so on. When it is identified, it is evaluated as accounting for from 2% up to 5% of overall thermoplastic consumption.

Technically the mechanical engineering market is truly heterogeneous, putting all the properties of all thermoplastics to good use. Applications are very diverse, covering:

- all types of functionalities
- a broad diversity of shapes and forms, from miniaturized to giant parts
- mechanical, optical, physical or chemical properties obtainable with either thermoplastics or thermoplastic composites.

Most mechanical engineering applications are produced in small or medium runs.

Several exceptional features explain the high level of thermoplastics and thermoplastic elastomers used for the mechanical engineering market:

- Technical motivations: using thermoplastics is favoured by:
  - ease and freedom of design allowing a broad integration of functionalities
  - ease of processing and assembly
  - impact resistance
  - low density and attractive performance/weight ratio leading to weight reduction
  - low or zero maintenance
  - non-rusting (but beware of ageing)
  - insulating properties
  - transparency
  - mechanical and acoustic damping
  - elasticity and sealing properties of TPEs and particularly TPVs
  - the replacement of conventional materials because of an exceptional combination of properties unattainable for metals, wood, ceramics and glass
  - adaptation to mass production and small series
  - weldability
  - cost cutting

  - the possibility to associate several thermoplastics to integrate several functionalities thanks to the exceptional combination of properties, for example, co-moulding a hard thermoplastic and a soft TPE.
- Aesthetics: thermoplastics allow:
  - much more design freedom than conventional insulating materials
  - decoration possibilities: transparency, bulk colouring, printability, paintability, in-mould decoration
  - pleasing finish.
- Economic features: thermoplastics provide:
  - an economical response to mass production
  - reduction of manufacturing times
  - reduction of finishing costs: plastics allow the integration of functions and, consequently, lead to reduction of assembly costs
  - higher productivity due to adapted processes, integration of functions, fewer processing steps . . .

Thermoplastics also have some general handicaps:

- high raw material cost (but attractive final cost)
- behaviour differs significantly from that of steel
- susceptibility to fire of organic polymers
- recycling bringing some particular problems due to economic conditions, polymer modifications and reinforcements.

To progress in the mechanical engineering industry, plastics must improve their performance characteristics, ease of processing, productivity and recycling, for example:

- better mechanical performances
- better thermal resistance in the long term and better durability to favour long-term service without maintenance
- ease of processing: improved flow properties and processability leading to cycle time reductions and productivity gains
- better fire behaviour, lower smoke emission and more widespread use of halogen-free grades
- low finishing costs: bulk colouring, an intelligent design and an effective maintenance of the moulds, dies and other tools reduce or avoid finishing operations, cutting the finishing costs
- recycling: more-effective solutions are sought.

Let us quote some mechanical engineering application examples for some thermoplastics. These examples can be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for a specific problem and test the right grade under real service life conditions.

Polyethylene

- Large-sized objects, tanks, cisterns: hydraulic tanks, septic tanks, chemical tanks . . .
- Chemical pipes . . .
- Crosslinked foams, extruded and moulded parts . . .
- UHMWPE: gears, bearings, antifriction parts for light loads . . .

PE foam

- Machine soundproofing . . .
- Impact and vibration damping . . .

Polypropylene

- Casings, caps, framework of ventilation, fan blades, air filters, filters and pumps of industrial dishwashers, softeners, washing machines, detergent product vats, parts of pumps used for handling chemicals, frames, rollers of cables, parts with film hinge, electrical components, translucent parts, cases, pipes . . .

PP foam

- Damping and protection; air, water and dust proofing, thermal insulation, soundproofing for industrial machinery . . .
- Reusable packaging or shuttle packaging for heavy parts such as doors, windscreens, rear mirrors . . .
- Damping blocks, intermediate layers . . .

PMP

- Trays for chemical treatments, floating balls for chemical bath insulation . . .
- Films for industrial applications . . .

COC

- Transparent mouldings, sensors . . .

EVA

- Tyres (light uses), kneepads, insulation, ring seals, protective caps, clips, cable binders, lids, all kinds of closures, bellows, rail pads, O-rings, soundproofing . . .
- Glues . . .
- Foams . . .

EMA

- Tool handles, screwdriver handles . . .

CPE

- Extruded profiles: gasketing, tubing . . .
- Moulded shapes: pipe fittings . . .
- Hoses for chemical transfer and storage . . .

PVC

- Pipes, parts, containers for contact with chemicals . . .
- Padding . . .
- Coated metal racks and shelving . . .
- Protective strips, trims . . .
- Anti-abrasion coating . . .

PVC foam

- Machine soundproofing . . .
- Impact and vibration damping . . .
- Insulation of tanks, pipes . . .
- Scale models . . .

PVC-C

- Components for cooling towers, laboratory sinks, pumps . . .
- Pipes for paper and surface treatment sectors, electroplating plants, photographic, semiconductor and chemical industries . . .

PS

- Handles . . .
- Tubing for corrosive liquids . . .
- Tank covers . . .
- Insulators, cable separators . . .
- Lenses . . .
- Studs, heels . . .
- Sign panels . . .

EPS

- Heat insulation, soundproofing . . .
- Models and mock-ups . . .
- Advertising elements . . .

ABS

- Tubing, pipes and fittings for aggressive environments and corrosive liquids . . .
- Insulators . . .
- Housings . . .
- Handles . . .
- Enclosures.

SAN

- Outer covers for instruments, machines and lamps . . .
- Lenses . . .
- Handles . . .

PA

- Antifriction parts: bearings, rods . . .
- Gears, screws and bolts, pulleys, collars, valve casings, rings, clips, ventilators, cooling fans, tanks and containers . . .

PA 11 or 12

- Anticorrosion, protection: offshore drilling, offshore oil & gas production and test lines, gas & water injection lines, gas lift lines, pipes, fittings, valves, lined pipes; powdering within the health care equipment, oil industry; internal coating in new and refurbished injection tubing, production tubing and flow lines; production risers, choke & kill lines, nitrogen lines, hydraulic lines; buried gas pipelines; co-extruded pipes with MDPE and HDPE to increase their performances; dirty water and effluent pipes used in aggressive environments . . .
- Antifriction parts: bearings, rods . . .
- Pneumatic and hydraulic hoses; petrochemical, fuel handling and hydraulic applications; gears, collars, valve casings, rings, clips . . .
- Powdering . . .

Aromatic PA

- Systems for glass production . . .
- Filter technology . . .
- Machine tools . . .
- Leisure industry applications . . .

Thermoplastic polyester

- Housings for airflow mass meter, connectors, gears, meters and sensors . . .
- Vacuum nozzles . . .
- Valve bodies . . .
- Motor parts . . .
- Lighting and lamp fittings . . .
- Textile bobbins . . .

PMMA

- Transparent technical and decorative parts for lights, instrument panels, dials, indicators, tachometer covers, inspection holes, peepholes, portholes, domes, panes, caps, casings, hoods and electrical parts . . .
- Nameplates, medallions . . .
- Signs: internally illuminated outdoor signs, indoor and outdoor signs, diffusers, side-lit signs, very thin illuminated displays, fluorescent signs . . .
- Glazing applications, shatter-resistant glazing and protective glazing, windows and skylights, sight glasses, sight gauges . . .
- Acoustic screens . . .
- Transparent pipelines, moulds, models, gauges, product prototypes, demonstration models . . .
- Cast and extruded sheets, cell-cast sheets, stretched sheets, films down to 50 microns used in protection, communications . . .

PC

- Protective glazing, vandal-proof windows, shatter-resistant glazing, windows and skylights, sight glasses, sight gauges, portholes, high temperature and pressure windows, portholes in pressure chambers . . .
- Films for technical uses: keyboards, instrument panels, control boards, insulating layers and cards . . .
- Light globes, lighting diffusers, light-control lenses, outdoor lighting fixtures . . .
- Photography, camera lenses, binoculars, magnifying glasses . . .
- Transparent technical parts: indicators, dials, inspection holes, peepholes, domes, panes, caps, casings, hoods and electrical parts . . .
- Transparent and decorative parts for vending machines, machinery panels, knobs and housings, housewares . . .
- Equipment housings . . .
- Brackets, structural parts, covers, handles, rollers, machine guards, fittings . . .
- Power tools . . .
- Jet pump impellers and diffusers . . .
- Face shields, safety helmets . . .
- Static dissipative grades: covers, guards, access panels, machine windows and doors, static control shields, glove boxes, electronic equipment, process instrumentation, conveyor line covers, clean room windows and doors, partitions and pass through modules . . .

POM

- Rollers, bearings, bushings, conveyor plates, wear pads . . .
- Timing screws . . .

- Washers . . .
- Housing parts, handles and knobs . . .
- Couplings, pump impellers . . .
- Gears, sprocket wheels, gearwheels, cams, springs . . .
- Small pressure vessels, coil formers . . .
- Nuclear engineering components, gears, cams . . .
- Packaging machinery star wheels . . .
- Poultry processing parts, valve stems, food conveyors . . .
- Clips, lugs, conveyor components . . .
- Aerosol components, aerosol valves and heads . . .
- Sound-damping mountings . . .
- Ball cocks, faucets, faucet cartridges, faucet underbodies, valve stems . . .
- Irrigation equipment and valves . . .
- Pump and filter housings, milk pump impellers, plumbing systems . . .
- Fittings, hinges, shower heads . . . .
- Coffee spigots . . .
- Antifriction parts, bearings, bushings, rods, zippers . . .

PPE

- Housing parts, handles and knobs . . .
- Machine housings, pump and filter housings, impellers, fluid and material handling components, water pump housings and impellers in machinery and engineering, impellers, plumbing systems . . .
- Frames, ventilating parts . . .
- Water purification equipment parts . . . .
- Gears . . .
- Plastic parts in central heating systems . . .

Perfluorinated thermoplastics (PTFE or TFE, PFA, FEP)

- Washers, flanges, baffles . . .
- Gaskets, seals, rings, O rings, D rings, U seals, V seals, cup seals . . .
- Encapsulated O-ring and other parts, lined products . . .
- Self-lubricating components, bearings, bushings . . .
- Lantern rings for pumps, bellow-type seals for centrifugal pumps; hydraulic, pneumatic, earthmoving equipment; cylinder valves for O_2, CO_2, refined gases, chlorine, ammonia . . .
- Bellows for glass columns, glass valves, pipelines . . .
- Valve and pump components, balls for non-return valves . . .
- PTFE/woven-glass composites . . .
- Assemblies for piping systems, sprinklers, mixers . . .
- Heavy wall tubing; plain, coloured, striped tubing fabrications for instrumentation; automotive push-pull cables; industrial and process hydraulics and other fluids . . .
- Piping liners for glass-lined reactors, stainless steel reactors, glass equipment and mixers . . .
- Membranes, filter media, filter bags, cartridges, microfiltration membranes, vents and adsorbent products . . .

ETFE

- Linings of components used in chemical processing, sleeves . . .
- Pump housings, compressor linings and components . . .

- Extruded tubing, pipes, hoses, fittings, fluid handling, profiles . . .
- Injection- and blow-moulded articles . . .
- Containers, vessels, process vessels, tank construction and linings, columns, elbows, tees . . .
- Fasteners . . .
- Instrument components . . .
- Cryogenic applications, super-cold refrigeration components . . .
- Valves, seats, seals, gaskets, diaphragms, liquid gauge seals . . .
- Bearings, thrusts . . .
- Heat-shrinkable films, oriented films . . .

PCTFE

- Cryogenic applications, super-cold refrigeration components . . .
- Valves, seats, seals, gaskets, diaphragms . . .
- Bearings, thrusts . . .
- Pipes . . .

ECTFE

- Linings of components used in chemical processing, sleeves . . .
- Pump housings, compressor linings and components . . .
- Extruded tubing, pipes, hoses, fittings, fluid handling, profiles . . .
- Injection- and blow-moulded articles . . .
- Containers, vessels, process vessels, tank construction and linings, columns . . .
- Cryogenic applications, super-cold refrigeration components . . .
- Valves, seats, seals, gaskets, diaphragms . . .
- Bearings, thrusts . . .

PVDF

- Linings of components used in chemical processing, pump housings, compressor linings and components . . .
- Extruded tubing, pipes, hoses, fittings, fluid handling, profiles . . .
- Injection- and blow-moulded articles . . .
- Containers, vessels, process vessels, tank construction and linings, columns, elbows, tees . . .
- Fasteners . . .
- Instrument components . . .
- Valves, seats, seals, gaskets, diaphragms, liquid gauge seals . . .
- Cocks . . .
- Bearings, thrusts . . .
- Fibres, screens . . .

PVF

- Weather-resistant film for glazing panels, glazing for solar panels . . .
- UV screening films, surface covering for PVC film, surface protection of signs . . .
- Gas sampling bags . . .
- Label materials for harsh environments . . .

Cellulosics

- Trims . . .
- Diffusers, luminaries . . .

- Hand tools, screwdriver handles, buttons, handles, hammer heads . . .
- Metallized parts, vacuum metallized parts, reflectors . . .

Polysulfone

- Fluid handling, coupling and fitting applications . . .
- Manifolds, distributor valves . . .
- Lighting fixtures, portholes . . .
- Chemical process equipment, semiconductor process equipment components . . .
- Plumbing fixtures, faucet components . . .
- ESD trays . . .

PPS

- Thrusters of pumps, hot water pumps . . .
- Bearings (PTFE lubricated) . . .
- Precision parts for mechanical and regulation components . . .
- Sterilizable laboratory equipment . . .
- Hairdryer grilles and components, cutting heads for electric shavers . . .
- Air outlet grilles for microscopes . . .

PEEK

- Impeller wheels for regenerative pumps, pump rotors, laundry system wheels, submersible pump insulation, dry transformer insulation . . .
- Glue-gun bushings . . .
- Quick coupling systems . . .
- Conductivity sensors . . .
- Seals, compressor valve plates . . .
- Heat exchanger parts, flexible surface heaters . . .
- Gaskets, oil field pipe flanges and gaskets . . .
- High-temperature labels . . .

PEI

- Water-pump impellers, expansion valves . . .
- Hot water reservoirs, heat exchange systems . . .
- Fire helmets . . .
- Tableware and catering, reusable food service, food trays, soup mugs, steam insert pans or gastronome containers, cloches, microwavable bowls, utensils, ovenware, cooking utensils and re-usable airline casseroles . . .
- Filaments for fire-resistant padding . . .

PAI

- Non-lubricated bearings, seals, bearing cages, rotating and sliding components, bushings, seal rings, wear pads, piston rings, hook joints for transmission seal rings . . .
- Tag axle assembly of cement trucks and heavy vehicles . . .
- Vanes in air motor . . .
- Reciprocating compressor parts . . .
- Gears, valve plates, intake valves . . .
- Impellers, rotors . . .
- Material handling components . . .
- Terminal strips . . .

- Ceramic coated piston for 5-HP engine . . .
- Insulators . . .
- Fibres for heat and fire protection, clothing for fighter pilots, army and police forces; smoke filtration . . .

PI

- Paper for fire-resistant uses . . .
- Brakes on textile winding-machine, pump pads, joint seatings, manipulator inserts for glass bottle demoulding, gears of variable speed transmissions, toothed wheels . . .
- Piston rings of ethylene compressors, dry bearings, sliding plates, guides for cast solid films in self-lubricated PI . . .
- Guiding rollers of grinder bands, sealing discs of valves in an industrial Freon compressor, segments of air compressors . . .
- Racks and handling cases for PCB treatment . . .
- Valve seats, piston rings for hydraulic installations for the chemical industry, seals and other parts for high-vacuum installations usable up to 300°C without lubrication . . .
- Cryogenic insulation in PI foams . . .
- Joints and linings for vacuum pumps . . .

LCP

- Chip carriers . . .
- Sensors . . .
- High-performance motor components, transmission system components, pump components . . .
- Guides . . .
- Components for fuel handling, fuel or gas barrier structures . . .
- Sterilizable trays and equipment . . .
- Miniature gears . . .

PBI

- High heat bushings, valve seats, ball valve seats, contact seals, insulator bushings . . .
- Thermal isolators, high heat insulator bushings for hot runner plastic injection moulds . . .
- Guide rollers . . .
- Semiconductor industry, vacuum chamber applications; clamp rings for gas plasma etching equipment, wafer retaining rings for gas plasma etching, wafer carriers, vacuum tips . . .

TPS

- General-purpose boots and bellows . . .
- General-purpose gasketing, seals . . .
- Workbench feet, end caps, feet and pads for light loads . . .
- Impermeable liners, protective sheets . . .

TPO

- Workbench feet, appliance feet, supports and pads . . .
- Handles, soft-touch overmoulding . . .
- General-purpose profiles, tubes, pipes, sheathing . . .

TPV

- Boots and bellows . . .
- Grips, handles, feet, pads . . .

- Foamed seals, integrated seals . . .
- Bumpers or edge accessories, cord holders . . .
- Vibration mounts . . .
- Wheel treads . . .
- Tubing . . .
- Industrial sheet goods . . .
- Coated fabrics . . .
- Pipe seals . . .
- Caster wheels . . .

TPV PP/NBR-V

- Boots and bellows for oil contact . . .
- Seals for oil filters; seals, tubes, pipes, profiles for oil contact . . .
- Mounts for damping noise and vibration, shock absorbers . . .

TPV PP/IIR-V

- Goods with low permeability to moisture, air and oxygen for butyl rubber replacement . . .

TPE/PVC

- General-purpose boots and bellows . . .
- Trims . . .
- Tubes . . .
- Glazing . . .
- Grips, handles, overmoulding . . .
- Feet, pads, mounts . . .
- Seals, integrated seals, window encapsulations . . .
- Shock-proofing casings . . .

TPU

- Gaskets and seals, hydraulic seals . . .
- Hoses and tubing, hydraulic hoses, fire hose liners, flexible tubing . . .
- Films and sheets . . .
- Motor and vibration mounts . . .
- Caster wheels . . .
- Drive belts . . .
- Conveyor belts, food processing equipment, mining screens . . .
- Protective clothing, weatherproof clothing . . .
- Shock-proofing casings . . .
- Magnetic media . . .

MPR

- Damping mounts for noise and vibration . . .
- Seals . . .
- Coated fabrics, films and sheets . . .
- Soft handles and grips . . .

COPE

- Seals, gaskets, packing . . .
- Hoses and tubing, flexible tubing, hose jackets, convoluted tubing, hydraulic hoses, pneumatic tubing . . .

- Tool handles and grips for pliers, screwdrivers . . .
- Profiles . . .
- Gears, sprockets, caster wheels . . .
- Bearings, plugs, pads, feet, damping mounts . . .
- Fuel tanks, oil field parts . . .
- Films, sheets, thin and flexible membranes, diaphragms . . .
- Roller covering . . .
- Belting . . .
- Shock-proofing casings . . .
- Handcuff holders . . .
- Railway pads . . .

PEBA

- Hoses and tubing, flexible tubing, hose jackets, convoluted tubing, hydraulic hoses, pneumatic tubing . . .
- Profiles . . .
- Gears, sprockets, caster wheels, low-noise gear wheels . . .
- Bearings, plugs, pads, feet, damping mounts . . .
- Films, sheets, thin and flexible membranes, diaphragms . . .
- Belting, conveyor belts . . .
- Shock-proofing casings . . .

2.12.7 Sports and leisure

The sports and leisure market consumes approximately 2% of all thermoplastics. It is sensitive to the economic situation, weather conditions and the phenomenon of fashion, and appears increasingly competitive. Nevertheless, the crises of growth that the sports industry encounters do not seem to weigh on the penetration of thermoplastics in this sector. The market analysis, however, emphasizes significant disparities of consumption according to the type of activity:

- football, rugby, basketball, tennis, golf, badminton: clothes, shoes, balls, protection, possibly flooring . . .
- diving: flippers, tubes, masks, wet suits . . .
- aquatic sports and sailing, sailing boards, dinghies, inflatable beach articles, paragliding: equipment, clothes, protection, footwear, boards of all kinds, paddles, hulls of canoes, helmets . . .
- hiking, cycling, mountain biking, horse riding, climbing: accessories, equipment, clothes, shoes and boots, protection . . .
- winter sports, ski, snowboard, toboggan: equipment, accessories, shoes, protection
- gymnastics, fitness: accessories, equipment, protection . . .

The broad range of applications shows that the thermoplastics are appreciated for general properties such as lightness, impact resistance, aesthetics, final cost and ease of processing, and for very versatile characteristics according to the grades or families, such as flexibility or rigidity, damping or elasticity, high friction or easy slip, and transparency. With the appearance of a broad choice of colours, fashion supports the use of thermoplastics of intense, well-defined and varied colours.

Winter sports represent a significant share of the sports and leisure market where the majority of commodity and engineering thermoplastics are used.

Let us quote some application examples for some thermoplastics in this sector. These examples can be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade under real service life conditions.

Polyethylene

- Hulls of boats, canoes, buoys, sailboards, fun boards . . .
- Luges, ski pads . . .
- Beach shoes . . .
- Swimming pool covers . . .
- Toys . . .

PE foam

- Life jackets, life suits . . .
- Safety padding . . .
- Buoys . . .
- Gym mats, padding, damping and insulating mats . . .
- Stuffing of rucksack in foam-coated textile . . .
- Toys: 2D and 3D puzzles, floating toys . . .

Polypropylene

- Rigid shells of snow boots . . .
- Floats of boards . . .
- Luggage, suitcases, vanity cases . . .
- Lawn furniture, lawn products, garden furniture, garden tools . . .
- Toys . . .

PP foam

- Padding of helmets and seats for babies and children . . .
- Safety padding . . .

EVA

- Swimming pool hoses . . .
- Injected parts: transparent, filled to a greater or lesser degree, possibly crosslinked and/or foamed in microcellular form for tyres (light uses), kneepads, footwear, soles, sports and technical items, buoys, flexible toys, protective caps . . .

EMA

- Footwear components: thermoformed shoe inserts, football boot soles, protective pads for shoes and boots . . .
- Sporting goods, scratch-resistant golf balls, skittle and bowling pin covers, ski boots . . .

PVC

- Garden hoses . . .
- Toys, dolls, fishing lures, fancy goods . . .
- Flooring for badminton and other specialized courts/playrooms . . .
- Inflatable covers, structures and devices . . .
- Shoe soles . . .
- Coated fabrics for clothing, leather working, opaque curtains, tarpaulins . . .
- Films and sheets for adhesive tapes, translucent curtains, school and office stationery . . .
- Upholstery, covering, padding . . .

PVC foam

- Life jackets, life suits.
- Safety padding.
- Buoys.
- Gym mats, safety padding, damping and insulating mats . . .
- Protective devices for various sports such as hockey, basketball, soccer, boxing . . .
- Padding of helmets and seats for babies and children . . .

PS

- Lenses . . .
- Studs, heels . . .

EPS

- Cores of sea sailboards, surfboards or beach boards with GFRP skins . . .
- Buoys and lifejackets . . .
- Puzzles . . .

ABS

- Fuselage of recreational plane . . .
- Recreational vehicles, boats . . .
- Shells of helmets . . .

SAN

- Writing and drawing equipment . . .

PA

- Wheels, saddle stems, crank gears for bicycles . . .
- Ski boots . . .
- Roller skates, toys . . .
- Snowmobile bumpers . . .
- Hovercraft propellers . . .
- Grass and leaf blower parts and housings . . .
- Filaments for fishing . . .

PA 11 or 12

- Ski boots, toys, snowmobile parts . . .
- Leisure industry applications . . .

PMMA

- Optical components for sunglasses, watch glasses, lenses, magnifying glasses, camera lenses . . .
- Glazing applications, shatter-resistant glazing for aircraft, boats, protective glazing . . .
- Transparent thermoformed products . . .
- Writing and drawing instruments . . .
- Piano keys . . .
- Arts and fashion: embedment of items, sculptures, decorative inclusions, jewels, knick-knacks . . .
- Toys . . .
- Films laminated on ABS, PVC or other plastic sheets that are thermoformed into parts requiring resistance to outdoor weathering: motorcycle shrouds, recreational vehicle panels . . .

- Deeply formed components subsequently backed with glass fibre reinforced polyester: camper tops, furniture and recreational vehicle bodies.

PC

- Architectural glazing, roofs of verandas, stadiums; aircraft, boat, mass transit glazing . . .
- Aesthetic applications . . .
- Face shields, safety helmets . . .
- Garden equipment . . .
- Furniture, office & institutional furniture . . .
- Protective films for boards and sailing boards . . .

POM

- Clock and watch parts, watch gears . . .
- Quality toys . . .
- Mechanical pen and pencil parts . . .
- Garden sprayers . . .
- Ski bindings, shoe components, sole plates for golf shoes . . .

PVDF

- Weathering protection for other thermoplastics and metals . . .

Cellulosics

- Pen/stationery supplies, pen barrels, writing instruments, squares . . .
- Recreational parts . . .
- Costume jewellery . . .
- Toys and sporting goods . . .

PAI

- Ball bearings for America's Cup yachts . . .

PI

- Non-flammable scenery, coloured-filter holders for studios and theatres . . .

LCP

- Miniature gears for watches . . .

TPS

- Workbench feet, end caps, appliance feet and pads . . .
- Impermeable liners, protective sheets . . .
- Shoe soles . . .
- Toys . . .

TPO

- Workbench feet, appliance feet, supports and pads . . .
- Handles, soft-touch overmoulding . . .
- Toys . . .

TPV

- Grips, buttons, bumpers, seals, feet, gaskets . . .
- Shockproof, water-resistant shields . . .
- PP/IIR-V: consumer goods requiring low permeability to moisture, air and oxygen, competing with butyl rubber: for example, inner tubes for bikes, bladders for balloons . . .

TPE/PVC

- Grips, handles, overmoulding . . .
- Feet, pads, mounts . . .
- Seals, integrated seals . . .
- Shoe soles . . .
- Leather-like goods . . .
- Toys . . .
- Shock-proofing casings . . .

TPU

- In-line skates . . .
- Ski boots, sports shoe soles . . .
- Swim fins . . .
- Goggles . . .
- Gaskets and seals . . .
- Inflatable rafts . . .
- Life vests . . .
- Weatherproof clothing . . .
- Shock-proofing casings . . .
- Toys . . .
- Magnetic media . . .

MPR

- Injection- and blow-moulded parts, seals and gaskets resisting oils, handles of motorbikes, cable guides . . .
- Damping mounts for noise and vibration . . .
- Toys, tyres for scale models . . .
- Soft handles and grips . . .

COPE

- Sunglasses: bridges for lenses, rear frames and arms, goggles . . .
- Headphones . . .
- Suitcase handles . . .
- Grips, pencil grips . . .
- Front straps for ski boots . . .
- Snowboard cover laminates . . .
- Shoe binding system components, tensioner ski binding . . .
- Soling . . .
- Caterpillars for snowmobiles . . .
- Shock-proofing casings . . .

PEBA

- Goggles, glass frames . . .
- Soling, outsoles for American football, soccer, rugby, baseball footwear . . .
- Snowshoe deckings, athletics shoes and equipment . . .
- Sport balls, golf balls . . .
- Ski parts, ski boots components . . .
- Athletic footwear components . . .

- Damping systems, vibration and shock absorption in sports equipment, damping of tennis rackets . . .
- Grips, pencil grips . . .
- Shock-proofing casings . . .

2.12.8 Medical market

The medical market consumes roughly 2% of all thermoplastics. It is subjected to the same requirements as the whole of the health industry: evolution of health services, compliance with specific standards and regulations, more rigorous cost controls, ageing of the population, increased resistance of pathogenic agents. The globalization of the medical industry offers new opportunities and challenges to the plastic suppliers. To reduce costs and to improve their competitiveness, manufacturers of medical materials work in partnership with producers to examine, among other things, the possibilities to improve the products, materials, equipment and design methods.

Table 2.37 points out some interesting properties for the medical applications of commodity thermoplastics.

Table 2.37 Interesting properties for the most-common medical applications

	PVC	EVA	PE, PP	PET
Steam sterilization	+	−	+/−	+
Gamma-ray sterilization	+	+	+/−	+
Flexibility	+	+/−	−	−
Transparency	+	+	+/−	+
Welding by HF	+	+	−	−
Printability	+	+	−	−
Practical experience of use	+	+/−	+	+/−

Thermoplastics are found in very diverse products, some being specific to medical applications, others being general-purpose parts and components as for other machinery or electric devices. Let us mention for example:

- flexible tubing for solutions
- pouches for blood and various liquids
- permeable membranes
- implants, prostheses
- pharmaceutical packaging: blisters, tubes, boxes . . .
- bottles, tanks, bulbs
- films, shrinkable films, gloves
- transdermal patches
- semi-rigid connectors
- various parts and plastic components, machine housings . . .

An example of the possibilities for plastics to respond to a specific problem is the replacement of almost 100% of the stoppers, capsules, joints and other closure systems used for pharmaceutical products. The replacement of glass is the most-significant opportunity for the development of thermoplastics but new possibilities could appear in medical self-care systems and blood sample tubes. A 50–70% increase in the use of plastics should come from existing mass-produced and low-cost products. Let us quote, for example:

- PVC for tubes and pouches for blood, but PVC is handicapped by environmental regulations and trends

- polypropylene for pharmaceutical and medical packaging
- polystyrene for tubes and other test and laboratory equipment
- thermoplastic polyester for bacteriology equipment
- polyethylene foam for the waterproof layers of sanitary towels and nappies
- gloves and general-purpose films.

It has taken the surgery sector a long time to adopt plastic products. Engineering thermoplastics with high impact resistance, UHMWPE and some fibre-reinforced grades are starting to be used in applications where conventional materials are predominant, for example, implants, the instruments used to insert suture clips, and the casings of apparatus of paramount importance. Thus, UHMWPE is used for internal prostheses and a blood pump used during open-heart operations includes several plastic parts – polycarbonate for the pump barrel and polypropylene for the permeable membranes.

One factor in the reduction of healthcare expenditure is home medical care, which involves adaptations of the methods of care. These uses dictate particular requirements for sterility, safety, reliability, weight and facility of use. Plastics can bring solutions in the fields of single-use products, unbreakable equipment and weight reduction, for example, in the syringes, tubes and pumps for drug injections and apparatus for ambulatory dialysis.

The launch of new resins being rare, progress on materials intended for medical applications is by way of formulation, alloys and modifications of existing resins. Thus, new radiation-stable polypropylene grades are available for the manufacture of cups, boxes, baskets, mixers, etc. that are radiation sterilized. And polyesters with better environmental stress cracking resistance are extending their potential in the area of medical testing.

In less-specialized areas:

- Films of polyester for blisters and containers can be thinner without harming the integrity of the packed products.
- Co-extruded films of polypropylene or other polyolefins and a flexible polyester are solutions for pouches for intravenous drug-delivery systems.
- Medical equipment and its packaging are undergoing significant evolution with regard to their design, which is being re-examined to reinforce the advantages of plastics:
  - ○ economical production of structures with thin walls and reinforcement ribs – these measures have, moreover, the advantage of reducing the weight of waste to be eliminated after use
  - ○ function integration – the elimination of a part brings significant economies by the reduction of tooling and assembly steps.
- Processing is also evolving to contribute to cost and waste savings without heavy investments:
  - ○ multiplication of the number of cavities in a mould
  - ○ improvement of mould cooling
  - ○ reduction of cycle times
  - ○ better control of processes by statistical processing of recorded parameters (SPC).
- The use of recycled materials, confined to parts without contact with medical components, is possible thanks to co-injection or co-extrusion.

Plastics also make it possible to re-examine the policy of medical wastes. The incineration of plastics, provided these resins are incinerated with negligible impact on the environment, poses fewer problems than the incineration of glass, which leaves significant residues.

The re-use or otherwise of equipment is the subject of controversy because of the risks of contamination. Re-use limited to the treatment of only one patient is a solution under consideration. The economic advantages of this procedure are accompanied by a reduction in final waste. For its application, it is necessary to use thermoplastics with sufficiently high performance to withstand several sterilizations and uses. The polyetherimides, LCPs, PEEKs and polysulfones could be appropriate. The use of biodegradable thermoplastics is under evaluation.

TPEs have lower consumption in medical applications in Europe (2% of their overall consumption) compared to the USA (12%), where they progress more quickly at the rate of 12% per annum.

In addition to the functional tests common to any application, the TPEs that are proposed for medical applications must satisfy certain specific tests of biocompatibility and aptitude for sterilization.

Table 2.38 summarizes the significant properties of the TPEs for medical or food uses. These results are very general and have an indicative value only. The designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade under real service life conditions.

Table 2.38 Significant properties of TPEs for medical or food uses

	Toxicity	Resistance	
		Hydrolysis	Solvents
Styrenics	Good	Good	Medium
Alloys	Good	Good	Good
TPU (ether)	Good	Good	Medium
COPE	Good	Medium/good	
PEBA	Good	Good	Medium
	Sterilization behaviour		
	Steam at 121°C	Steam at 131°C	Irradiation
Styrenics	Weak	Weak	Fair
Alloys	Good	Fair	Fair
TPU (ether)	Good	Good	Fair
COPE	Good	Good	Fair
PEBA	Good	Good	Fair

The main driving forces in favour of TPEs are:

- ease of processing
- design freedom
- purity of suitable grades; to pass the compatibility or toxicity tests, the TPEs do not generally need to be washed
- the cost of the function.

Let us quote some application examples for some thermoplastics. These examples can be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade under real service life conditions.

Polyethylene

- Films and sheets . . .
- Blow-moulded containers, bottles for drugs . . .
- UHMWPE for prostheses . . .

PE foam

- Electrode pads for electrocardiogram testers.
- Waterproofing layers for sanitary towels and disposable nappies.

Polypropylene

- Nonwovens . . .
- Blow-moulded and sheet-thermoformed products for personal care, health, medical and labware applications . . .
- Medical disposable trays, containers for irrigation, parenteral, haemodialysis solutions . . .
- High-clarity parts for medical and food applications . . .

Films

- Oriented, bi-oriented and cast films and foils for medical packaging . . .
- Clean polypropylene for packaging and casting cup applications, hospital disposables and other bedside applications, safety syringes, pre-filled syringes, general-purpose syringes; autoclave- or radiation-sterilizable parts in the presence of aqueous solutions; vials and bottles; contact lens casting cups and packaging . . .
- Laboratory wares, blood and centrifuge tubes, test tubes, beakers and pipette tips . . .

PMP

- Cells for blood tests, syringes, centrifugation tubes, needle hubs, transparent tubes and tubing connectors, nebulizer parts, urine samplers . . .
- Laboratory ware: trays for chemical treatments, animal cages . . .
- Transparent tubes and pipes . . .

COC

- Medical, laboratory and care applications: transparent pre-filled syringes, pharmaceutical containers and packages, primary packaging of pharmaceuticals, medical devices, diagnostic disposables, laboratory ware . . .

PVC: the medical sector consumes 4% of all PVC

- Fluid bags and containers for blood, plasma, intravenous solutions, urine incontinence . . .
- Blood vessels for artificial kidneys, heart and lung bypass sets . . .
- Tubing, catheters, cannulas, endotracheal tubing, feeding and pressure monitoring tubing . . .
- Artificial skin for emergency burns treatment . . .
- Drip chamber components . . .
- Inflatable splints, prosthetics . . .
- Surgical and examination gloves, inhalation masks, overshoes, protective sheeting and tailored covers, mattress and bedding covers, anti-bump protection bars . . .
- Blisters and dosage packs for pharmaceuticals and medicines, single-dose medication packaging, shatter-proof bottles and jars . . .

PVDC

- Barrier films for food, pharmaceuticals, chemicals . . .

PS

- Medical and laboratory parts . . .
- Lenses . . .

Aromatic PA

- Glass production . . .
- Medical technology . . .

PMMA

- Optical components, sunglasses, lenses, magnifying glasses . . .
- Packaging for tablets, pills, capsules, suppositories, urine containers, sterilizable equipment . . .
- Implants . . .
- Hip prostheses . . .
- Percutaneous polymethylmethacrylate vertebroplasty . . .
- Intraocular lenses . . .
- Membranes for continuous haemodiafiltration . . .
- Composite cements for orthopaedic surgery . . .
- Polymethacrylimide (PMI) rigid foams as core material for composites used for X-ray tables . . .

PC

- Glazing . . .
- Sunglasses, magnifying glasses, lenses, lenses for eyeglasses . . .
- Dialysis equipment parts, compact heart-lung systems . . .
- Medical tubing . . .
- Gamma-ray sterilizable reusables . . .
- Instrument covers, handles, machine guards, fittings . . .

Perfluorinated thermoplastics (PTFE or TFE, PFA, FEP)

- Synthetic blood vessels and patches for soft tissue regeneration; surgical sutures for use in vascular, cardiac, general surgery and orthopaedic procedures . . .
- Knitted, woven, braided or sewn fibres: compression packing, sewing thread, membranes, filter media, filter bags, cartridges, microfiltration membranes, vents and adsorbent products . . .

CTFE

- Syringes, sterilizable packaging; membranes, tubes . . .
- Oxygen tents . . .
- Prosthesis . . .
- Pharmaceutical packaging . . .
- Pouches for gas sampling . . .

Cellulosics

- Packaging, containers for healthcare, cosmetics, perfumery and personal care supplies . . .
- Ophthalmic, optical safety frames, spectacles, sunglasses . . .

Polysulfone

- Sterilizable containers, steam-cleaning equipment components . . .
- Haemodialysis equipment parts, membranes for artificial kidneys, blood purification . . .
- Endoscopic probe positioning ferrules . . .
- Surgical instrument handles . . .
- Orthopaedic implant trails . . .

PEEK

- Prosthetics . . .
- Surgical and dental instruments (up to 3000 autoclave sterilization cycles) . . .
- Endoscope components . . .
- Port access systems . . .
- Haemodialysers, dialysis machine components . . .

PEI

- Reusable medical devices, sterilization trays . . .
- Stopcocks . . .
- Dentistry devices . . .
- Pipettes . . .

LCP

- Surgical instruments, dental tools . . .
- Sterilizable trays and equipment . . .
- Drug-delivery systems and diagnostics . . .
- Miniature hearing aid parts . . .

TPO

- Syringe plunger tips, epidural syringe plungers . . .
- Seals, gaskets and diaphragms, blood filter seals overmoulded on a PC base . . .
- Medical equipment components, homeopathic drug dispensers . . .
- Medical tubing . . .
- Endoscopic camera holders, epidural needle fixation devices . . .
- Medical clogs . . .

TPV PP/IIR-V

- Specific applications relating to low gas permeability, pharmacopoeia compliance, damping properties.

TPU

- Medical tubing . . .
- Biomedical apparatus components . . .

COPE

- Breathable films for medical disposables . . .

PEBA

- Delivery catheters . . .
- Medical instruments . . .
- Medical bandages . . .
- Surgical garments, sheeting, mattress covers . . .
- Breathable films for medical disposables . . .

2.12.9 Furniture & bedding

The furniture & bedding sector consumes approximately 1–4% of the thermoplastics total. Thermoplastics find outlets in various categories of furniture:

- outdoor furniture: garden and street furniture
- storage units and small furniture

- kitchen and bathroom furniture
- movable furniture
- institutional and professional furniture
- fittings, accessories, supplies and hardware for furniture.

Outdoor furniture

Thermoplastics can offer:

- low or reasonable cost
- weather resistance adapted to lifetime
- mechanical performances and aesthetics
- design freedom
- adaptation to mass production
- lightness and ease of assembly of the delivery kits
- minimum or zero maintenance.

For street furniture, it is necessary to provide a greater mechanical resistance (vandalism, intensive use, safety of fixings) and, possibly, fire resistance.

The seats, tables, loungers and other pieces of garden furniture are currently the prerogative of polypropylenes.

The seats of bus shelters can be made out of polypropylene, HDPE, PVC or polyamide.

The structures of play areas (ladders, stationary motorbikes, labyrinths, huts . . .) can be in highly coloured HDPE or polypropylene.

Indoor furniture

The main reasons to use thermoplastics are the same as for outdoor furniture, with some differences:

- Higher costs are acceptable if particular properties are obtained. For example, engineering thermoplastics such as modified and reinforced polyamides can be used for demanding and top-of-the-range applications.
- Durability of colouring and appearance requirements are more stringent.
- Processes for small series or large parts are appreciated.
- Good resistance to moisture, greases and healthcare products are required for kitchen and bathroom furniture.

Coffee tables, travelling tables and modular storage elements can be made out of ABS, PMMA (when transparency is sought) and PVC.

Small storage units and medicine chests can be made out of HIPS, ABS, possibly polyethylene for bottom-of-the-range articles.

Bathroom stools are often in HDPE.

Newspaper racks, CD racks, bedside units and valet stands . . . can be made out of transparent or smoked PMMA, ABS, polycarbonate.

Lighting devices and accessories can be made out of PMMA and polycarbonate.

Certain beds are made out of thermoformed ABS or are covered with a PVC film or sheet mimicking wood.

Chairs, backrests, seats, armchairs can be made out of polypropylene, PMMA, ABS, possibly combined with a metal structure.

Decorative profiles can be made out of PVC, PS or ABS.

Some inflatable furniture uses sheets or films of PVC or polyethylene.

The penetration of thermoplastics in contemporary furniture remains limited by the perception that costs are prohibitive, and the difficulty of convincing both the profession and the public. Present in contemporary furniture at the end of the 1930s, plastics made their first breakthrough in the 1960s with German products and under the influence of Italian design. About the middle of the 1970s, the tendency was reversed, involving a rejection of plastics, which were labelled as bottom-of-the-range materials. Today, designers are again turning to these materials, which can represent 30% of the furniture of certain resolutely contemporary stores. Stools, seats, mobile pieces of furniture, nested tables, as well as dustbins, vases, lamps . . . can be made out of plastic, possibly combined with a more traditional material such as metal.

To reduce the costs of the small series, it is necessary to seek, as in other industries, new methods of design with integration of functions, simplification of assemblies and finishing operations, and a judicious choice of processing method. For example, the assembly of plastic panels on a metal structure makes it possible to obtain bulky objects with very low investments. The use of thermoforming or other techniques existing in packaging (the principle of blister packaging) makes it possible to achieve large parts (e.g. a seat made out of thermoformed polypropylene) or double-shells at moderate prices.

The use of waste and recycled materials is also a route to be exploited and already allows the realization of low-cost tiles by simple compression of wastes.

Let us quote some application examples for some thermoplastics. These examples can be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for a specific problem and test the right grade under real service life conditions.

Polyethylene

- Street and bathroom furniture, seats . . .
- Accessories: pegs, dowels, nuts, spacers, inserts, plate bearings, casters . . .
- Inflatable furniture . . .

Polypropylene

- Garden furniture . . .
- Indoor and outdoor carpeting, carpet backing . . .
- Accessories: table feet, hinges, lighting brackets . . .

EMA

- Clothes hangers . . .

PVC

- Upholstery, coverings, padding . . .
- Patio furniture . . .
- Coated metal racks and shelving . . .
- Inflatable furniture . . .
- A new and fast-developing application is ‘synthetic wood’ (i.e. wood-plastic composites; WPC) made from rigid PVC heavily filled with wood flour, extruded in wood-like profiles that can be sawn, nailed and screwed just like natural wood.

PVC foam

- Panels for showrooms . . .
- Scenery . . .
- Shop fittings . . .

Styrenics, PS, HIPS, ABS

- Coffee tables, travelling tables, modular storage elements, small storage units, medicine chests . . .

- Clips, wardrobe bars, drawers . . .
- Thrusts, slides, handles of doors and drawers, bolts . . .
- Decorative rods, bands, profiles . . .

SAN

- Bathroom fittings, sanitary ware, soap dispensers, shower cubicles, shelves . . .
- Components for furniture . . .

PA

- Antifriction parts: bearings, rods . . .
- Hinges, slides . . .
- Armchair frames . . .

PMMA

- Transparent furniture . . .
- Knobs, small furniture . . .

PC

- Garden equipment . . .
- Furniture, office & institutional furniture . . .

POM

- Bearings, bushings, wear pads . . .
- Fittings, hinges, shower heads . . . .

Cellulosics

- Decorative rods, bands, profiles . . .

TPS

- Feet, end caps, pads . . .

TPO

- Feet, supports and pads . . .
- Handles, soft-touch overmoulding . . .

TPV

- Grips, handles . . .
- Feet, pads . . .

TPE/PVC

- Grips, handles . . .
- Feet, pads . . .
- Leather-like goods . . .

COPE

- Bedsprings . . .

PEBA

- Bedsprings . . .

2.12.10 Agriculture

The agricultural market consumes approximately 2–4% of all thermoplastics and, apart from packaging, can be divided into three main types of uses:

- plasticulture: films, pots and other accessories
- pipes
- machinery.

Plasticulture

Thermoplastics make it possible to satisfy various functions of agriculture and plant breeding:

- Mulching: transparent or black LDPE, double-layered white and black LDPE for reflective purposes, photodegradable LDPE.
- Tunnels: plasticized PVC, LDPE, EVA.
- Flat covers: nonwoven PP, punched LDPE films.
- Greenhouses with simple walls: LDPE, EVA, PVC, multilayer LDPE/EVA, LDPE/recyclate.
- Greenhouses with multiple walls: PMMA, PC.
- Membranes for water reserves: PVC, PE, EVA.
- Ensilage films: LDPE, plasticized PVC.
- Cups, pots: PS, PP.
- Artificial soils: EPS.
- Mulching of radiant tubes for heating by warm water: PP.
- Watering: polyethylene, flexible PVC tube reinforced with polyester yarn.
- Drainage: rigid PVC.
- Agricultural pulverization of weedkillers, insecticides, fertilizers: reinforced PVC, PE, EVA, COPE.
- High-pressure couplings: reinforced PVC.
- Pneumatic control: PA, PE.
- Machinery is a heterogeneous sector that puts all the properties of all thermoplastics to good use. Applications are very diverse, covering all types of functionalities and a broad diversity of shapes and forms, from miniaturized (nozzle of atomizer) to giant parts (combine harvester). Requirements can be severe needing high-performance mechanical, thermal, optical, physical or chemical properties obtainable with certain thermoplastics and thermoplastic composites.

To progress in the agricultural sector, plastics must improve their performance characteristics, ease of processing, productivity and recycling, for example:

- more precise and stringent specifications
- better mechanical performances
- better thermal resistance in the long term and better durability to favour long-term service without maintenance
- development of new processing technologies: bi-, tri- or quadri-extrusion, alloys, multi-material components, better control of the reinforcement
- ease of processing: improved flow properties and processability leading to cycle time reductions and productivity gains
- low finishing costs: bulk colouring, intelligent design and effective maintenance of the moulds, dies and other tools to reduce or avoid finishing operations, and cut finishing costs
- recycling: more-effective solutions are sought.

As in many sectors of industry, plastic components that replace metal components are increasingly numerous.

Let us quote some application examples for some thermoplastics. These examples can be commercialized, in development, potential or related to very specific uses. The designer must verify the possibility to use the quoted thermoplastic family for their specific problem and test the right grade under real service life conditions.

Polyethylene

- Films for tunnels and other agricultural applications . . .
- Large-sized objects: cisterns, tanks . . .
- Water or sewer pipes, sheaths . . .

PE foam

- Machine soundproofing . . .
- Impact and vibration damping . . .

PE fibres

- Ropes for fish-farming, anchorage . . .

Polypropylene

- Polypropylene filaments, fibres, fabrics, partially and fully oriented yarns perform well in cordage, netting, woven bags . . .
- Polypropylenes are cost-effective polymers for casings, caps, framework of ventilation, fan blades, air filters, filters and pumps of agricultural machines, pipes . . .

PP foam

- Damping and protection; air, water and dust proofing, thermal insulation, soundproofing . . .

EVOH

- Co-extrusion with polyamides, polypropylene, polyethylene, EVA, thermoplastic polyester, polycarbonate, polystyrene, ionomers for packaging of fertilizers, herbicides and other chemicals.

PVC

- Garden hoses and pipes . . .
- Fishing lures . . .
- Inflatable covers, structures and devices . . .

PVC foam

- Machine soundproofing . . .
- Impact and vibration damping . . .
- Insulation of tanks, pipes . . .

EPS

- Artificial soil for horticulture . . .
- Heat insulation, soundproofing . . .

ABS

- Tubing, pipes and fittings for aggressive environments and corrosive liquids . . .
- Housings . . .
- Handles . . .

PA

- Antifriction parts: bearings, rods . . .
- Technical parts: gears, screws and bolts, pulleys, collars, valve casings, rings, clips, ventilators, cooling fans, tanks and containers . . .

PA 11, 12

- Hydraulic, fuel and water hoses; air brake hoses; monolayer and multilayer plastic fuel lines . . .
- Antifriction parts: bearings, rods . . .
- Technical parts: pneumatic and hydraulic hoses; fuel handling and hydraulic applications; gears, collars, valve casings, rings, clips . . .

PMMA

- Transparent and decorative parts for agricultural machines . . .
- Lenses for lights . . .
- Instrument panels, dials, indicators, tachometer covers . . .
- Nameplates, medallions . . .
- Cast and extruded sheets, cell-cast sheets for greenhouses . . .

PC

- Transparent and decorative parts for agricultural machines . . .
- Glazing for greenhouses . . .
- Machine lighting: lenses . . .
- Nameplates and bezels . . .
- Garden equipment . . .

POM

- Rollers, bearings, bushings, conveyor plates, wear pads . . .
- Housing parts, handles and knobs . . .
- Couplings, pump impellers . . .
- Gears, sprocket wheels, gearwheels, cams, springs . . .
- Poultry processing parts, food conveyors . . .
- Clips, lugs, conveyor components . . .
- Aerosol components, aerosol valves and heads . . .
- Irrigation equipment and valves . . .
- Garden sprayers . . .
- Milk pumps . . .
- Filter housings . . .
- Antifriction parts, bearings, bushings, rods, zippers . . .

PPE

- Housing parts, handles and knobs . . .
- Machine housings, pump housings and impellers, fluid and material handling components, water pump housings and impellers in machinery . . .
- Frames, ventilating parts . . .

Polysulfone

- Fluid handling, coupling and fitting applications, potable water fittings . . .
- Manifolds, distributor valves . . .
- Lighting fixtures, portholes . . .

- Porous filaments or membranes for micro- and ultrafiltration and reverse osmosis, membranes for wastewater recovery . . .

PPS

- Thrusters of pumps, hot water pumps . . .
- Bearings (PTFE lubricated) . . .

TPS

- Rack and pinion boots . . .
- Weather-stripping, window seals . . .
- Feet, end caps, pads . . .

TPO

- Feet, supports and pads . . .
- Handles, soft-touch overmoulding . . .

TPV

- Grips, handles, feet, pads for garden devices . . .
- Feet, pads . . .
- Foamed seals . . .
- Motor and vibration mounts . . .

TPE/PVC

- Grips, handles . . .
- Feet, pads . . .
- Seals, integrated seals . . .
- Motor and vibration mounts . . .
- Grips, handles, overmoulding . . .

TPU

- Constant velocity boots . . .
- Mounts . . .
- Gaskets and seals, hydraulic seals . . .
- Hoses and tubing, hydraulic hoses, flexible tubing . . .
- Motor and vibration mounts . . .
- Drive belts . . .
- Conveyor belts . . .
- Cattle tags . . .

MPR

- Damping mounts for noise and vibration . . .
- Soft handles and grips . . .

COPE

- Constant velocity joint (CVJ) boots, rack and pinion bellows . . .
- Caterpillars . . .
- Seals, gaskets, packing . . .

PEBA

- Hoses and tubing, flexible tubing, hose jackets, convoluted tubing, hydraulic hoses, pneumatic tubing . . .
- Bearings, plugs, pads, feet, damping mounts . . .

References

Technical guides, newsletters, websites

3M, Akzo Plastics, Allied Signal, Allrim, Amcel, APC (AmericanPlasticsCouncil.org), Amoco, Arkema, Arco Chemical, Astar, Atochem, Atofina, Bakelite GmbH, BASF, Bayer, BF Goodrich, BIP, Bisco, BP Chemicals, Bryte, Ceca, Celanese, Ciba, Cray Valley, Culver City Corp, Degussa, Devcon, Dow, DSM, Du Pont de Nemours, DuPont Dow, Dynamit Nobel, Eleco, Emerson & Cumming, EMS, Enichem, Epotecny, Eval, Exatec, Exxon, Ferro, Ferruzzi, FiberCote, Framet Futura, General Electric Plastics, General Electric Silicones, Hexcel, Hoechst, Hüls, ICI, Irathane, Isomeca, Kommerling, Kuraray, La Bakélite, Loctite, Lohmann, Mecelec, Menzolit, Mitsui Chem, Monsanto, Montedison, Naphtachimie, Neste, Nief Plastic, Nippon Gohsei, Nippon Mitsubishi, Nonacor, Norflys, Orkem, Owens Corning, Perstop, Phillips Petroleum, PlasticsEurope, PPG, PRW, Raschig, Recticel, Repsol, Rhodia, Rhône Poulenc, Rohm, Schulman, Scott Bader, Shell, Sika, Sintimid, SNIA Tecnopolimeri, SNPE, Solvay, spmp, Stratime, Symalit, Synres, Synthésia, T2L, Technochemie GmbH, Telenor, The European Alliance for SMC, Thieme, Toray, Tramico, Tubize Plastics, Tubulam, Ube, Union Carbide, Uniroyal, Vetrotex, Vyncolit, Wacker, Wilson Fiberfil, YLA.

Reviews

[1] *Plastics Additives & Compounding* (Elsevier Ltd)
[2] *Modern Plastics Encyclopaedia* (McGraw-Hill Publications)
[3] *Modern Plastics International* (Canon Communications LLC, Los Angeles, CA, USA)
[4] *Reinforced Plastics* (Elsevier Ltd)

Chapter 3

Basic criteria for the selection of thermoplastics

Polymers have some specific properties due to their organic nature. Thermoplastics, as seen in Chapter 1, are independent organic macromolecules with some sensitivity to environmental parameters: temperature, moisture, deleterious solids, liquids, gases and other chemical products. They are also sensitive to mechanical loading, especially cyclic loads. Their specific properties, such as electrical or optical properties, are also important for their applications.

All the properties are influenced by the additives used with the thermoplastic matrices, notably the reinforcements but also stabilizers, plasticizers, colorants and others.

Thermomechanical behaviour is most probably the most widely exploited property of engineering thermoplastics. Figure 3.1 shows the behaviour of two types of thermoplastic, one amorphous and the other semicrystalline, versus temperature. We can see several steps moving from low to high temperatures:

- a high modulus plateau corresponding to a brittle material
- a first decrease of the modulus that depends on the material morphology:
  - ○ leading to a ductile state for the amorphous material
  - ○ leading to a second pseudo-plateau for the semicrystalline thermoplastic
- a final drop for the semicrystalline material.

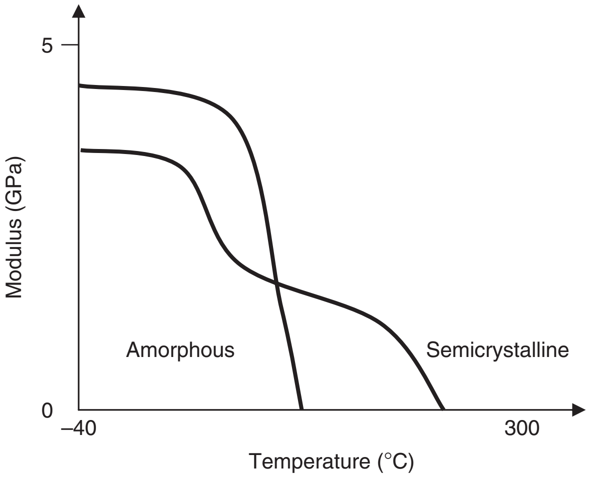


Figure 3.1. Examples of modulus variations versus temperature for an amorphous and a semicrystalline thermoplastic

This is important for the majority of applications because:

- the softening at ‘high’ temperature limits the mechanical performances
- the brittleness at ‘low’ temperature can lead to failure after light impacts
- the damping properties broadly vary with temperature and become weaker or non-existent at low temperatures.

The selection of thermoplastics and composites to design a new part requires impartial and comparative testing methods.

3.1 Evaluation of plastic properties

The property measurement methods are standardized and only allow comparisons: the test specimens are produced under the best possible conditions, the deleterious factors are isolated to avoid any synergy, the duration of tests is inevitably limited, etc. In real life, this is practically never the case and the results found in any literature will have to be verified, checked, interpreted and corrected with safety margins.

Lastly, it is necessary to take account of the dispersion of the results and, particularly for the composites, of property anisotropy.

Failure of parts is led by the ratio of the actual mechanical stress on the part versus the mechanical stress at break of the weakest point. In Figure 3.2, the two materials (A) and (B) have the same average tensile strength, but one (B) has more widely dispersed individual values with a broader risk of failure because the lowest values of tensile strength are inferior to the actual stress in the part.

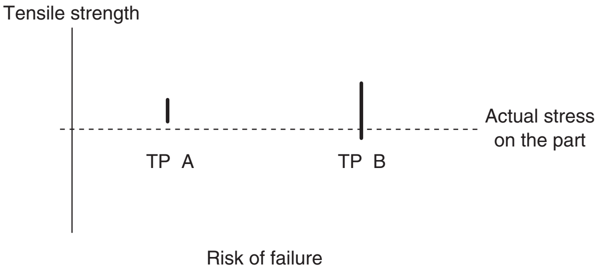


Figure 3.2. Effect of data dispersion on the risk of failure

3.1.1 Thermal behaviour

A temperature rise causes two different phenomena:

- Immediate physical effects (see Figure 3.1):
  - ○ decay of the modulus and other mechanical and physical properties, physicochemical softening
  - ○ dimensional stability: reversible thermal expansion and, eventually, irreversible shrinkage and warpage.
- Long-term effects:
  - ○ physical: irreversible creep and relaxation to a greater or lesser extent
  - ○ chemical: irreversible degradation of the material, decrease in mechanical properties, even after a return to the ambient temperature.

The maximum service temperatures depend on the duration of service time and the possible simultaneous application of mechanical stresses.

A fall in temperature has only physical effects:

- increase in the modulus and rigidity
- reduction in the impact resistance; the material can become brittle
- eventually, crystallization for semicrystalline polymers.

Conventional heat measurements are:

- continuous use temperature (CUT)
- UL temperature index
- heat deflection temperature (HDT)
- vicat softening temperature (VST)
- accelerated ageing.

Continuous use temperature (CUT)

The continuous use temperature is an arbitrary temperature resulting from general experience and observation. It is the maximum temperature that an *unstressed* part can withstand for a very long time without failure or loss of function even if there is a significant reduction in the initial properties.

This subjective value is not measurable and is deduced from ageing test interpretations and information collected in the technical literature.

To give some idea, continuous use temperatures for thermoplastics are in a range from 50°C up to 400°C for exceptional families.

UL temperature index

The temperature index, derived from long-term oven-ageing test programmes, is the maximum temperature that causes a 50% decay of the studied characteristics in the very long term. The UL temperature index depends on:

- the grade
- the thickness of the tested samples
- the characteristics studied.

Influence of grade

For two grades of mineral-filled nylon 66, of the same thickness and for the same properties, the UL temperature indices are 65°C and 80°C.

For three grades of epoxy resins, of the same thickness and for the same properties, the UL temperature indices are 160°C, 170°C and 180°C.

Influence of thickness

The UL temperature indices increase with the thickness of the samples. For example, for a defined polymer grade, the UL temperature indices are:

- 200°C for a 2.1 mm thickness.
- 50°C for a 0.4 mm thickness.

Influence of the characteristics studied

There are three categories of UL temperature indices:

- electrical properties only
- electrical and mechanical properties, impact excluded
- electrical and mechanical properties, impact included.

For the same grade in the same thickness, the three indices can be identical or different. Table 3.1 displays some examples.

Table 3.1 Examples of UL temperature indices

	Thickness (mm)	Electrical, mechanical properties, including impact (°C)	Electrical, mechanical properties, excluding impact (°C)	Electrical properties (°C)
PTFE	0.8	180	180	180
Polycarbonate	1.6	110	125	125
PVC	2	50	80	80

To give a general idea, UL temperature indices of thermoplastics are in a range of 50°C up to more than 200°C for exceptional families.

Like all the laboratory methods, the temperature index is an arbitrary measurement that must be interpreted and must constitute only one of the elements by which judgement is made.

Heat deflection temperature (HDT)

The HDT is the temperature at which a standard deflection occurs for defined test samples subjected to a given bending load and a linear increase in temperature. The stresses usually selected are 0.46 MPa (HDT B) or 1.8 MPa (HDT A) and must be indicated with the results. In any case, the polymer cannot be used under this load at this temperature.

Generally, HDTs are in a range of 20°C up to more than 400°C for exceptional families. For a given thermoplastic family, HDT is affected by reinforcement fillers and plasticizers.

Vicat softening temperature (VST)

The Vicat softening temperature is the temperature at which a standard deflection occurs for defined test samples subjected to a given linear temperature increase and a compression loading from a defined indenter of a specified weight. The load used is often 10 N (Vicat A) or 50 N (Vicat B) and must be indicated with the results. In either case the polymer cannot be used under this compression load at this temperature.

For a given thermoplastic family, VST is affected by reinforcement fillers and plasticizers.

HDT and VST are not strictly linked but there is a certain relationship and when HDT is low, VST is also low.

Accelerated ageing

Conventional accelerated ageing tests consist in exposing defined samples to controlled-temperature air in ovens protected from light, ozone and chemicals, for one or more given times. The degradation is measured by the variation at room temperature of one or several physical or mechanical characteristics during the ageing. The variations of impact resistance, hardness, tensile or flexural strength are the most frequently studied.

Sometimes, properties are measured at the ageing temperature, which is a more severe method.

Accelerated ageing is an arbitrary measurement that must be interpreted and must constitute only one of the elements used in making a judgement:

- Under identical conditions, the properties do not all degrade at the same rate.
- It is impossible to establish a direct relationship between the accelerated ageing of a part and its real lifespan. For an unknown polymer, the results of accelerated ageing must be compared with those obtained on a known polymer of a very similar formula.

3.1.2 Low-temperature behaviour

There are many methods to test low-temperature behaviour and the possibility to use a thermoplastic at low temperature depends on the service conditions. Some grades can be used at −200°C or less if there are no impacts. Some other thermoplastics can be brittle at ambient temperature like the polystyrene used for yoghurt packaging.

It is necessary to distinguish:

- short-term tests: brittle point, low-temperature impact test, low-temperature rigidity, and elastic recovery for elastomers such as silicone
- long-term tests: crystallization tests, which make it possible to detect a slow crystallization by the evolution of hardness with time.

Brittle point

The – very fuzzy – definition of the brittle point is based on a more or less sudden reduction in the impact resistance or the flexibility. The indicated values must be carefully considered.

- Low-temperature impact tests: cooled samples are subjected to a conventional impact test. Generally, the temperatures most often used are −20°C, −30°C or −40°C.
- Low-temperature brittleness or toughness: the samples are cooled to a temperature far lower than the supposed temperature of brittleness, and then gradually warmed up. At each selected step temperature, the test specimens are subjected to a specified impact. The temperature at which specimens deteriorate or fail is the 'brittle point'. In some other tests, the lowest temperature to which specimens can be cooled without deterioration is regarded as the limiting temperature of 'toughness' or 'no brittleness'.
- Low-temperature film flexibility: the film or sheet is rolled up on a specified mandrel at one or several temperatures.

Rigidity in torsion: 'Clash & Berg', 'Gehman' tests

These tests are based on the evolution of the static or dynamic torsion modulus when the temperature decreases. Results can be:

- plotted versus the temperature
- expressed as the value of the modulus for specified temperatures
- recorded as the temperatures for which the modulus is 2, 5, 10, 100 . . . times higher than that measured at room temperature.

Crystallization test

The crystallization test consists of measuring the evolution of hardness at a specified temperature over several weeks. This method is of special interest for those polymers that can slowly crystallize at service temperatures.

3.1.3 Density

Density is a basic characteristic of thermoplastics, important for engineering, economic and structural reasons:

- Weight saving is one of the reasons leading to polymer choice.
- Density is a consequence of structure and allows low, medium and high density polyethylene material to be distinguished.
- Prices are based on weight and, often, the part design is based on volume.

For dense thermoplastics, densities are in the range of 0.8 g/cm^3 to more than 2.0 g/cm^3. For cellular materials such as foams, densities can be as low as 10 kg/m^3.

3.1.4 Mechanical properties

A lot of characteristics are currently deduced from the stress/strain curves.

Figure 3.3 shows the case for two tensile behaviours:

- one for a brittle polymer, when the break point arises immediately after the yield point or coincides with it
- the other for a ductile polymer, when the break point is far from the yield point.

Although resulting from low-speed tests, these curves give results only under instantaneous loads whereas in real life the parts are exposed to long-term stresses or strains. For this, it is necessary to refer to the long-term mechanical properties.

Conventional mechanical measurements are:

- elastic modulus
- yield point

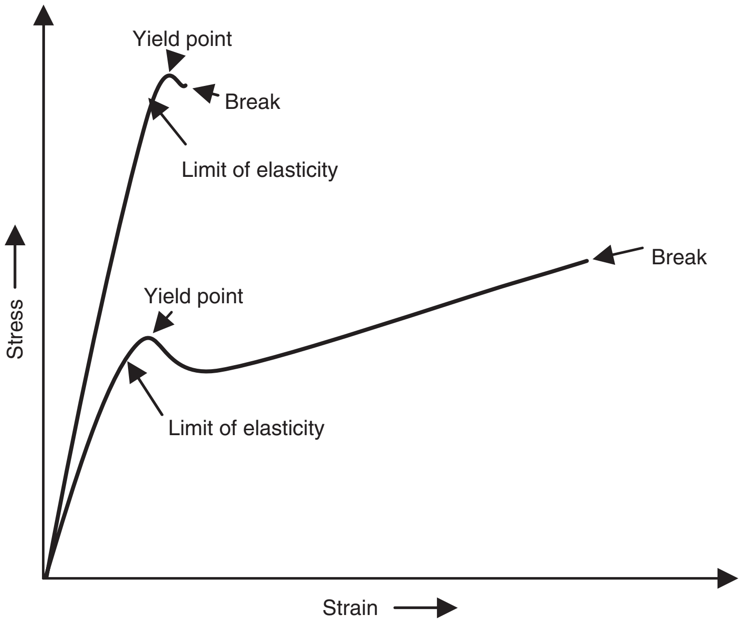


Figure 3.3. Tensile behaviour of polymers

- stress and strain at yield
- ultimate stress and strain
- impact test.

The loading types generally used now are:

- tensile
- flexural
- compression. In this case, it is generally a unidirectional compression. Bulk compression is rarely used, except for modelling.

The performance level is closely linked with the use of reinforcing materials. Figure 3.4 schematizes the position of three different categories of thermoplastics versus moduli and strengths:

- engineering plastics possibly filled with short glass fibres
- General-purpose composites such as BMC, SMC, GMT . . .
- unidirectional composites for high-tech applications.

Elastic modulus

The elastic modulus is the slope of the tangent at the origin of the stress/strain curve. The tensile or compression modulus is often called Young's modulus whereas the torsion modulus is often called shear modulus or Coulomb's modulus.

Yield point

The yield point is the first point of the stress/strain curve for which there is an increase in the strain without an increase in the stress. Parts must always operate well below this point during service.

Stress and strain at yield

Stress and strain at yield are the values of the stress and strain corresponding to the yield point.

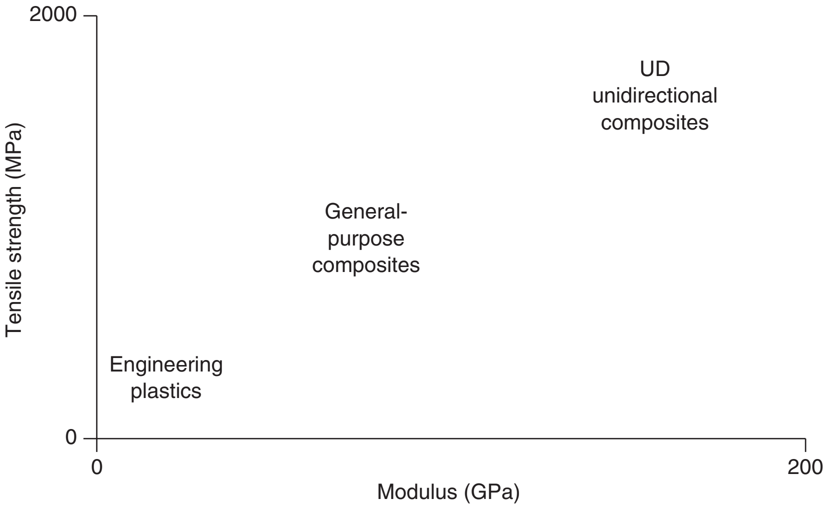


Figure 3.4. Examples of moduli and tensile strengths of thermoplastics and composites

Ultimate stress and strain

Ultimate stress and strain, or stress and strain at break, are the values corresponding to the breaking of the samples.

Interlaminar shear strength

The interlaminar shear strength (ILSS) is the value of the shear strength producing a delamination between two composite layers along the plane of their interface. The measurement is made by a three-point deflection test with the supports very close together.

Impact test

Impact tests measure the energy absorbed during a specified impact of a standard weight striking, at a given speed, a test sample clamped with a suitable system. The hammer can be a falling weight or, more often, a pendulum. In this case, the samples can be smooth or notched. The results depend on the molecular orientation and the degree of crystallization of the material in the sample, its size, the clamping system, the possible notch and its form, the mass and the strike speed. The values found in the literature, even for instrumented multi-axial impact (ISO 6603–2:2000), can only be used to help choose and do not replace tests on real parts.

The Izod and Charpy impact tests are mostly used. A defined pendulum strikes the specimen sample, notched or un-notched, clamped with a defined device. The absorbed energy is calculated and expressed:

- in kJ/m^2: the absorbed energy divided by the specimen area at the notch
- J/m: the absorbed energy divided by the length of the notch, which is also the thickness of the sample.

There is no true correlation between the two methods as we can see in Figure 3.5, which displays the notched versus un-notched impact strength of various grades of polycarbonates, acrylics, polyphenylene sulfide and nylon.

The notched impact tests tend to measure the notch sensitivity rather than the real impact strength of the material. It corresponds better to parts with sharp edges, ribs and so on.

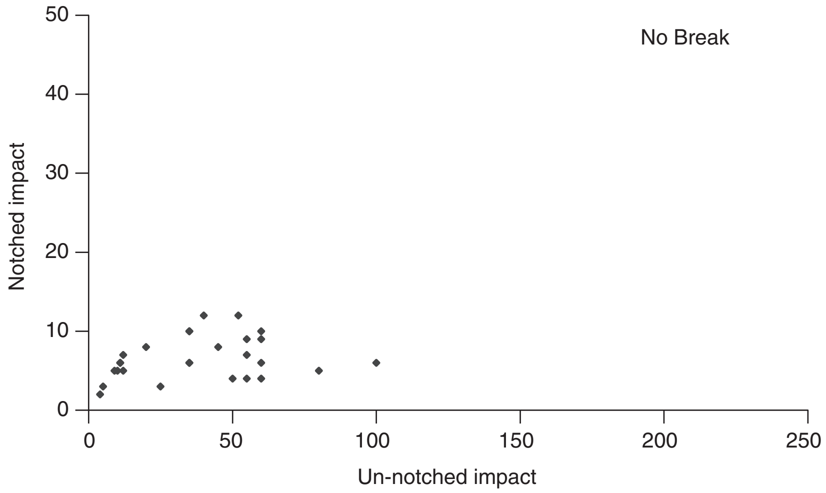


Figure 3.5. Impact strength of un-notched and notched samples

Hardness

The most usual test methods are:

- Shore A for soft polymers
- Shore D for hard polymers
- IRHD, International Rubber Hardness
- Rockwell R, M and others
- Ball indentation.

There are no mathematical correlations between the various methods. Figure 3.6 displays examples for Rockwell M and Shore D.

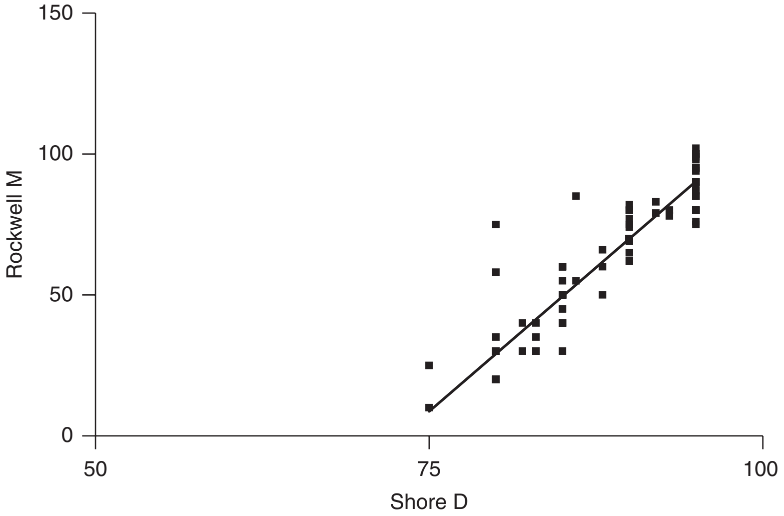


Figure 3.6. Hardness: examples of Rockwell M versus Shore D for some thermoplastics

3.1.5 Long-term mechanical properties

Thermoplastics have a viscoelastic behaviour that increases with temperature: their properties are a function of the duration of load application.

Creep

Creep is the time-dependent strain induced by a constant mechanical loading. The strain is a function of the stress level, the time for which the stress is applied, and the temperature. The results can be presented graphically in various ways by combining these three parameters or in quantified forms: creep modulus and creep strength, for example.

The creep modulus for a specified stress, time and temperature is the value of the stress divided by the strain measured after the selected time.

The creep strength for a specified time and temperature is the value of the strength leading to failure after the time under consideration.

Creep modulus and strength values are broadly inferior to their counterparts measured by dynamometry.

Figures 3.7 (a)–(d) show some aspects of creep for polypropylene and polyethylene:

- (a) and (b) are the same strain results plotted against arithmetic or logarithmic scales for time
- (c) shows examples of creep strain according to load
- (d) shows examples of creep strength versus time according to the temperature. It is not comparable with (a) (b) and (c).

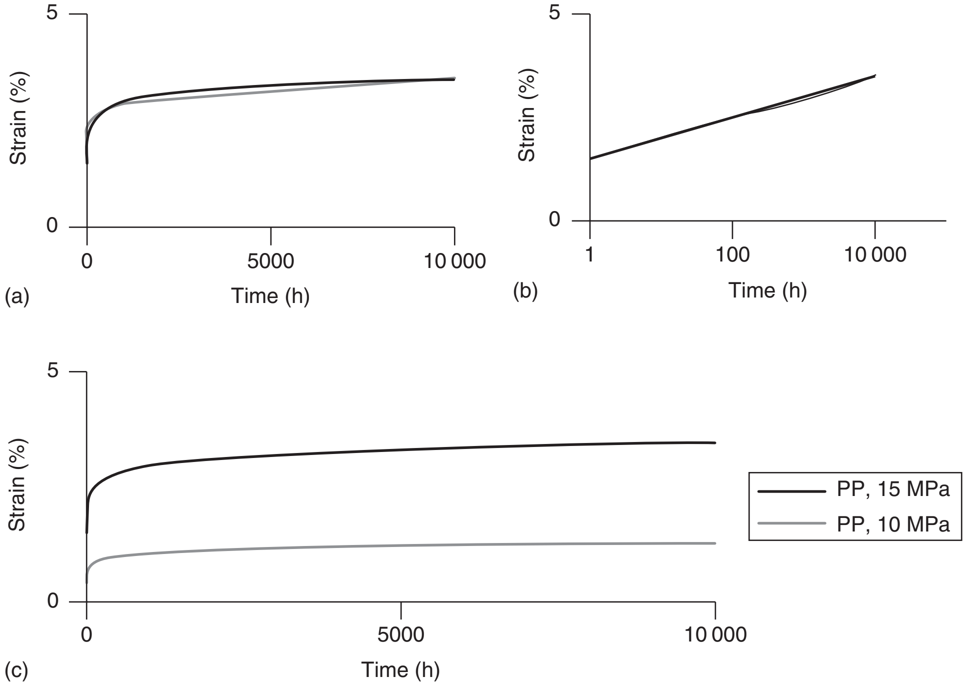


Figure 3.7. (a) Creep strain versus time: example of polypropylene at 23°C under 10 MPa in tensile loading; (b) Creep strain versus time: example of polypropylene at 23°C under 10MPa in tensile loading; (c) Creep strain versus time: example of polypropylene at 23°C under 10 and 15MPa in tensile loading

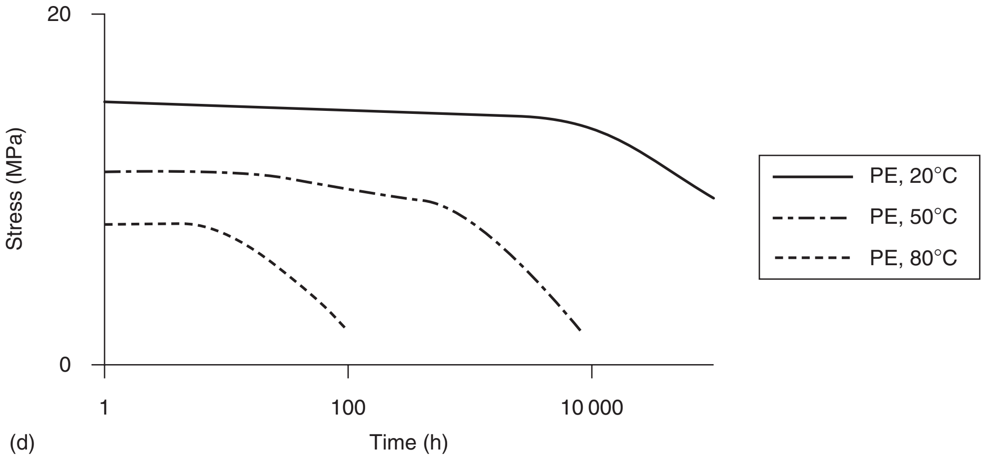


Figure 3.7.(Contd) *(d) Creep strength versus time: example of polyethylene at 20°C, 50°C and 80°C*

Relaxation

Relaxation is the time-dependent stress resulting from a constant strain. The stress is a function of the strain level, the application time and the temperature. The results of tests at a defined temperature can be presented as a load versus time curve or a stress retention versus time curve.

The stress retention for a defined time and temperature is the actual measured stress divided by the original stress at time zero.

Figure 3.8 shows a diagrammatic example of the stress retention, expressed as a percentage, with a fast drop at the beginning of the test followed by a gentle slope.

Fatigue

The repeated mechanical loading of a polymer leads to a speedier failure than an instantaneous loading. The Wohler curves (or SN curves) plot the level of stress or strain (S) leading

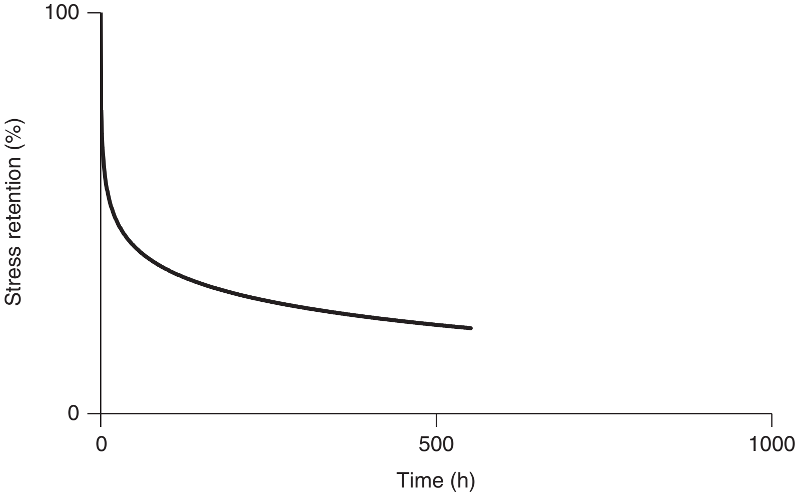


Figure 3.8. *Relaxation: diagrammatic example of stress retention versus time*

to failure after N cycles of repeated loading. Two basic types of tests coexist at defined stress or at defined strain.

Thermoplastics being sensitive to creep, the fatigue tests at defined strain are less severe than those at defined stress for comparable original stresses.

The results depend on the stress type and level, the frequency, the surrounding temperature, and the geometry of the sample. We must note that the temperature of the material rises under the dynamic loading with the usual consequences, such as modulus reduction and ageing.

Depending on the thermoplastic, stress can:

- continuously decrease during fatigue testing, or
- decrease abruptly at the beginning of the fatigue test and then gently decrease, or
- decrease abruptly at the beginning and then stabilize.

Three diagrammatic examples are displayed in Figure 3.9 for 100 000 to 10 000 000 cycles. The fast drop in strength at the start is not visible because it generally appears before 100 000 cycles.

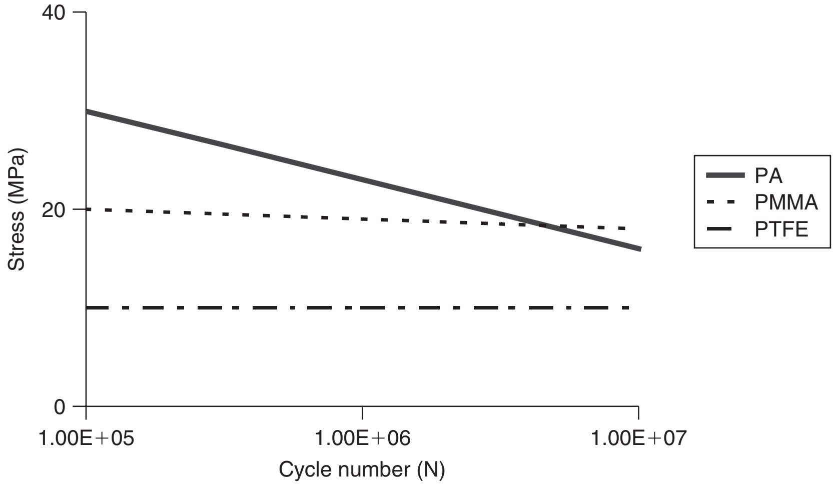


Figure 3.9. SN curves: diagrammatic examples based on PA, PMMA and PTFE

3.1.6 Long-term light and UV resistance

Polymers are organic materials and are sensitive to natural or artificial UV sources. This is of primary importance for outdoor exposure of unprotected parts and for some industrial applications such as electrical welding, photocopier light exposure devices . . .

Additives such as special fillers (carbon blacks, for example), UV stabilizers and so on can enhance the basic resistance of the matrix to UV.

Under quite precise conditions (angle of incidence, positioning, temperature, water vapour, surface water . . .), tests can be done by exposure:

- to the natural light of the sun, or
- to the radiation of xenon lamps (Xenotest, WeatherOmeter) or others.

The effects of ageing appear mainly in three ways:

- mechanical property degradation
- modification, for clear grades, of aspect and colour, chalking, yellowing, browning, discoloration . . .
- surface crazing and cracking.

The interpretation of the results is difficult because of:

- climate diversity
- the risks of industrial or domestic pollution in real life
- the lack of correlation between artificial and natural ageing
- the different degradation kinetics of the various properties.

3.1.7 Chemical resistance by immersion or contact

The action of a chemical on a plastic can induce three concomitant phenomena:

- absorption of the liquid by the plastic, which leads to swelling of the part
- extraction by the liquid of some material components (plasticizers in particular, anti-degradants, monomers and oligomers, colorants). This extraction can reduce the apparent swelling of the part, or even lead to a retraction
- pollution of the liquid by the immersed polymer: desorption of particles and ingredients.

The tests themselves consist of immersing the sample in the liquid under consideration for a given time at a given temperature.

The generated effects can be highlighted in several ways:

- evaluation of the volume, weight or dimension swelling of the sample
- percentage of extracted materials
- degradation of the mechanical characteristics, either immediately, or after drying.

For these tests, the service liquids (solvent, oil, hydraulic fluid, acid, base . . .) can be used but, to ease the establishment of specifications and comparative tests, reference solvents, oils or fuels are often used. The most current are IRM 901, 902 or 903 oils (which replace ASTM 1, 2 and 3 oils), fuels or solvents ASTM A, B, C.

Environmental stress cracking

When a plastic exposed to air is subjected to a stress or a strain below its yield point, cracking can occur after a very long duration. The simultaneous exposure to a chemical environment under the same stress or strain can lead to a spectacular reduction of the failure time. The accelerated cracking in this way corresponds to 'environmental stress cracking' (ESC).

3.1.8 Electrical properties

Polymers are naturally insulating and can be characterized by:

- The volume resistivity and surface resistivity
- The dielectric strength
- The arc resistance.

Volume resistivity – ASTM D257 and IEC 93

The volume resistivity is the electrical resistance of a polymer sample of unit area and unit thickness when electrodes placed on two opposite faces apply an electrical potential across it. The volume resistivity is expressed in ohm.cm.

Classification of polymers varies depending on the country and application. Each case must be examined in its context and the following data are only examples:

- insulating polymers: resistivity higher than $10^9\,\Omega$.cm
- conductive polymers: resistivity lower than $10^5\,\Omega$.cm
- polymers for electrical heating: resistivity lower than $10^2\,\Omega$.cm

Surface resistivity – ASTM D257 and IEC 93

The surface resistivity is the electrical resistance between two electrodes placed on the same face of a polymer sample. The surface resistivity is expressed in ohms (or sometimes in ohms per square).

Classification of polymers depends on the country and application. Each case must be examined in its context and the following data are only examples:

- insulating polymers: resistivity higher than 10^{12} ohm per square
- dissipative polymers: resistivity in a range from 10^5 up to 10^{12} ohm per square
- anti-electrostatic parts for coalmines: resistivity lower than 10^9 ohm per square
- conductive polymers: resistivity lower than 10^5 ohm per square.

Dielectric strength

The dielectric strength is the maximum voltage before breakdown divided by the thickness of the sample. It is expressed in kV/mm.

Arc resistance

The arc resistance is the time necessary to make the polymer surface conductive by the action of a high-voltage, low-current arc. It is expressed in seconds.

3.1.9 Gas permeability

The determination of the gas permeability under given conditions of pressure and temperature is based on the measure of the gas flow rate through a polymer membrane of defined size. The permeability is expressed in $m^2/Pa.s$.

The gas permeability depends on the chemical natures of the polymer and the gas (air, nitrogen, CO_2, moisture . . .). For the same polymer, the results are often very different, depending on the gas.

3.1.10 Flammability

Fire behaviour depends, initially, on the nature of the polymer. However, the use of fireproofing agents, special plasticizers and specific fillers can modify this behaviour very significantly.

Tests relate to:

- the tendency for combustion: UL94 ratings, oxygen index
- the smoke opacity
- the toxicity and corrosivity of the smoke.

UL94 fire ratings

The UL94 fire ratings provide basic information on the material's ability to extinguish a flame, once ignited. The positioning of the sample (horizontal: H; or vertical: V), the burning rate, the extinguishing time and dripping are considered.

The main categories are:

- V0: the most difficult to burn, extinguished after 10 s, no drips
- V1: extinguished after 30 s, no drips
- V2: extinguished after 30 s, flaming particles or drips permitted

- 5V: extinguished after 60 s, flaming particles or drips permitted
- HB: burning horizontally at a 76 mm/min maximum rate.

The UL rating depends on the exact grade and the sample thickness. For the same grade of polyphenylene sulfide, the UL ratings are:

- V1 for a 1.6 mm thickness
- V0 for a 6 mm thickness.

Oxygen index

The oxygen index is the minimum percentage of oxygen in an atmosphere of oxygen and nitrogen that sustains the flame of an ignited polymer sample.

Generally, oxygen indices range from 17 up to more than 60.

There is no true link between UL94 rating and oxygen index but a thermoplastic with a low oxygen index cannot satisfy to UL94 V0. For a random choice of 100 classified grades of various plastics, the results are as follows:

- 50% of the grades have an oxygen index inferior to 30 and a UL94 rating of:
  - HB for 49%
  - V2 for 1%.
- 14% of the grades have an oxygen index between 30 and 39 and a UL94 rating of:
  - V1 for 4%
  - V0 for 10%
- 36% of the grades have an oxygen index greater than 39 and a UL94 rating of V0.

Smoke opacity

Smoke opacity is measured by optical density.

3.1.11 Optical properties

The most usual optical properties are:

- light absorption: the percentage of light absorbed by the polymer versus the incident light intensity
- light transmission: the percentage of light transmitted through the polymer versus the incident light
- haze, which is induced by light scattering within the polymer. A water haze can be caused by absorbed moisture
- gloss: the capacity of the polymer surface to reflect light in given directions.

3.2 Evaluation of plastic structural properties

Structural properties such as molecular weight, viscosity, plasticity and crystallinity are important tools to evaluate:

- processability
- evolution of performance after processing
- causes of failure and degradation during service life.

Rheological behaviour, viscosity and plasticity under given conditions are affected by the nature of the polymer, the average molecular weight, its distribution, and the molecular structure, branching, stereo-arrangement . . .

3.2.1 Morphology and structure of polymers

Determination of the average molecular weight and its distribution can be assessed by gel permeation or size-exclusion chromatography on solution polymers. The crystallinity of a polymer can be measured by DSC, density or X-ray diffraction.

Gel permeation or size-exclusion chromatography (GPC or SEC)

The dissolved polymer molecules are separated on the basis of their size relative to the pores of a packing material contained in a column. The chromatograms can be converted to molar mass distributions, average molar masses, M_n, M_v, M_w and M_z, long-chain branching and its distribution.

Differential scanning calorimetry (DSC) or differential thermal analysis (DTA)

A sample of the polymer to be studied and an inert reference material are heated and cooled in an inert environment (nitrogen) according to a defined schedule of temperatures (scanning or isothermal). The heat-flow measurements allow the determination of the temperature profile of the polymer, including melting, crystallization and glass transition temperatures, heat (enthalpy) of fusion and crystallization. DSC can also evaluate thermal stability, heat capacity, specific heat, crosslinking and reaction kinetics.

One must remember that static methods like DSC and dynamic ones like DMTA lead to very different data for some characteristics such as glass transition.

Rheology

The rheological properties of polymers can be studied:

- in the molten state with rheometers and MFI or MFR devices
- in the solid state by dynamic mechanical thermal analysis (DMTA)
- in dilute solutions by viscometry.

Capillary rheometers

Capillary rheometers are in the form of a barrel where the operator puts the polymer sample. After heating to equilibrate its temperature, the sample is pushed by a piston through a die at chosen rates. Various sizes and shapes of dies are available. Capillary rheometers measure the rheological properties under broad ranges of conditions of temperature, pressure, stress, strain and time, allowing the adoption of parameters near to those for processing.

Usually, measured properties are, for example:

- shear viscosity from low to high shear rates as near as possible to processing conditions
- die swell
- flow disturbances such as melt fracture, sharkskin . . . at high shear rates corresponding to processing conditions
- elastic modulus G′, viscous modulus G″ and phase angle (tan delta) as functions of frequency and temperature.

Figure 3.10 displays some examples of viscosity versus shear rate for two different grades of polypropylene at 190°C and 250°C.

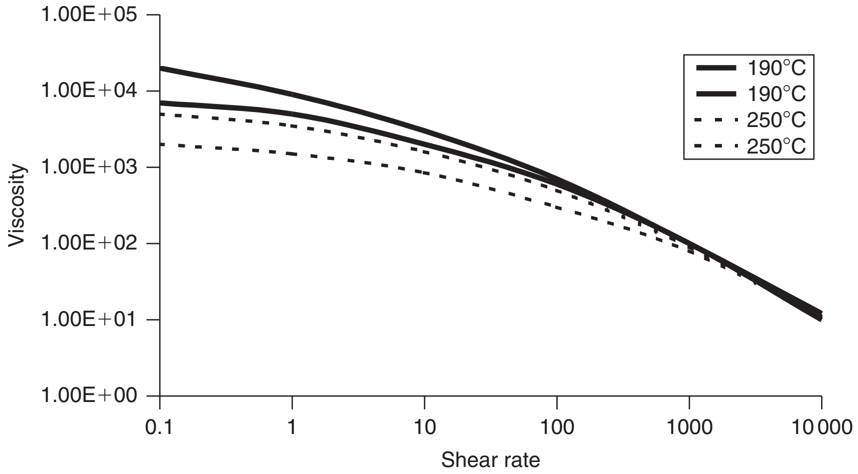


Figure 3.10. Viscosity examples for two PPs versus shear rate and temperature

Conclusions can be drawn concerning:

- processability
- molecular mass and its distribution
- chain branching.

Melt flow index (MFI), melt flow rate (MFR)

More common and simpler than rheometers, MFI/MFR equipment, like rheometers, is in the form of a barrel where the operator puts the polymer sample. After heating to equilibrate its temperature, the sample is pushed by a piston through a die at an undefined rate, the piston being simply powered by a loading weight. The choice of the loading weights and temperatures is limited and, consequently, the shear rate is not controlled and is often much lower than in the actual processing. The method needs large amounts of material and the duration of each measurement is long, providing average characteristics.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical testers apply a small sinusoidal stress or strain to a small sample of the polymer to be examined and measure resonant frequency and damping versus temperature and forced frequency. Instrument software computes dynamic storage modulus (G′), dynamic loss modulus (G″) and tan delta or damping factor. Measurements over a wide range of frequency and temperature provide a fingerprint of the polymer with sensitivity highly superior to DSC.

One must remember that static methods like DSC and dynamic methods such as DMTA lead to very different data for the same characteristics, such as glass transition.

Thermal analysis techniques (DSC, TGA, DMTA . . .) operating on mini or micro samples can detect pinpoint heterogeneities in final parts that bulk analysis methods such as rheometry are unable to do. Transient variations of moulding parameters, local design mistakes, internal stresses that influence the properties of the final product, notably impact behaviour, dimensional stability, warpage . . . can be displayed.

3.3 ISO standards concerning polymer testing

The TPEs are often tested with elastomer standards; some thermoplastics and TPEs are used as adhesives. Sometimes PE and more rarely PVC are crosslinked. Consequently, the following standards, while mainly concerning thermoplastics and composites, also include adhesives and elastomers.

3.3.1 Moulding of test specimens

ISO 294-2:1996 Plastics – Injection moulding of test specimens of thermoplastic materials – Part 2: Small tensile bars

3.3.2 Mechanical properties

Tensile properties

ISO 37:1994 Rubber, vulcanized or thermoplastic – Determination of tensile stress–strain properties

ISO 527-1:1994 Plastics – Determination of tensile properties – Part 1: General principles

ISO 527-2:1994 Plastics – Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics

ISO 527-3:2001 Plastics – Determination of tensile properties – Part 3: Test conditions for films and sheets

ISO 527-4:1997 Plastics – Determination of tensile properties – Part 4: Test conditions for isotropic and orthotropic fibre-reinforced plastic composites

ISO 527-5:1997 Plastics – Determination of tensile properties – Part 5: Test conditions for unidirectional fibre-reinforced plastic composites

ISO 1798:1997 Flexible cellular polymeric materials – Determination of tensile strength and elongation at break

ISO 1926:1979 Cellular plastics – Determination of tensile properties of rigid materials

ISO 4587:2003 Adhesives – Determination of tensile lap-shear strength of rigid-to-rigid bonded assemblies

ISO 5893:2002 Rubber and plastics test equipment – Tensile, flexural and compression types (constant rate of traverse) – Specification

ISO 6237:2003 Adhesives – Wood-to-wood adhesive bonds – Determination of shear strength by tensile loading

ISO 6922:1987 Adhesives – Determination of tensile strength of butt joints

Flexural properties

ISO 178:2004 Plastics – Determination of flexural properties

ISO 1209-1:1990 Cellular plastics, rigid – Flexural tests – Part 1: Bending test

ISO 1209-2:1990 Cellular plastics, rigid – Flexural tests – Part 2: Determination of flexural properties

ISO 3597-2:2003 Textile-glass-reinforced plastics – Determination of mechanical properties on rods made of roving-reinforced resin – Part 2: Determination of flexural strength

ISO 5893:2002 Rubber and plastics test equipment – Tensile, flexural and compression types (constant rate of traverse) – Specification

ISO 6721-3:1995 Plastics – Determination of dynamic mechanical properties – Part 3: Flexural vibration – Resonance-curve method

ISO 6721-5:1996 Plastics – Determination of dynamic mechanical properties – Part 5: Flexural vibration – Non-resonance method

ISO 14125:2001 Fibre-reinforced plastic composites – Determination of flexural properties

Compression properties

ISO 844:2001 Rigid cellular plastics – Determination of compression properties

ISO 3386-1:1986 Polymeric materials, cellular flexible – Determination of stress–strain characteristics in compression – Part 1: Low-density materials

ISO 3386-2:1997 Flexible cellular polymeric materials – Determination of stress–strain characteristics in compression – Part 2: High-density materials

ISO 5893:2002 Rubber and plastics test equipment – Tensile, flexural and compression types (constant rate of traverse) – Specification

ISO 7743:2004 Rubber, vulcanized or thermoplastic – Determination of compression stress-strain properties

ISO 13362:2000 Flexible cellular polymeric materials – Determination of compression set under humid conditions

Shear properties

ISO 1827:1991 Rubber, vulcanized or thermoplastic – Determination of modulus in shear or adhesion to rigid plates – Quadruple shear method

ISO 1922:2001 Rigid cellular plastics – Determination of shear strength

ISO 4587:2003 Adhesives – Determination of tensile lap-shear strength of rigid-to-rigid bonded assemblies

ISO 6237:2003 Adhesives – Wood-to-wood adhesive bonds – Determination of shear strength by tensile loading

ISO 6238:2001 Adhesives – Wood-to-wood adhesive bonds – Determination of shear strength by compressive loading

ISO 6721-6:1996 Plastics – Determination of dynamic mechanical properties – Part 6: Shear vibration – Non-resonance method

ISO 6721-8:1997 Plastics – Determination of dynamic mechanical properties – Part 8: Longitudinal and shear vibration – Wave-propagation method

ISO 6721-10:1999 Plastics – Determination of dynamic mechanical properties – Part 10: Complex shear viscosity using a parallel-plate oscillatory rheometer

ISO 9311-2:2002 Adhesives for thermoplastic piping systems – Part 2: Determination of shear strength

ISO 9653:1998 Adhesives – Test method for shear impact strength of adhesive bonds

ISO 9664:1993 Adhesives – Test methods for fatigue properties of structural adhesives in tensile shear

ISO 10123:1990 Adhesives – Determination of shear strength of anaerobic adhesives using pin-and-collar specimens

ISO 11003-1:2001 Adhesives – Determination of shear behaviour of structural adhesives – Part 1: Torsion test method using butt-bonded hollow cylinders

ISO 11003-2:2001 Adhesives – Determination of shear behaviour of structural adhesives – Part 2: Tensile test method using thick adherents

ISO 13445:2003 Adhesives – Determination of shear strength of adhesive bonds between rigid substrates by the block-shear method

ISO 14129:1997 Fibre-reinforced plastic composites – Determination of the in-plane shear stress/shear strain response, including the in-plane shear modulus and strength, by the plus or minus 45 degree tension test method

ISO 15108:1998 Adhesives – Determination of strength of bonded joints using a bending-shear method

ISO 15310:1999 Fibre-reinforced plastic composites – Determination of the in-plane shear modulus by the plate twist method

Torsion properties

ISO 458-1:1985 Plastics – Determination of stiffness in torsion of flexible materials – Part 1: General method

ISO 458-2:1985 Plastics – Determination of stiffness in torsion of flexible materials – Part 2: Application to plasticized compounds of homopolymers and copolymers of vinyl chloride

ISO 4663:1986 Rubber – Determination of dynamic behaviour of vulcanizates at low frequencies – Torsion pendulum method

ISO 6721-2:1995 Plastics – Determination of dynamic mechanical properties – Part 2: Torsion-pendulum method

ISO 11003-1:2001 Adhesives – Determination of shear behaviour of structural adhesives – Part 1: Torsion test method using butt-bonded hollow cylinders

Interlaminar properties

ISO 3597-4:2003 Textile-glass-reinforced plastics – Determination of mechanical properties on rods made of roving-reinforced resin – Part 4: Determination of apparent interlaminar shear strength

ISO 14130:1997 Fibre-reinforced plastic composites – Determination of apparent interlaminar shear strength by short-beam method

ISO 15024:2001 Fibre-reinforced plastic composites – Determination of mode I interlaminar fracture toughness, GIC, for unidirectionally reinforced materials

Hardness

ISO 48:1994 Rubber, vulcanized or thermoplastic – Determination of hardness (hardness between 10 IRHD and 100 IRHD)

ISO 868:2003 Plastics and ebonite – Determination of indentation hardness by means of a durometer (Shore hardness)

ISO 2039-1:2001 Plastics – Determination of hardness – Part 1: Ball indentation method

ISO 2039-2:1987 Plastics – Determination of hardness – Part 2: Rockwell hardness

ISO 2439:1997 Flexible cellular polymeric materials – Determination of hardness (indentation technique)

ISO 6123-1:1982 Rubber or plastics covered rollers – Specifications – Part 1: Requirements for hardness

ISO 7267-1:1997 Rubber-covered rollers – Determination of apparent hardness – Part 1: IRHD method

ISO 7267-2:1986 Rubber-covered rollers – Determination of apparent hardness – Part 2: Shore-type durometer method

ISO 7267-3:1988 Rubber-covered rollers – Determination of apparent hardness – Part 3: Pusey and Jones method

ISO 7619:2004 Rubber – Determination of indentation hardness by means of pocket hardness meters

Impact testing

ISO 179-1:2000 Plastics – Determination of Charpy impact properties – Part 1: Non-instrumented impact test

ISO 179-2:1998 Plastics – Determination of Charpy impact properties – Part 2: Instrumented impact test

ISO 180:2000 Plastics – Determination of Izod impact strength

ISO 974:2000 Plastics – Determination of the brittleness temperature by impact

ISO 2897-1:1997 Plastics – Impact-resistant polystyrene (PS-I) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 2897-2:2003 Plastics – Impact-resistant polystyrene (PS-I) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 6402-2:2003 Plastics – Impact-resistant acrylonitrile/styrene (ASA, AES, ACS) moulding and extrusion materials, excluding butadiene-modified materials – Part 2: Preparation of test specimens and determination of properties

ISO 6603-1:2000 Plastics – Determination of puncture impact behaviour of rigid plastics – Part 1: Non-instrumented impact testing

ISO 6603-2:2000 Plastics – Determination of puncture impact behaviour of rigid plastics – Part 2: Instrumented impact testing

ISO 7765-1:1988 Plastics film and sheeting – Determination of impact resistance by the free-falling dart method – Part 1: Staircase methods

ISO 7765-2:1994 Plastics film and sheeting – Determination of impact resistance by the free-falling dart method – Part 2: Instrumented puncture test

ISO 8256:1991 Plastics – Determination of tensile-impact strength

ISO 9653:1998 Adhesives – Test method for shear impact strength of adhesive bonds

ISO 11343:2003 Adhesives – Determination of dynamic resistance to cleavage of high strength adhesive bonds under impact conditions – Wedge impact method

ISO 13802:1999 Plastics – Verification of pendulum impact-testing machines – Charpy, Izod and tensile impact-testing

ISO 14631:1999 Extruded sheets of impact-modified polystyrene (PS-I) – Requirements and test methods

3.3.3 Thermomechanical properties

HDT

ISO 75-1:2004 Plastics – Determination of temperature of deflection under load – Part 1: General test method

ISO 75-2:2004 Plastics – Determination of temperature of deflection under load – Part 2: Plastics and ebonite

ISO 75-3:2004 Plastics – Determination of temperature of deflection under load – Part 3: High-strength thermosetting laminates and long-fibre-reinforced plastics

Vicat softening temperature

ISO 306:1994 Plastics – Thermoplastic materials – Determination of Vicat softening temperature (VST)

Low temperature

ISO 812:1991 Rubber, vulcanized – Determination of low-temperature brittleness

ISO 974:2000 Plastics – Determination of the brittleness temperature by impact

ISO 1432:1988 Rubber, vulcanized or thermoplastic – Determination of low temperature stiffening (Gehman test)

ISO 2921:1997 Rubber, vulcanized – Determination of low-temperature characteristics – Temperature-retraction procedure (TR test)

Crystallization

ISO 6471:1994 Rubber, vulcanized – Determination of crystallization effects under compression

ISO 3387:1994 Rubber – Determination of crystallization effects by hardness measurements

ISO 11357-3:1999 Plastics – Differential scanning calorimetry (DSC) – Part 3: Determination of temperature and enthalpy of melting and crystallization

ISO 11357-7:2002 Plastics – Differential scanning calorimetry (DSC) – Part 7: Determination of crystallization kinetics

3.3.4 Long-term properties

Accelerated ageing

ISO 188:1998 Rubber, vulcanized or thermoplastic – Accelerated ageing and heat resistance tests

ISO 2440:1997 Flexible and rigid cellular polymeric materials – Accelerated ageing tests

ISO 6914:2004 Rubber, vulcanized – Determination of ageing characteristics by measurement of stress at a given elongation

ISO 9142:2003 Adhesives – Guide to the selection of standard laboratory ageing conditions for testing bonded joints

Creep

ISO 899-1:2003 Plastics – Determination of creep behaviour – Part 1: Tensile creep

ISO 899-2:2003 Plastics – Determination of creep behaviour – Part 2: Flexural creep by three-point loading

ISO 2285:2001 Rubber, vulcanized or thermoplastic – Determination of tension set under constant elongation, and of tension set, elongation and creep under constant tensile load

ISO 7616:1986 Cellular plastics, rigid – Determination of compressive creep under specified load and temperature conditions

ISO 7850:1986 Cellular plastics, rigid – Determination of compressive creep

ISO 8013:1988 Rubber, vulcanized – Determination of creep in compression or shear

ISO 10066:1991 Flexible cellular polymeric materials – Determination of creep in compression

Compression and tension set

ISO 815:1991 Rubber, vulcanized or thermoplastic – Determination of compression set at ambient, elevated or low temperatures

ISO 1856:2000 Flexible cellular polymeric materials – Determination of compression set

ISO 2285:2001 Rubber, vulcanized or thermoplastic – Determination of tension set under constant elongation, and of tension set, elongation and creep under constant tensile load

Relaxation

ISO 3384:2001 Rubber, vulcanized or thermoplastic – Determination of stress relaxation in compression at ambient and at elevated temperatures

Fatigue and dynamic mechanical properties

ISO 6721-4:1994 Plastics – Determination of dynamic mechanical properties – Part 4: Tensile vibration – Non-resonance method

ISO 6721-9:1997 Plastics – Determination of dynamic mechanical properties – Part 9: Tensile vibration – Sonic-pulse propagation method

ISO 3385:1989 Flexible cellular polymeric materials – Determination of fatigue by constant-load pounding

ISO 4666-1:1982 Rubber, vulcanized – Determination of temperature rise and resistance to fatigue in flexometer testing – Part 1: Basic principles

ISO 4666-2:1982 Rubber, vulcanized – Determination of temperature rise and resistance to fatigue in flexometer testing – Part 2: Rotary flexometer

ISO 4666-3:1982 Rubber, vulcanized – Determination of temperature rise and resistance to fatigue in flexometer testing – Part 3: Compression flexometer

ISO 6943:1984 Rubber, vulcanized – Determination of tension fatigue

ISO 8659:1989 Thermoplastics valves – Fatigue strength – Test method

ISO 9664:1993 Adhesives – Test methods for fatigue properties of structural adhesives in tensile shear

ISO 15850:2002 Plastics – Determination of tension-tension fatigue crack propagation – Linear elastic fracture mechanics (LEFM) approach

Light resistance

ISO 4582:1998 Plastics – Determination of changes in colour and variations in properties after exposure to daylight under glass, natural weathering or laboratory light sources

ISO 4892-1:1999 Plastics – Methods of exposure to laboratory light sources – Part 1: General guidance

ISO 4892-2:1994 Plastics – Methods of exposure to laboratory light sources – Part 2: Xenon-arc sources

ISO 4892-3:1994 Plastics – Methods of exposure to laboratory light sources – Part 3: Fluorescent UV lamps

ISO 4892-4:1994 Plastics – Methods of exposure to laboratory light sources – Part 4: Open-flame carbon-arc lamps

3.3.5 Fluid contact behaviour

Chemical behaviour

ISO 175:1999 Plastics – Methods of test for the determination of the effects of immersion in liquid chemicals

ISO 4661-2:1987 Rubber, vulcanized – Preparation of samples and test pieces – Part 2: Chemical tests

ISO 6252:1992 Plastics – Determination of environmental stress cracking (ESC) – Constant-tensile-stress method

ISO/TR 7620:1986 Rubber materials – Chemical resistance

Gas, humidity and vapour permeability

ISO 1663:1999 Rigid cellular plastics – Determination of water vapour transmission properties

ISO 2556:1974 Plastics – Determination of the gas transmission rate of films and thin sheets under atmospheric pressure – Manometric method

ISO 6179:1998 Rubber, vulcanized or thermoplastic – Rubber sheets and rubber-coated fabrics – Determination of transmission rate of volatile liquids (gravimetric technique)

ISO 15105-1:2002 Plastics – Film and sheeting – Determination of gas-transmission rate – Part 1: Differential-pressure method

ISO 15106-1:2003 Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 1: Humidity detection sensor method

ISO 15106-2:2003 Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 2: Infrared detection sensor method

ISO 15106-3:2003 Plastics – Film and sheeting – Determination of water vapour transmission rate – Part 3: Electrolytic detection sensor method

3.3.6 Electrical properties

ISO 1853:1998 Conducting and dissipative rubbers, vulcanized or thermoplastic – Measurement of resistivity

ISO 2878:1987 Rubber, vulcanized – Antistatic and conductive products – Determination of electrical resistance

ISO 2882:1979 Rubber, vulcanized – Antistatic and conductive products for hospital use – Electrical resistance limits

ISO 2883:1980 Rubber, vulcanized – Antistatic and conductive products for industrial use – Electrical resistance limits

ISO 3915:1981 Plastics – Measurement of resistivity of conductive plastics

3.3.7 Oxygen index, flammability, smoke generation

ISO 4589-1:1996 Plastics – Determination of burning behaviour by oxygen index – Part 1: Guidance

ISO 4589-2:1996 Plastics – Determination of burning behaviour by oxygen index – Part 2: Ambient-temperature test

ISO 4589-3:1996 Plastics – Determination of burning behaviour by oxygen index – Part 3: Elevated-temperature test

ISO 5659-1:1996 Plastics – Smoke generation – Part 1: Guidance on optical-density testing

ISO 5659-2:1997 Plastics – Smoke generation – Part 2: Determination of optical density by a single-chamber test

ISO/TR 5659-3:1999 Plastics – Smoke generation – Part 3: Determination of optical density by a dynamic-flow method

ISO 11907-1:1998 Plastics – Smoke generation – Determination of the corrosivity of fire effluents – Part 1: Guidance

ISO 11907-2:1995 Plastics – Smoke generation – Determination of the corrosivity of fire effluents – Part 2: Static method

ISO 11907-3:1998 Plastics – Smoke generation – Determination of the corrosivity of fire effluents – Part 3: Dynamic decomposition method using a travelling furnace

ISO 11907-4:1998 Plastics – Smoke generation – Determination of the corrosivity of fire effluents – Part 4: Dynamic decomposition method using a conical radiant heater

ISO 13774:1998 Rubber and plastics hoses for fuels for internal combustion engines – Method of test for flammability

3.3.8 Optical properties

ISO 1600:1990 Plastics – Cellulose acetate – Determination of light absorption on moulded specimens produced using different periods of heating

ISO 13468-1:1996 Plastics – Determination of the total luminous transmittance of transparent materials – Part 1: Single-beam instrument

ISO 13468-2:1999 Plastics – Determination of the total luminous transmittance of transparent materials – Part 2: Double-beam instrument

ISO 14782:1999 Plastics – Determination of haze for transparent materials

3.4 Analysis and diagnostic equipment

Thermoplastics are complex materials and need multiple technologies and equipment for their analysis and for diagnosis of failures. Let us quote, for example, without claiming to be exhaustive:

- Visual examination
  - optical microscopy, stereomicroscopy, micro and macro photography
  - microtome
  - electronic microscopy: scanning mode (SEM), transmission (TEM)
  - atomic force microscopy (AFM)
  - image analyser
  - particle size analyser.
- Physicochemical analysis
  - infrared, UV-visible spectrophotometry, IR microspectroscopy
  - gas chromatography, GC-MS
  - liquid chromatography: GPC, HPLC . . .
  - thin layer chromatography
  - mass spectrometry
  - NMR
  - X-ray fluorescence
  - elemental analysis C, H, N, S, O
  - Karl-Fischer humidity determiner
  - thermogravimetric analysis (TGA)
  - thermomechanical analysis (TMA)
  - dynamic mechanical thermal analysis (DMTA)

  - differential scanning calorimetry (DSC)
  - X-ray diffraction . . .
- Rheometry
  - rheometers: capillary, torque . . .
  - melt flow index, melt flow rate
  - viscometers: Brookfield and others
  - gel time determination equipment.
- Physical and mechanical testing
  - tension, compression and flexion dynamometers
  - dynamic testing machines
  - impact tests: Charpy, Izod, tensile-impact, possibly instrumented
  - hardness: Shore A and D, Rockwell, ball, Barcol, Vickers
  - softening temperatures: Vicat and HDT
  - low-temperature testers
  - abrasion and wear
  - gas permeability
  - photocolorimeter, brightness meter, yellowing index
  - light transmission, refractometer
  - acoustic emission equipment.
- Electrical properties
  - resistivity
  - arc resistance
  - dielectric strength.
- Fire behaviour
  - epiradiator, electric burner, radiant panel
  - oxygen index
  - flame propagation velocity: UL94 and other rating equipment
  - cone calorimeter
  - fume opacity equipment: NBS smoke chamber, fume meter, analysis of combustion fumes
  - specific equipment for specific industries: automotive . . .
- Ageing and long-term properties
  - ovens: dry and wet air
  - weathering: outdoor exposure, artificial exposure (Xenotest, WeatherOmeter, QUV Panel . . .)
  - ozone cabinets
  - creep
  - relaxation
  - chemical resistance, ESC.

3.5 Material selection

The first step is to prescribe specifications in an objective way:

- an undervaluation of the constraints leads to problems during use
- an overvaluation involves an overcharge due to the selection of materials that have unnecessarily high performance levels and costs, and due to part oversizing.

The following factors, among others, must be examined:
- targeted lifespan, end of life criteria
- temperature: extremes and average
- environment: outdoor exposure, light, moisture, ozone, corrosion, radiation . . .
- physical properties: transparency, thermal and electrical conductivity, gas permeability, tribological properties . . .
- mechanical properties: instantaneous, permanent or cyclic stresses, impact . . .
- chemical properties: risks of polymer corrosion, risks of environmental pollution by the plastic, food contact, desorption of ingredients in space vacuum, pollution of chemical and electrochemical baths, migration . . .
- electrical properties: influence of moisture, temperature and ageing
- dimensional tolerances
- weight
- price: does not only have to be considered per kilogram, but also according to the fundamental properties. The total lifetime cost, taking account of the expenses of assembly, maintenance, etc., is the true criterion.

It is necessary to remember that the combination of several factors often has a synergistic effect: a plastic resistant to a chemical in the absence of mechanical stress and at ambient temperature can crack quickly when exposed to the under load and be degraded more or less quickly in the event of a temperature rise.

Once the specification is established, a first pre-selection of the materials having the required minimal properties can be made using the following graphs (see Figures 3.11 to 3.38). For the selected polymer families, one should then refer to the corresponding monographs to determine those that satisfy all the points of the specifications.

Beware: because of a lack of space, not all thermoplastic families are plotted on each graph.

It is imperative that the final selection is made with the assistance of a polymer specialist.

3.6 Precision of the moulded parts

Plastics differ because of their morphology, structure, rheology, etc. The geometry of a part and the complexity of the corresponding mould vary. Consequently, the tolerances of a part depend on:
- polymer type
- part geometry
- processing concerns
- acceptable cost.

For example, the French standard NF T 58000 classifies:
- the various families of plastics into five categories according to the expected precision of the dimensions
- in each plastic category, there are four classes of precision:
  - ○ normal tolerances: normal checking of the processing and other procedures
  - ○ reduced tolerances: rigorous checking of the processing and other procedures
  - ○ precision tolerances: reinforced checking, use of special machines and tools, skilled workers, selection of the parts
  - ○ exceptional precision tolerances.

The costs increase with the required precision.

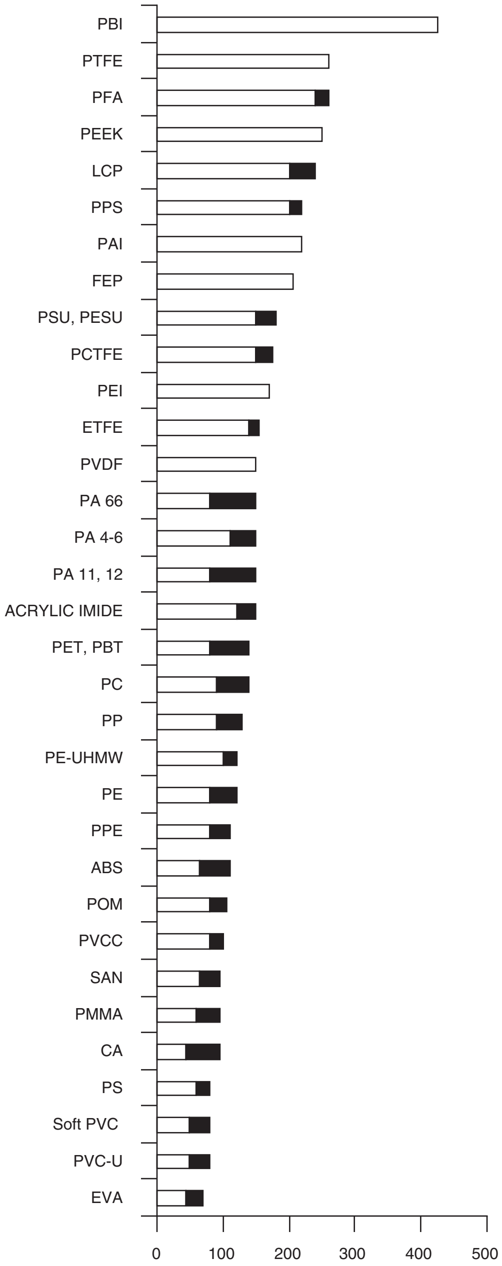


Figure 3.11. Examples of continuous use temperature in an unstressed state (°C)

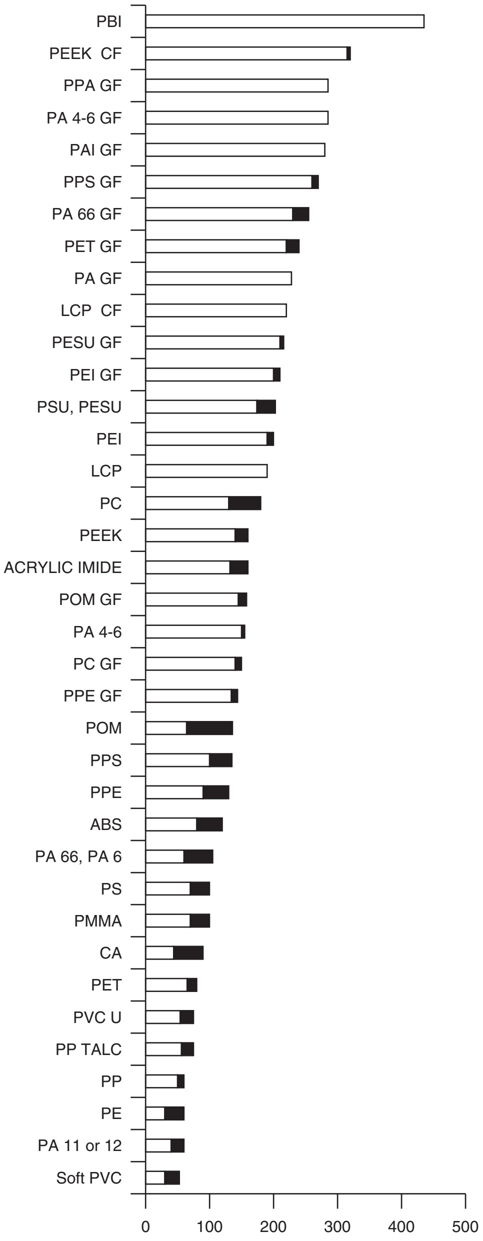


Figure 3.12. HDT A examples (°C)

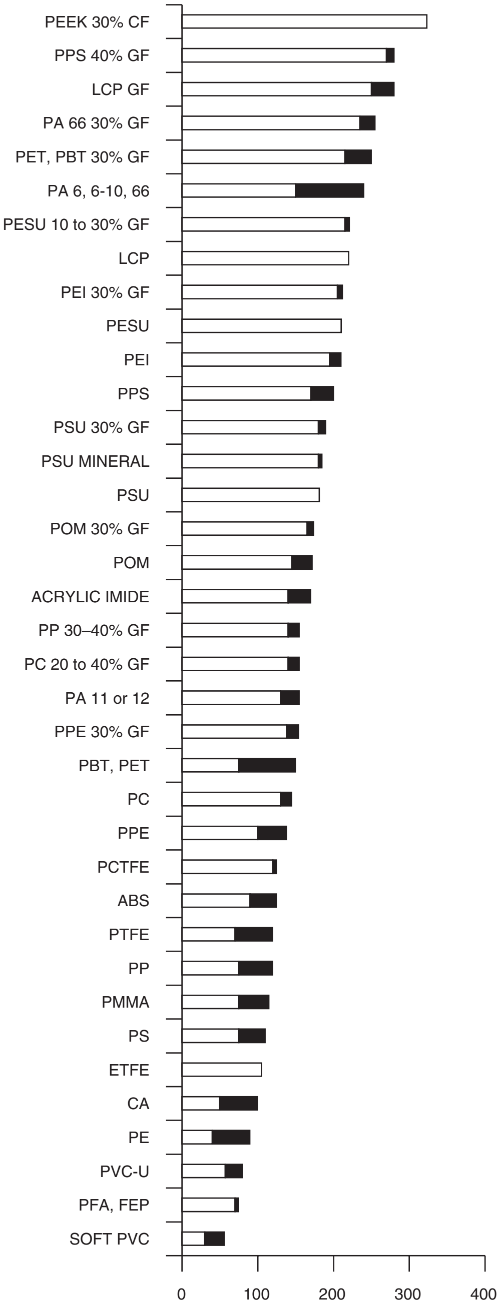


Figure 3.13. HDT B examples (°C)

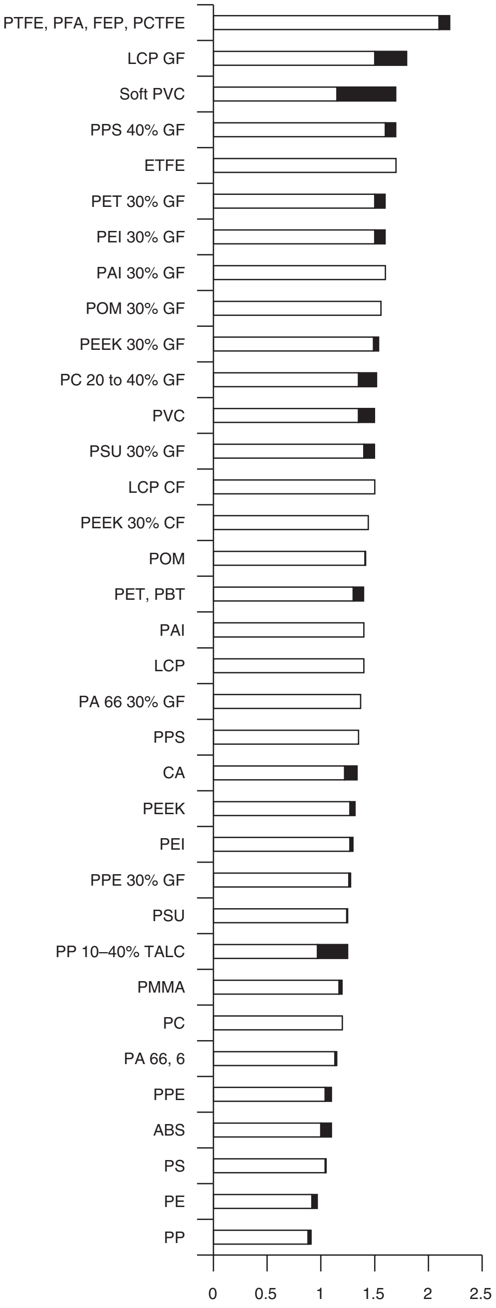


Figure 3.14. Density examples (g/cm^3)

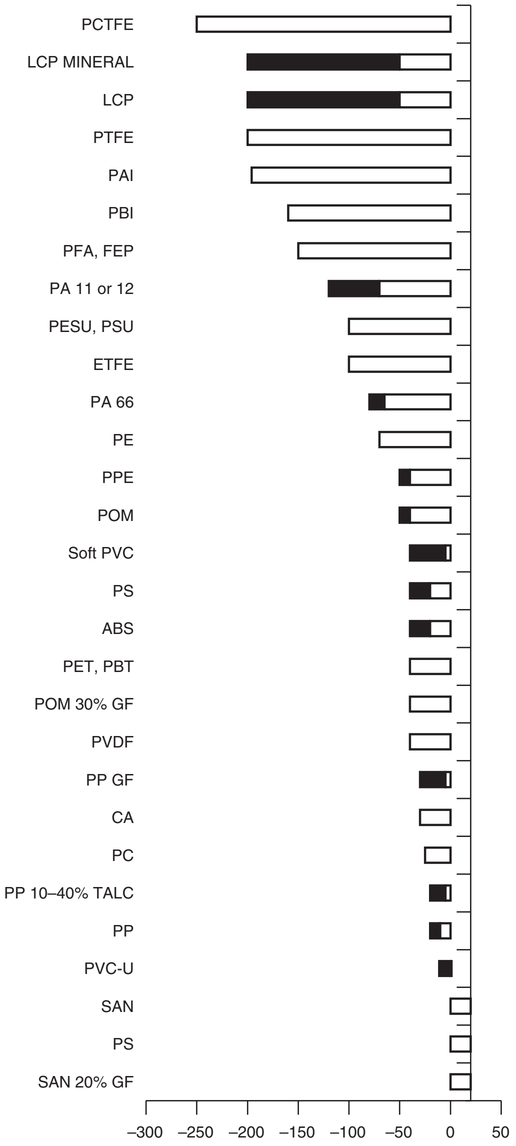


Figure 3.15. *Minimum service temperature examples (°C)*

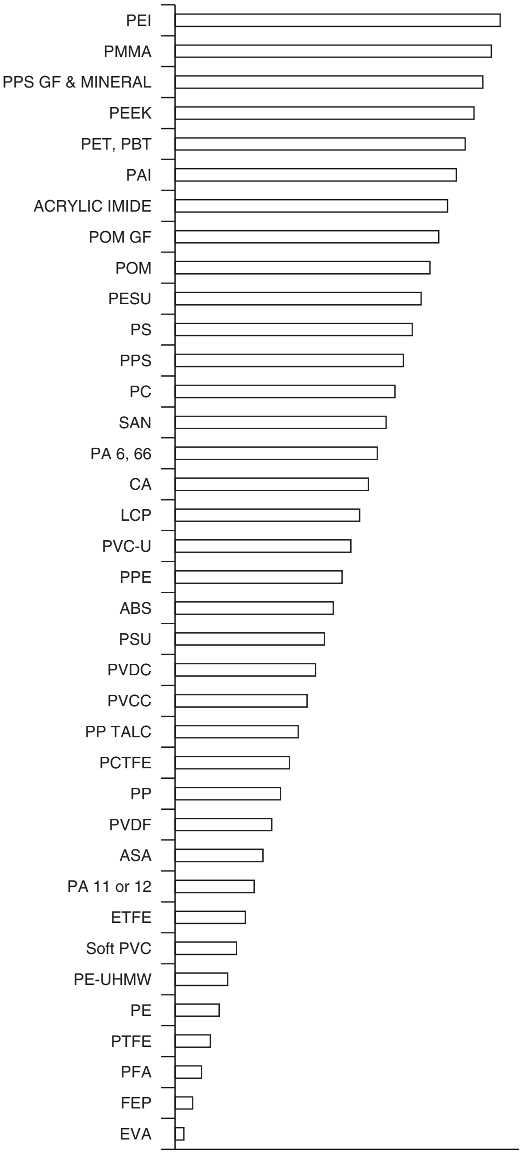


Figure 3.16. *Arbitrary hardness rating (no units)*

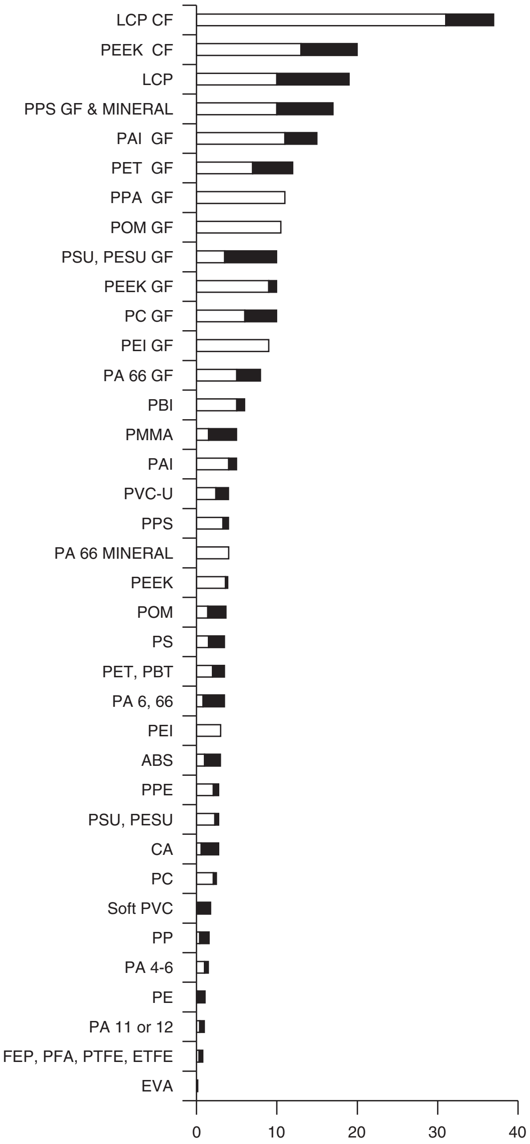


Figure 3.17. Tensile modulus examples (GPa)

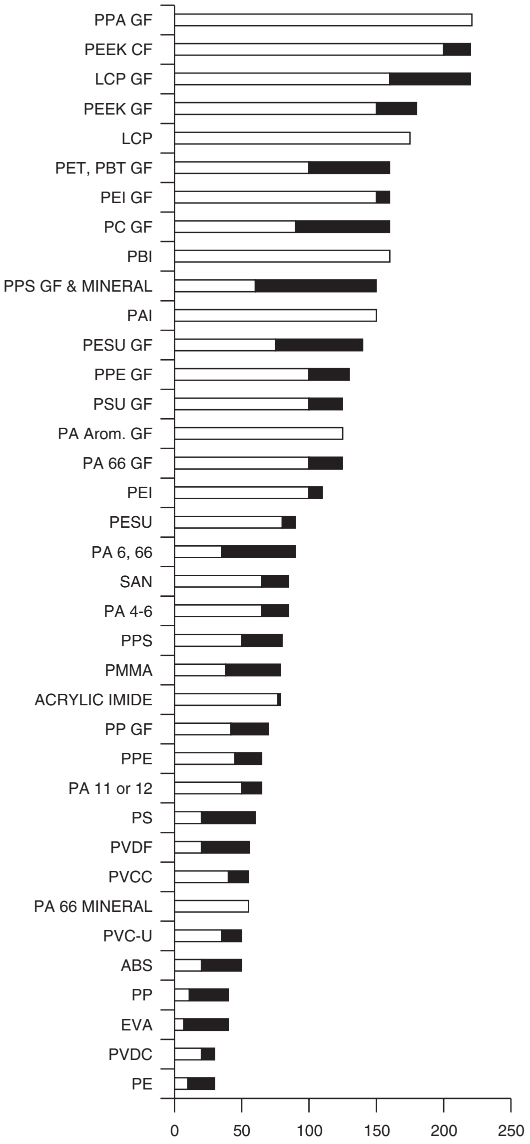


Figure 3.18. Stress at yield examples (MPa)

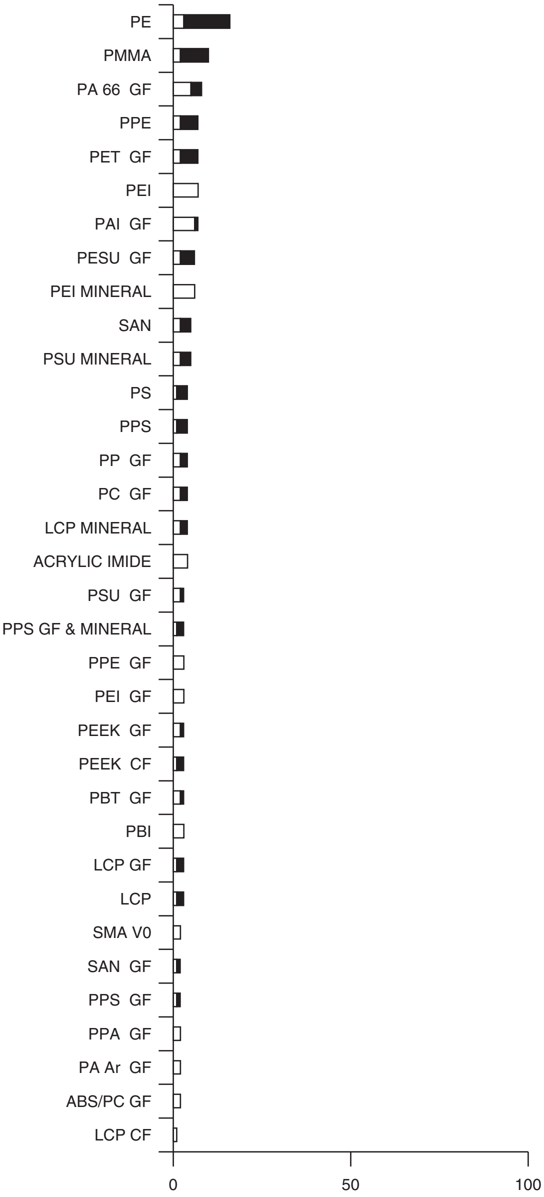


Figure 3.19. Strain at yield examples (%)

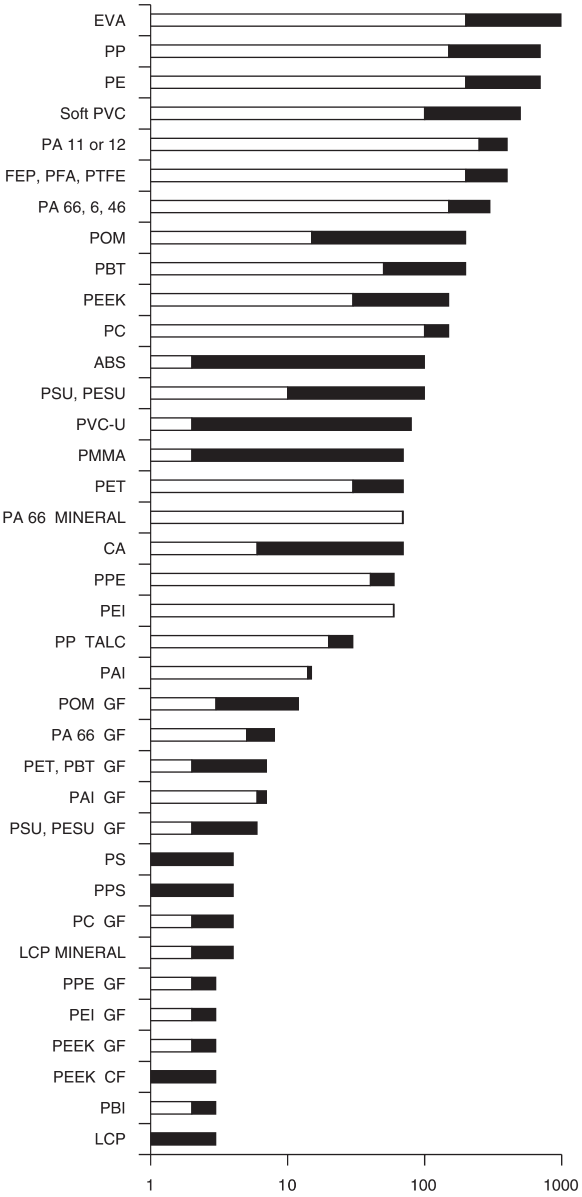


Figure 3.20. Elongation at break examples (%)

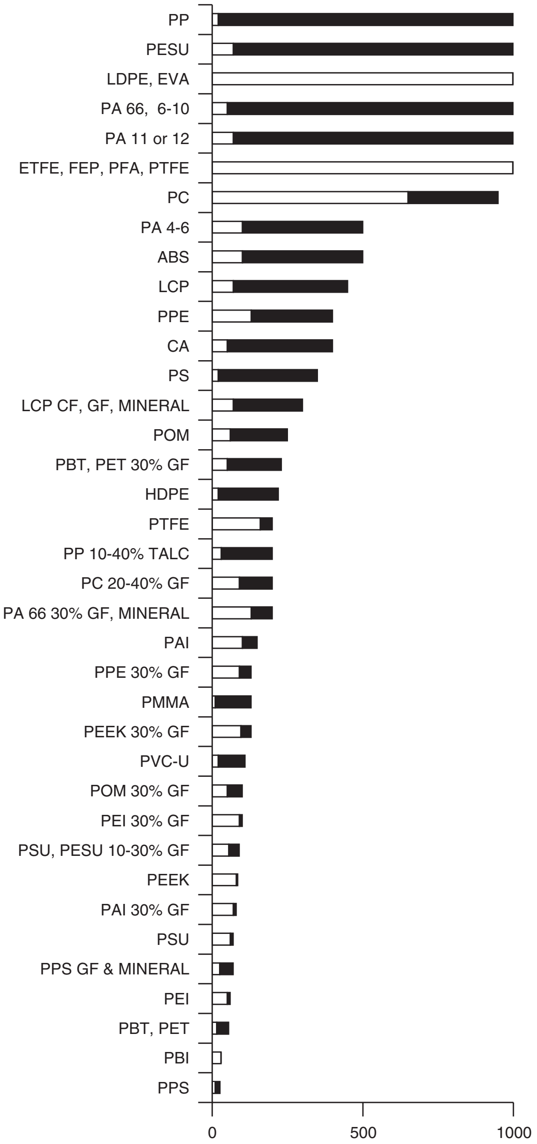


Figure 3.21. *Notched impact strength examples (J/m)*

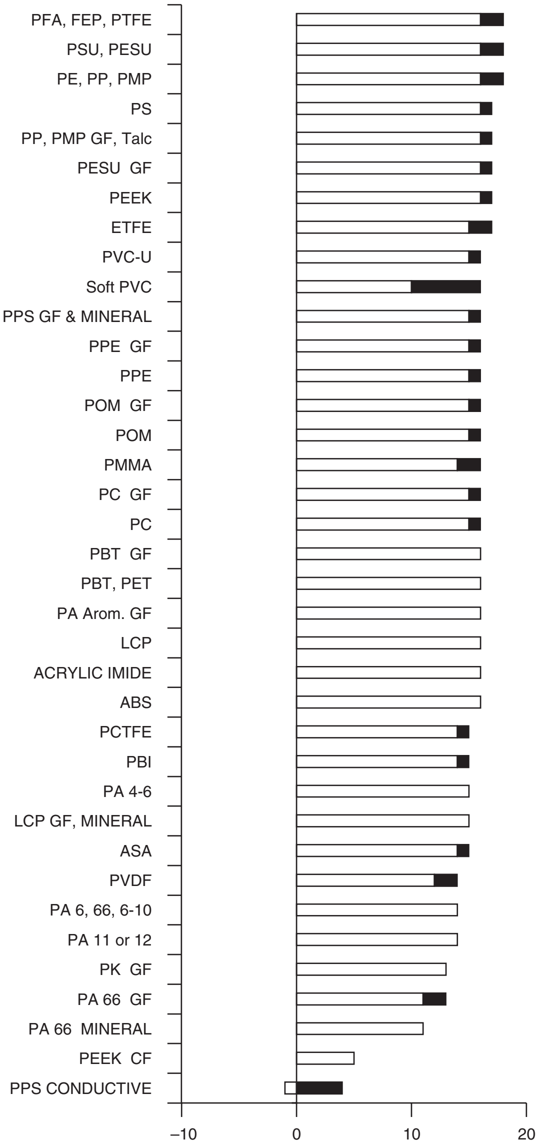


Figure 3.22. *Resistivity examples, log (ohm.cm)*

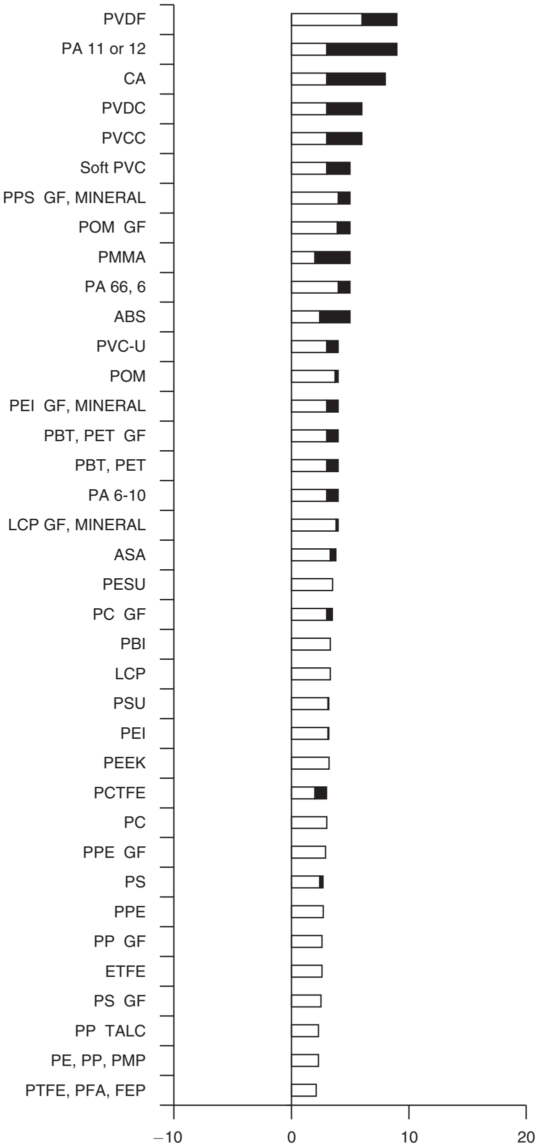


Figure 3.23. Dielectric rigidity examples (kV/mm)

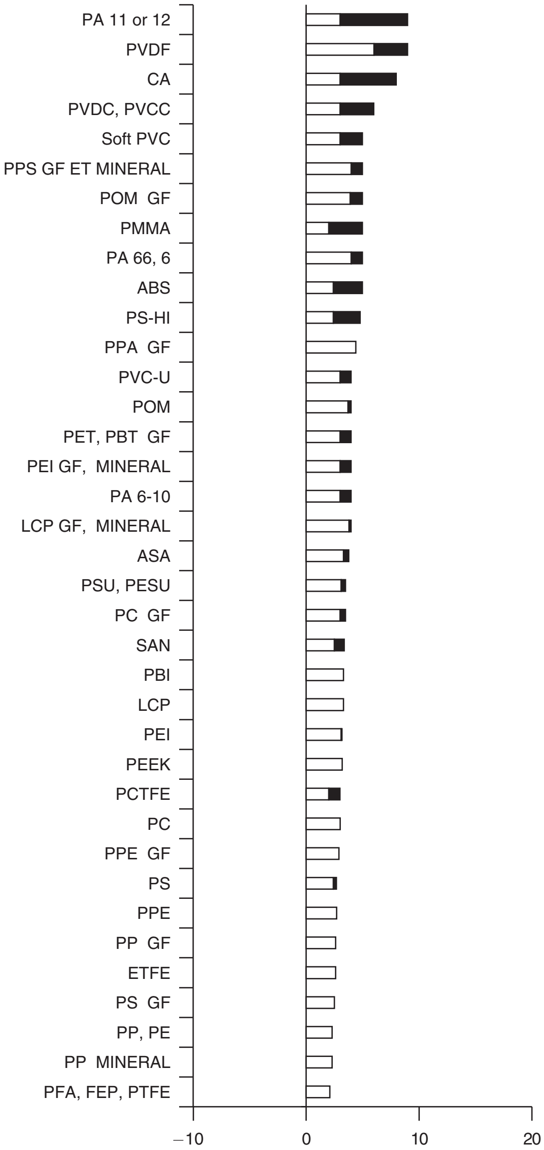


Figure 3.24. Dielectric constant examples (no units)

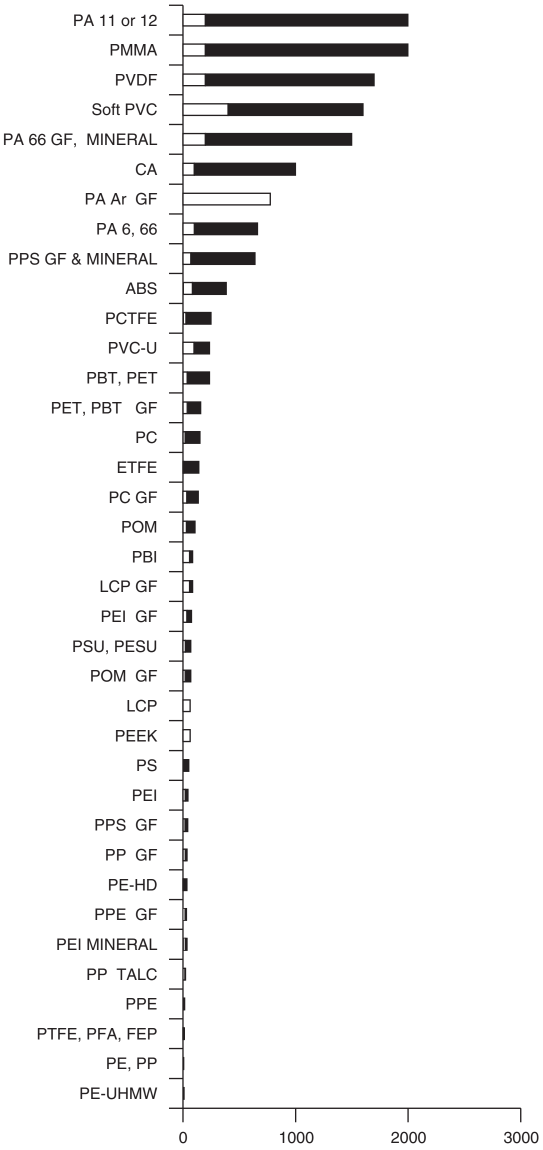


Figure 3.25. Dielectric loss factor examples (10^{-4})

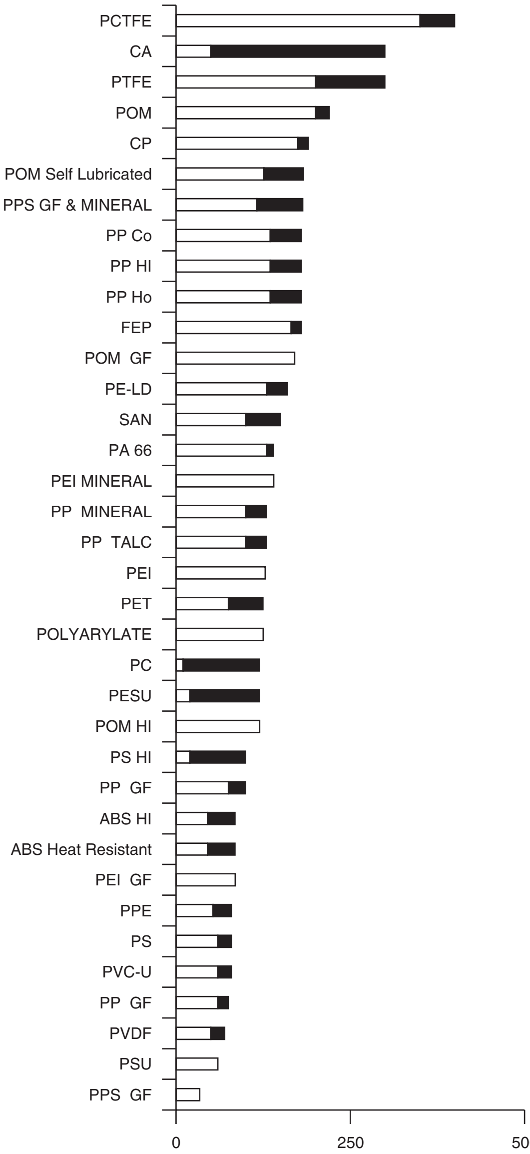


Figure 3.26. Arc resistance examples (s)

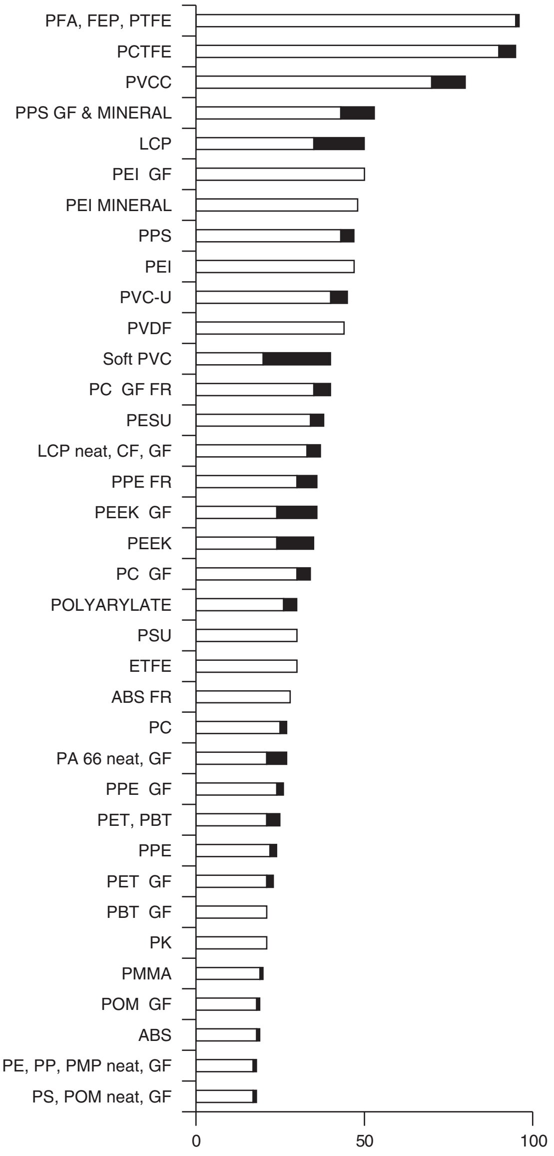


Figure 3.27. Oxygen index examples (%)

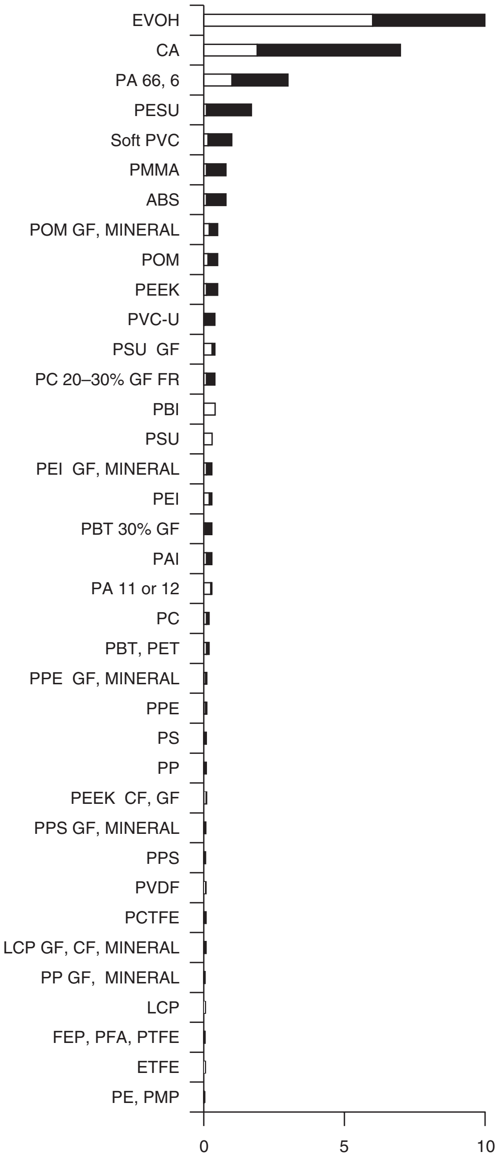


Figure 3.28. Water absorption examples, % after 24 h

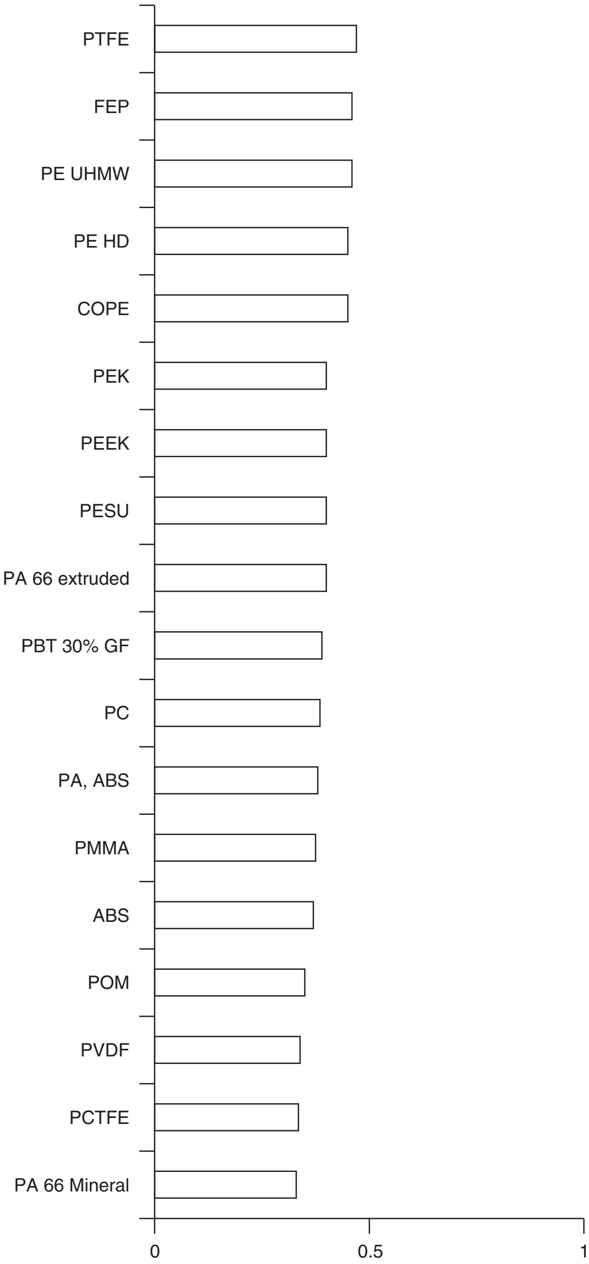


Figure 3.29. Poisson's ratio examples (no units)

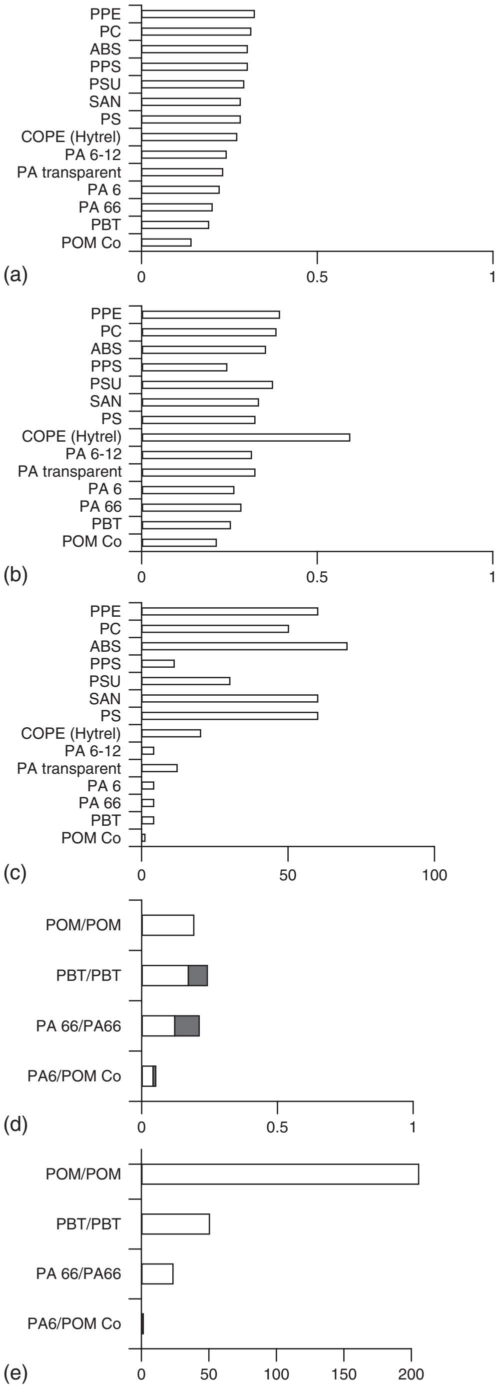


Figure 3.30. (a) Static coefficient of friction versus steel (no units); (b) Dynamic coefficient of friction versus steel (no units); (c) Friction versus steel: wear factor (arbitrary units); (d) Friction versus plastic: static and dynamic COF; (e) Friction versus plastic: wear factor (arbitrary unit)

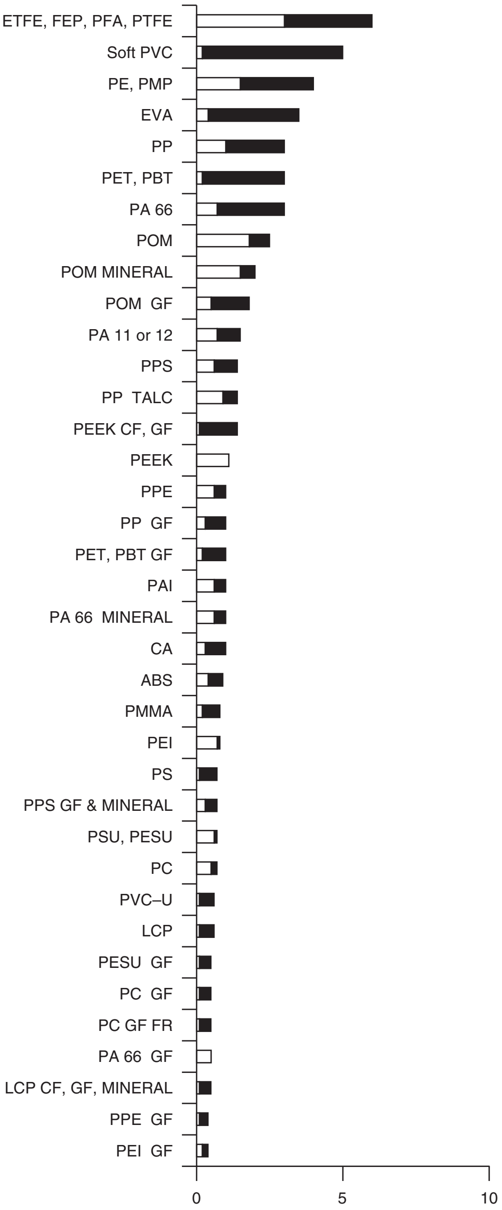


Figure 3.31. Shrinkage examples (%)

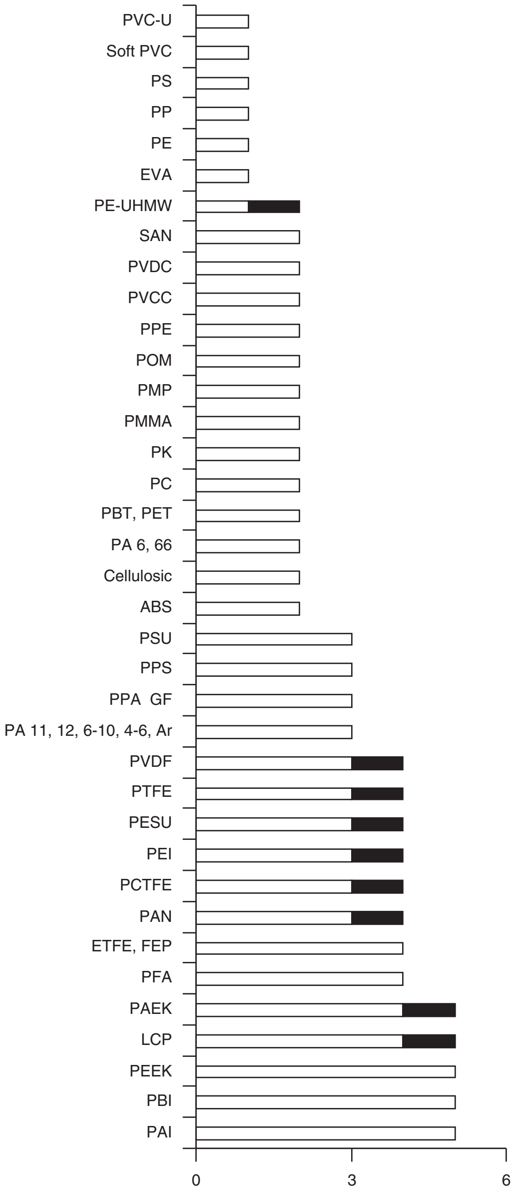


Figure 3.32. Price examples (arbitrary units)

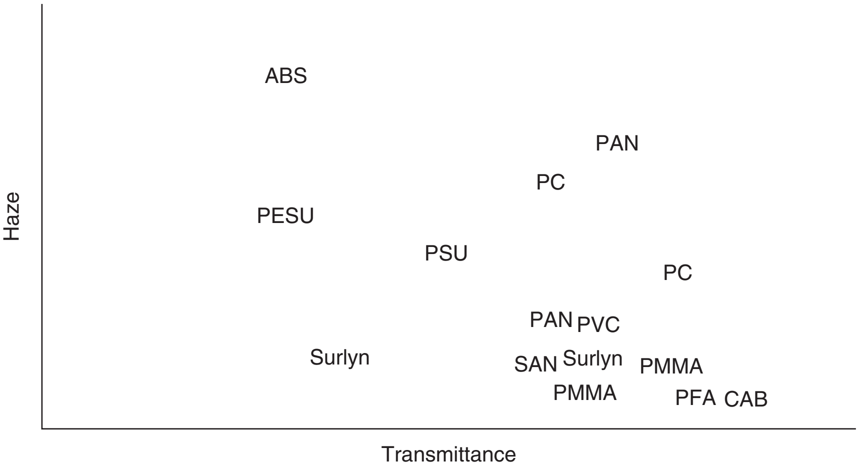


Figure 3.33. *Optical property examples*

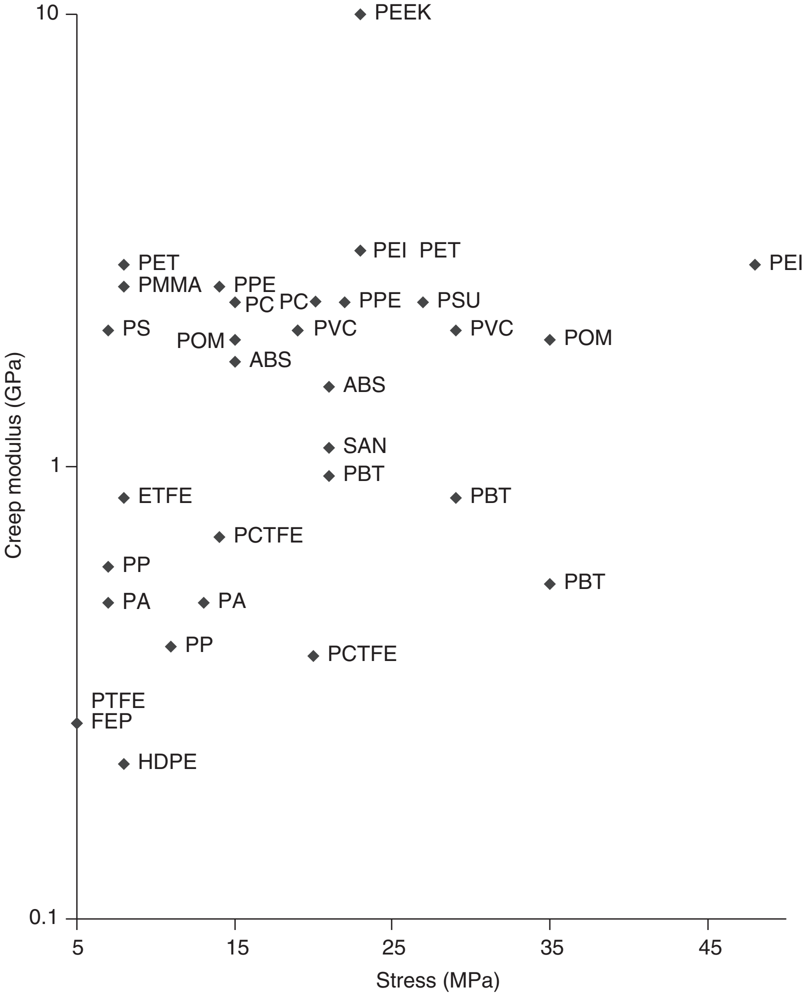


Figure 3.34. *Neat thermoplastics: 100 h creep modulus examples versus stress at 20°C*

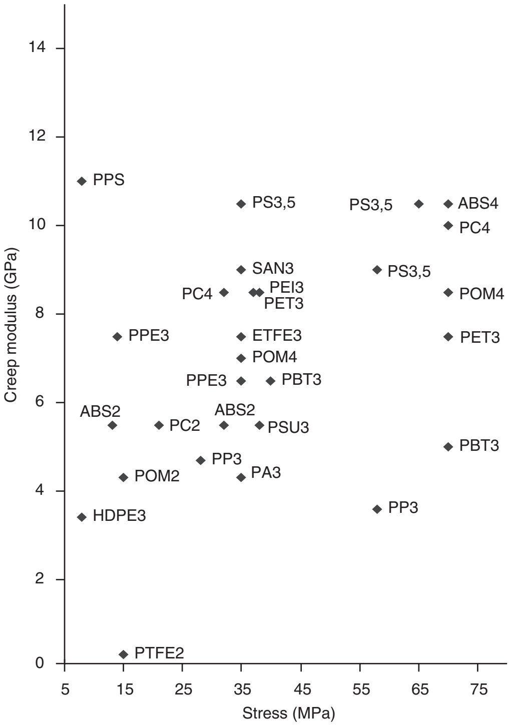


Figure 3.35. Reinforced thermoplastics: 100 h creep modulus examples versus stress at 20°C. A figure of 4 after the acronym indicates 40% glass fibre, etc.

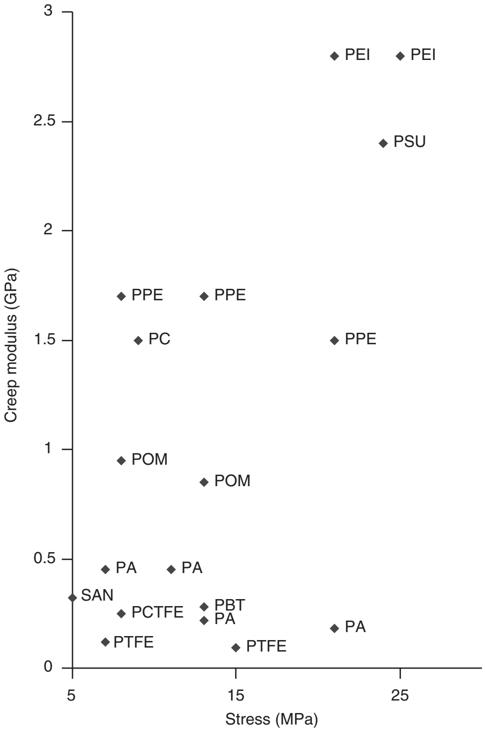


Figure 3.36. Neat thermoplastics: 100 h creep modulus examples versus stress at 65 ± 5°C

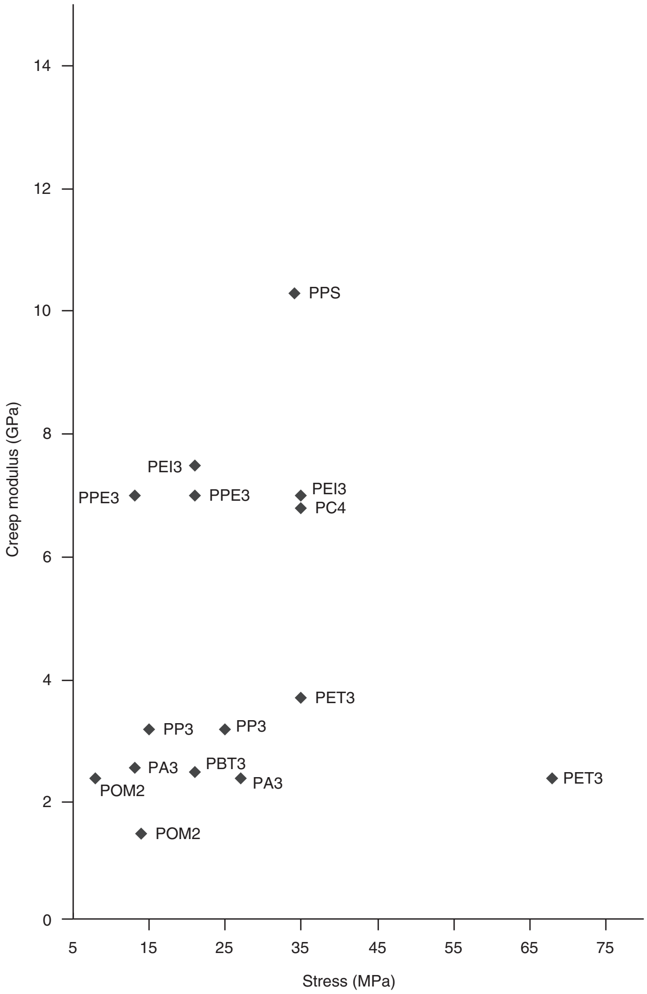


Figure 3.37. Reinforced thermoplastics: 100 h creep modulus examples versus stress at 65 ± 5°C. A figure of 4 after the acronym indicates 40% glass fibre, etc.

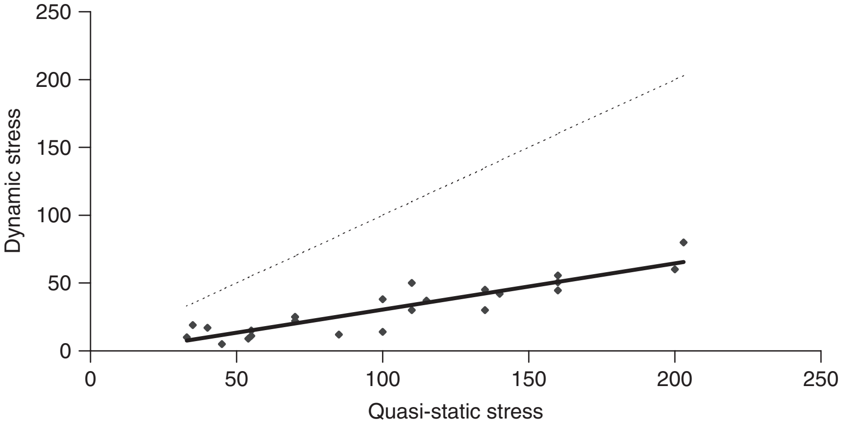


Figure 3.38. Examples of dynamic stress leading to failure at approximately 1 000 000 cycles at 20°C versus quasi-static stress at yield

Table 3.2, as an example, shows the tolerances for parts 10, 100 and 1000 mm long for the 'normal' and 'precision' classes.

Table 3.2 Examples of part tolerances for normal and precision classes

	Size (mm)	Tolerance class	
		Normal (±mm)	Precision (±mm)
Filled or neat ABS, amorphous PA, PC, PESU, amorphous PET,	10	0.20	0.07
PMMA, PPO, PS, PSU, rigid PVC, SB, SAN	100	0.50	0.20
Filled PA 6, 66, 6/10, 11, 12; PBT, PET, POM, PPS	1000	2.90	1.25
Mineral filled EP, MF, PF, UP	10	0.20	0.07
	100	0.50	0.20
	1000	2.90	1.30
Neat CA, CAB, CAP, PA 6, 66, 6/10, 11, 12; crystalline PBT, PET;	10	0.20	0.09
POM (<150 mm), EPDM modified PP PVC Shore D >50	100	0.60	0.29
	1000	4.40	1.90
Filled ETFE, PP, plasticized	10	0.20	0.09
High hardness TPE: PEBA, COPE, TPU	100	0.60	0.29
Filled PF and MF, prepregs	1000	4.40	1.90
Neat ETFE, FEP, PE, PFA, PP, plasticized PVC Shore D <50	10	0.20	0.11
TPE hardness Shore D <50	100	0.87	0.41
	1000	6.50	2.90

The same standard also fixes the tolerances for:

- angles, skins, ovalizations, ejection marks . . .
- shrink marks.

3.7 Schematic comparison of thermoplastic and composite properties

The following graphs and tables make it possible to quickly visualize some significant characteristics and to roughly position certain thermoplastics and their composites with respect to each other. The goal is only to make a first, very approximate, pre-rating. The reader must then consult the detailed monographs:

- to check the information whose graphical display may involve errors and approximations
- to seek results on other families and other grades that do not appear in the graphs for lack of space.

It must be recalled that:

- the visualized values for the unidirectional composites are those for the most favourable direction
- the procedures applied to thermoplastics are sometimes non-standard and this can affect the results recorded to some degree
- the indicated values are often examples that are not representative of the whole subfamily and are given purely as an indication
- in certain cases, the subfamily and commercial names of the grades specify only the reinforcement or the principal filler, whereas a secondary filler may be present in significant quantities and can influence the characteristics in a surprising way at first sight if one forgets this detail
- thermoplastics are sometimes used with reinforcements, some of which considerably modify the properties. It is necessary to be careful with the interpretation of the following

Table 3.3 Mechanical property examples for different reinforcements of polypropylene

	Reinforcement	Average tensile strength		Average impact strength	
		(MPa)	Variation (%)*	(J/m)	Variation (%)*
PP Ho	None	30	–	40	–
PP 10–40% Mineral	Spherical particles	21	−30	74	+85
PP 10–20% GF	Fibres	45	+50	97	+142
PP 30–40% GF	Fibres	56	+87	102	+155
PP 10–40% TALC	Platelets	24	−20	115	+187
PP Copolymer	Copolymer	32	+7	280	+600
PP High impact	Dispersed polymer	30	0	554	+1285

* Variation (%) relative to the value measured for neat homopolymer polypropylene.

graphs and to allot the property share to each component, matrix or reinforcement. Table 3.3 relating to various reinforced polypropylenes clearly shows the importance of the reinforcement

- lastly, be careful:
  - with the scales used as some are logarithmic
  - the ends of the bars in the graphs are maximum values of the given property for a thermoplastic family. Numerous grades in this family can have lower values.

Remember that the goal of the following figures is only to make a first, very approximate, pre-rating.

In Figure 3.33, the samples are films, sheets, bars or disks and the data are not strictly comparable and are only examples. Depending on the grade tested, several data points are possible for a given family depending on the test method used. These general indications are not necessarily representative of all the thermoplastic families and should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Figures 3.34 to 3.37: depending on the grade tested, several data points are possible for a given family depending on the test method used. These general indications are not necessarily representative of all the thermoplastic families and should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Figure 3.38: the samples are not comparable, methods are different and the data are only examples. Depending on the grade tested, several data points are possible for a given family depending on the test method used. Dynamic strength at failure is always inferior to static strength at break (indicated by the dashed line). These general indications are not necessarily representative of all the thermoplastic families and should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

3.8 Upgrading and customization of raw polymers

Each raw polymer has its set of interesting properties that can be modified in order to adapt to the requirements of each customer and application. Several routes are suitable:

- alloying of two compatible (or compatibilized) thermoplastics
- compounding with additives
- surface modification by painting, covering with film, metallization, surface treatment.

The upgrading of service properties mainly concerns:

- durability: stabilization, ageing, UV protection, hydrolysis . . .
- low-temperature behaviour, flexibility . . . : plasticization

- reinforcement: strength and modulus improvement
- toughening: impact strength improvement
- sensory properties: colour, gloss, odour . . .
- cost
- possibly, some specific characteristics such as fire behaviour, electrical or thermal characteristics, magnetic or tribological properties, biodegradability . . .

Figure 3.39 illustrates some examples of solutions to customize basic polymers.

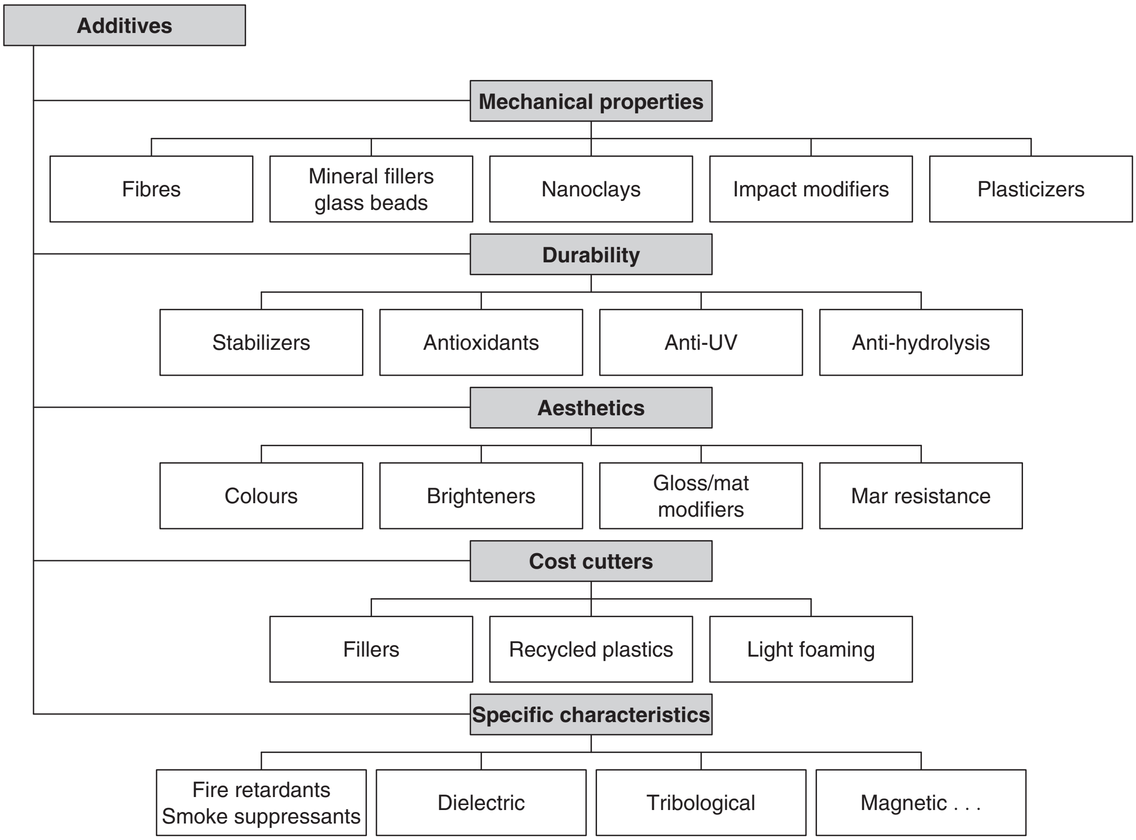


Figure 3.39. Widespread property upgrading and additive solution examples

For some specific thermoplastics, crosslinking is used to improve some properties induced by the formation of the 3D network.

3.8.1 Thermoplastic alloying

Thermoplastic families are diverse but their number is limited and often there are wide gaps between the properties of two basic polymer types. To bridge the gap, two polymer families can be mixed if they are compatible or if it is possible to compatibilize them with a third material.

Examples are numerous: ABS (the most widespread), ABS/PC, ABS/PA, ASA/PC, ASA/PVC, TPO, TPV, PPE (marketed grades are actually alloys with polystyrene or polyamide), PA/PP . . .

For a suitable mixing of two components, the properties of an alloy, including the cost, are generally intermediate between those of each component, as we can see in Figure 3.40 for an ABS/PC:

- mechanical properties: tensile strength (TS), elongation at break (EB), and notched impact strength
- thermomechanical properties: HDT A
- thermal properties: continuous use temperature (CUT).

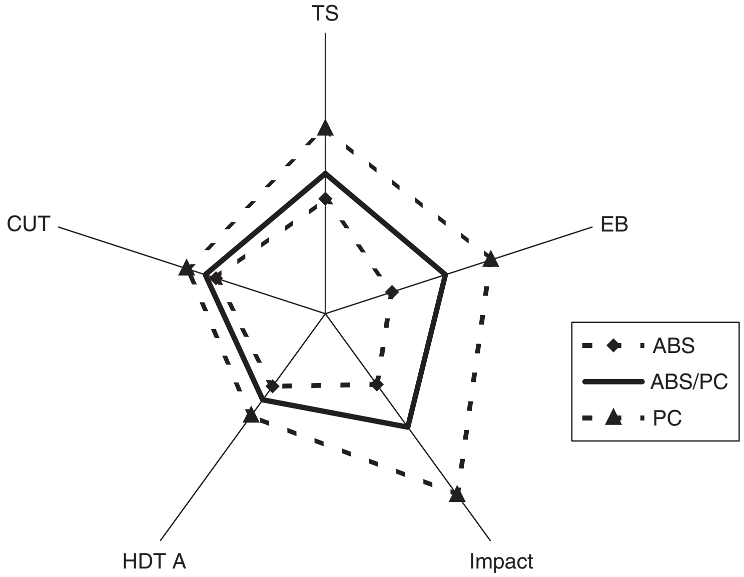


Figure 3.40. Property examples for ABS, PC and ABS/PC alloy

3.8.2 Compounding with additives

3.8.2.1 Mechanical property upgrading and customization: toughening, reinforcement, plasticization

The practical goals of the reinforcement are:

- to increase the modulus and strength
- to improve the HDT
- to reduce the tendency to creep under continuous loading
- to save costs by decreasing the material cost used to obtain the same stiffening.

The most up-to-date reinforcements are:

- fibres and assemblies containing fibres
- mineral fillers such as talc, calcium carbonate . . .
- glass microspheres . . .

Highly promising nanofillers, nanoclays and carbon nanotubes are also developing well.

Depending on the reinforcement, the main difficulties are:

- achieving an excellent adhesion between matrix and reinforcement
- the risk of shortened fibres broken during processing

- anisotropy due to the filler or fibre orientation and settling. With some processes, this is an advantage: a correct placement of the fibres permits reinforcement at specific points in the right direction.

Reinforcement with fibres

The principle of reinforcement is to transfer a part of the structural role to fibres that have much higher modulus and strength than the matrix. Figure 3.41, which plots tensile strength versus modulus for some typical fibres and matrices, clearly shows the gap between the performances of the matrix and glass or carbon fibres.

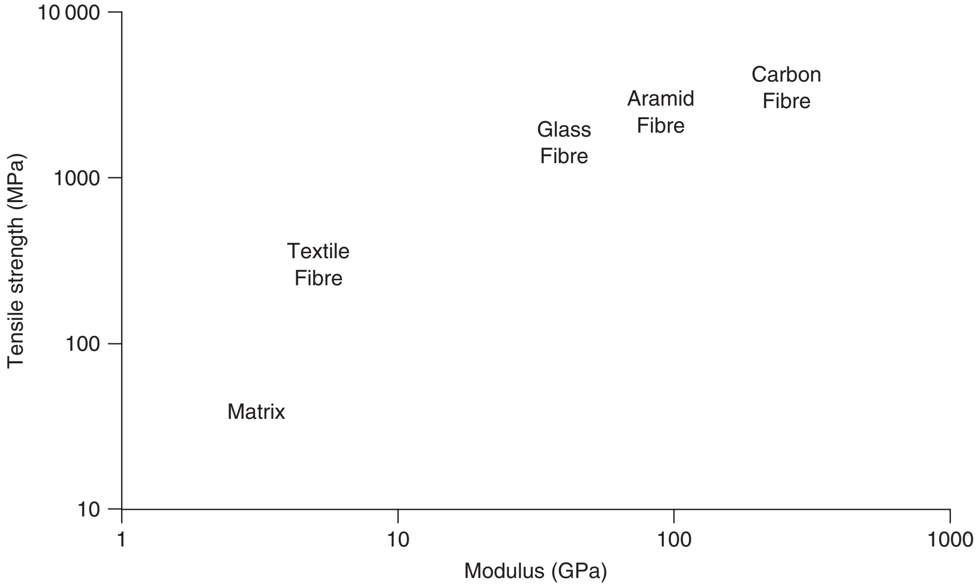


Figure 3.41. Fibres: examples of tensile strength versus modulus

Currently, glass fibres are the most widely used, accounting for 95% of the reinforcement fibres consumed by plastics. Aramid and carbon fibres account for nearly all the remaining 5%.

Natural fibres such as jute, flax and so on are developing to satisfy environmental trends.

Textile fibres like nylon and polyester are used to reinforce flexible materials such as soft PVC.

The properties of polymers reinforced with chopped glass fibres dispersed in the polymer matrix depend on:

- the nature of the fibre
- the fibre loading
- the aspect ratio (length versus diameter of the fibres)
- the sizing of the fibres to enhance adhesion to the matrix
- the real length of the fibres in the final part
- the quality of the fibre dispersion
- the anisotropy in the final part.

The properties of polymers reinforced with continuous filaments, rovings, fabrics and so on depend on:

- fibre type
- fibre loading
- the form of the fibre reinforcement (filament, roving . . .)
- orientation of the fibres
- the adhesion of the fibres to the matrix
- the anisotropy in the final part.

Table 3.4 shows some examples of the modulus and the strength reinforcement ratios for various reinforced thermoplastics and thermosets. The reinforcement ratio is the performance of the reinforced polymer divided by the performance of the neat polymer.

Table 3.4 Examples of reinforcement ratios based on tensile strength and modulus

Glass fibre	Strength	Modulus
None	1	1
Dispersed short GF	2.2	5
Dispersed long GF	3.3	6.7
Fabric reinforcement	5	5
Unidirectional reinforcement	20	20

Reinforcement and filling with mineral fillers

The reinforcement effect with mineral fillers is not as evident as with fibre reinforcement. Often the cost is significantly decreased but only a few properties are improved and others can be altered.

Table 3.5 shows some examples of the property effect ratios for mineral filler-reinforced polypropylene. The effect ratio is the performance of the reinforced polymer divided by the performance of the neat polymer. Properties of low-level glass fibre reinforced polypropylene are given for comparison.

Table 3.5 Examples of the effect of mineral fillers on polypropylene properties

	Effect ratio		
	Talc	Mineral	Glass fibre
Tensile strength	0.8	0.7	1.5
Tensile modulus	2.4	2.1	3.2
Notched impact strength	0.4	0.3	0.3
HDT A	1.2	1.1	2.0
Thermal conductivity	1.9	1.9	1.4
Coefficient of thermal expansion	0.5	0.4	0.5
Density	1.2	1.2	1.1
Shrinkage	0.5	0.4	0.3

Compared to neat polymer and glass fibre reinforced polymer:

- tensile strength decreases compared to neat polymer
- elongation at break is intermediate between neat and glass fibre reinforced polymer

- modulus increases and becomes intermediate between neat and glass fibre reinforced polymer
- impact strength decreases
- HDT increases and becomes intermediate between neat and glass fibre reinforced polymers
- coefficient of thermal expansion and shrinkage are reduced while thermal conductivity increases
- price decreases but density increases.

Reinforcement with glass beads

Glass beads act as a mineral filler with an aspect ratio of 1. Table 3.6 displays results for glass bead reinforced polyamide. The effect ratio is the performance of the reinforced polymer divided by the performance of the neat polymer.

Table 3.6 Examples of the effect of glass beads on polyamide properties

	Effect ratio
Tensile strength	1
Tensile modulus	1.5
Notched impact strength	0.4
Hardness	1.2
HDT A	1.2
Thermal conductivity	1.7
Coefficient of thermal expansion	0.6
Density	1.2
Shrinkage	0.6
Water absorption	0.4

These results are of the same order as those in Table 3.5 for mineral-filled polypropylene. Versus neat polymer:

- tensile strength is unchanged
- modulus increases and becomes intermediate between neat and glass fibre reinforced polymer
- impact strength decreases
- HDT slightly increases
- coefficient of thermal expansion and shrinkage are reduced while thermal conductivity increases
- density increases
- water absorption decreases due to the specific hygroscopic character of polyamide while glass beads are hydrophobic.

Nanofillers

Nanofillers are made up of:

- elementary particles in platelet form with thickness of the order of the nanometre and diameter of the order of 100 nm
- primary particles formed by stacking several elementary particles. The thickness is about 10 nm
- aggregates of numerous elementary particles.

To exceed the typical filler reinforcement and to obtain a real nanocomposite, it is necessary to destroy the primary particle structure during processing:

- either completely, by dispersing the elementary particles in the macromolecules – delaminated nanocomposite, or
- partially, by intercalating macromolecules between the elementary particles – intercalated nanocomposite.

The most-popular nanofiller is a natural layered silicate, montmorillonite, that is subjected to specific treatments. The properties of the final nanocomposite depend on the these treatments and the mixing efficiency.

Table 3.7 displays property examples for polyamide nanocomposites processed by various methods.

Table 3.7 Property examples for polyamide nanocomposites processed by various methods

	Neat PA	PA nanocomposites	
		Property	Reinforcement ratios
Tensile modulus (GPa)	2.7	3.3–4.3	1.2–1.6
Tensile stress at yield (MPa)	64	69–85	1.1–1.3
Elongation at break (%)	40	8–60	–
Izod notched impact (J/m)	37	36–50	1–1.3

Practically all the polymers can be processed to make nanocomposites. This emerging technology is developing in polyamide and TPO nanocomposites with applications in the automotive industry, and there are experiments with saturated polyesters, acrylics, polystyrenes . . .

The nanosilicates, because of their high aspect ratio, high surface area and nanometric scale, are reinforcing at low incorporation levels.

The main nanocomposite properties are:

- mechanical performances between those of the neat polymer and short glass fibre reinforced grades
- higher HDT than neat polymer but lower than short glass fibre reinforced grades
- density much lower than reinforced grades
- lower gas permeability
- better fire behaviour.

For an industrial example (see Table 3.8), the reinforcement ratios obtained with a loading of nanosilicate as low as 2% are attractive. The reinforcement ratio is the ratio of the nanocomposite performance versus that of the neat polymer.

Table 3.8 Example properties for a 2% nanosilicate-filled polyamide

	Property example	Reinforcement ratio
Density (g/cm^3)	1.15	1
Tensile strength (MPa)	100	1.25
Flexural modulus (GPa)	3.9	1.3
HDT A (1.8 MPa) (°C)	140	1.9

For a very similar density, the nanocomposite has significantly better thermomechanical properties than the neat polyamide.

Impact modifiers

Impact modifiers enhance impact strength at ambient temperature and reduce embrittlement at sub-zero temperatures. The principle is to distribute and dampen the energy of an impact by adding an elastomer or a rubbery polymer, which also reduces rigidity and some other properties.

The impact modifier is finely dispersed in the thermoplastic and particles absorb the energy of the impact. Numerous polymers are used, for example, ABS, MBS, CPE, SBS, SEBS, polyacrylate, polybutadiene, EPDM, ethylene-acrylate, modified polyolefins . . . The selected impact modifier must be compatible with the polymer to be enhanced, and adhere strongly to it. It must have enough cohesive strength and a glass transition temperature low enough to maintain high impact strength at low temperature.

Impact enhancers modify the balance of properties, notably stiffness, hardness, HDT (see Table 3.9), as well as, possibly, weatherability and thermal stability.

Some inorganic impact modifiers are also marketed, such as amorphous silicon dioxide.

Table 3.9 Examples of toughening effects on properties of polyamide and polyacetal

	Ratios: performance of impact grades divided by the same performance of unmodified grade	
	PA66	POM
Impact strength	5	2
Hardness, Rockwell M	0.5	0.7
Tensile strength	0.6	0.8
Elongation at break	1	2.9
Tensile modulus	0.4	0.6
HDT B	0.9	0.9

Plasticization

Plasticizers are mainly used to obtain a better flexibility at ambient and low temperature. However, they can also have other advantages, like the possibility to increase the amount of filler, which leads to cost savings, or, with specific grades, the possibility to bring other characteristics such as fire retardance, antistatic effect . . . Processing is generally enhanced, mixing and shaping being easier.

Unfortunately, they can have some drawbacks, such as decreased tensile strength and modulus, pollution, toxicity, migration or environmental risks, and the local and professional regulations, standards and specifications must be studied.

For specific polymers, halogen-free and phosphorus-free plasticizers can reduce the oxygen index. The transparency can be altered if the compatibility is low and/or the refractive index is inadequate.

The plasticization benefits can be reduced or even suppressed if the plasticizers disappear during service life by:

- volatilization, the more so as the temperature rises
- migration by contact with other solid materials, the more so as the temperature rises
- extraction by contact with fluids . . .

There are superabundant commercial products. Let us quote some of them:

- the esters:
    - the phthalates: diethylhexyl (also called dioctyl), DEHP (or DOP), is the most widely used; dimethyl, diethyl, dipropyl, dibutyl, dipentyl, dihexyl, diisoheptyl, dinonyl, diisononyl, butylbenzyl, dibenzyl . . .
    - the phosphates
    - other esters are used to some degree, for example: sebacates, adipates, azelates, glutarates, formates, hexoates, caprates, caprylates, tallates, trimellitates, tricitrates . . .
- petroleum oils, including the three main categories: paraffinics, aromatics, naphthenics
- low molecular weight rubbers or plastics (PE, PPO), liquid rubbers
- chlorinated hydrocarbons
- epoxidized soya bean oil
- fire-retardant additives such as tricresylphosphates, chlorinated waxes and others.

The choice of plasticizer types and levels is a subtle compromise between the bestowed advantages and drawbacks:

- compatibility with the polymer to be plasticized
- targeted processing, and rheological properties
- specified thermal, electrical and mechanical properties of the end product
- optical properties: light transmission, haze . . .
- fire behaviour: fire retardance, smoke, toxicity, corrosivity . . .
- chemical resistance
- ageing resistance to heat, humidity, light and UV
- volume cost
- toxicity and environmental risks
- stress cracking of other polymers by plasticizer migration, discoloration of rubber by contact
- contact with food and medical articles.

Table 3.10 displays three examples of PVC properties according to the degree of plasticization.

Table 3.10 Examples of PVC properties according to the degree of plasticization

	Negligible plasticization	Low plasticization	High plasticization
Density (g/cm^3)	1.35	1.35	1.15
Shrinkage (%)	0.3	0.8	5
Hardness, Shore D	75	70	15
Tensile strength (MPa)	45	25	10
Elongation at break (%)	40	200	500
Tensile modulus (GPa)	3	1	0.001
Notched impact strength (J/m)	20	NB	NB
HDT B (°C)	70	55	<30
Glass transition (°C)	60	−5	−50
Minimum service temperature (°C)	−5	−10	−40
Resistivity (ohm.cm)	15	15	10
Oxygen index (%)	40	40	20

NB: No break

3.8.2.2 Ageing protection: additives, films

Oxygen, heat, light and UV, shear and dynamic stresses attack polymers, degrading performances and aesthetics. Practical consequences of ageing generally are:

- mechanical property degradation, weakening, embrittlement . . .
- aesthetics degradation
- weight loss, shrinkage
- desorption and consumption of additives
- pollution of environment . . .

A durable protection is needed to avoid damage during processing, to satisfy the customer's specifications and requirements, and to give satisfaction during the complete service life of parts.

Protective additives can be classified as follows:

- processing stabilizers: antioxidants incorporated into the polymer to avoid heat degradation during processing
- antioxidants: added to the polymer to decrease thermo-oxidation during service life, avoiding molecular weight changes and loss of mechanical, physical and aesthetic properties
- light stabilizers: decrease degradation initiated by sunlight or UV exposure. Certain fillers absorb UV and act as filters protecting the polymer
- hydrolysis stabilizers: chemicals added to the polymer to avoid hydrolysis degradation during service life.

Another route to protect polymers from oxygen, light and UV is to encapsulate the part with a continuous film of another, more-resistant polymer to provide a barrier to oxygen. This technology is also used for decoration of plastic parts (in mould decoration or IMD, painting, multilayer sheets for thermoforming . . .). There is no protection against heat.

All these methods cannot totally inhibit polymer degradation. This is just a question of time, heat and exposure to light, water and other aggressive environments.

The efficiency of these additives depends on:

- the nature of the matrix
- the nature of the protective additive
- the actual level of additive in the part
- interaction with the other ingredients.

Table 3.11 shows examples of the very different efficiencies of eight antioxidants incorporated in the same polymer.

Table 3.11 Examples of antioxidant efficiencies in polypropylene films

	Air ageing at 130°C (hours to reach brittleness)	Efficiency ratio linked to control performance
Without protective agent	5	1
Protective agent A	34	7
Protective agent B	89	18
Protective agent C	91	18
Protective agent D	264	53
Protective agent E	456	91
Protective agent E+D	456	91
Protective agent E+A	552	110
Protective agent E+B	576	115

The other additives in the compound can also influence ageing as we can see in Table 3.12, which displays the effect of silica in combination with two different protective agents. In one case the silica degrades the ageing resistance and in the other silica enhances ageing behaviour.

Table 3.12 Examples of interaction between antioxidant and silica in polypropylene films

	Air ageing at 130°C (hours to reach brittleness)
Without protective agent	5
Silica	3
Protective agent E	456
Protective agent E + silica	336
Protective agent B	34
Protective agent B + silica	91

High part thickness decreases oxygen diffusion in the core of the polymer and reduces degradation, as can be seen in Figure 3.42.

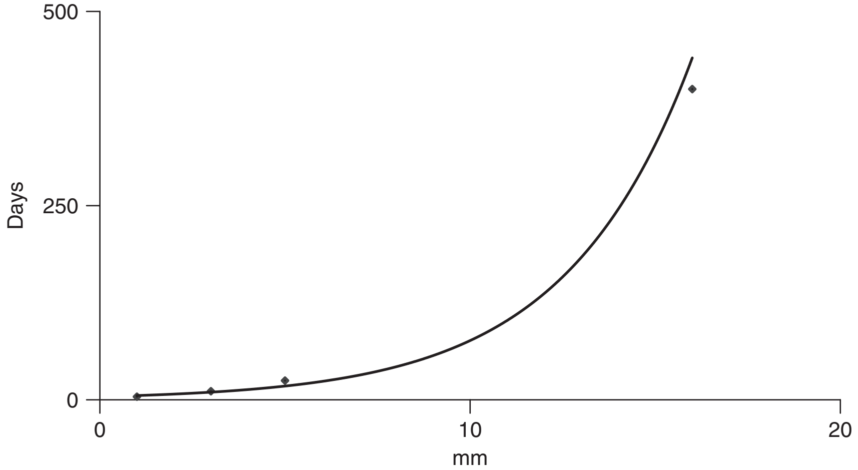


Figure 3.42. Ageing time (days) to reach the same degradation level versus sample thickness (mm)

Weathering is difficult to quantify because of the variation of the parameters according to the local conditions:

- hours of sun per annum
- irradiation energy
- UV level
- average and extreme temperatures
- hygrometry, rain
- ozone
- pollution, acid rain . . .

The technical consequences of weathering are similar to heat ageing with more pronounced surface degradation and notably:

- discoloration, yellowing, gloss loss, decreased transparency for transparent polymers
- chalking, crazing, hardening.

Table 3.13 shows examples of the efficiencies of anti-UV stabilization.

Table 3.13 Examples of UV degradation according to the polymer and exposure location

			% degradation		
			Tensile strength	Elongation at break	Impact
PC	Unstabilized	Arizona			93
	UV stabilized				3
PC white	Unstabilized	Florida	4	78	9
	UV stabilized		7	22	15
PE	Unstabilized	Florida	44	41	48
	UV stabilized		24	22	5

The other additives in the compound can also influence weathering as we can see in Table 3.14, which displays the effect of colorants in combination with UV stabilization. Ageing behaviour depends on the nature of the colorant and the UV-filtering action of the filler. Black compound is by far the best choice.

Table 3.14 Examples of UV exposure time to reach the same level of degradation of polypropylene according to the colorant

	Exposure time of coloured PP divided by exposure time of pure PP
Pure PP	1
Red A	1
Magenta	1
Blue C	1.8
Yellow	2
White	2.3
Red B	2.8
Brick-red	3.3
Blue D	3.5
Green	3.5
Black	12

3.8.2.3 Sensory properties

The market appeal of plastics is important for numerous applications such as packaging, automotive, appliances . . . Colour, transparency, gloss and odour contribute to make a plastic part attractive, unappealing or repulsive.

Colour can be obtained by adding colorants to compounds, or encapsulating the part with a continuous film of another coloured or printed polymer: in mould decoration (IMD), painting, multilayer sheets for thermoforming . . .

Colorants can be classified according to:

- their chemical structure: inorganic or organic
- their form: powders, masterbatches or concentrates in pellets, pastes, liquids, dustless powders, encapsulated . . .
- their function: colorants, brighteners, phosphorescent colorants, pearlescent colorants, metallic colorants . . .

Clarity and transparency can be enhanced by adding clarifiers.

Matting can be obtained by adding special mineral fillers, another secondary polymer that is miscible to a greater or lesser degree with the main polymer, or proprietary additives.

Glossy polymers can be obtained by polishing, post-moulding into perfectly polished moulds, lay out of films, IMD, FIM (film insert moulding), IMC (in mould coating), painting . . .

The choice of additives depends on numerous parameters concerning the nature of the polymer, the processing constraints (notably heat exposure, mixing technology), end-product aesthetics, and the durability under service conditions of the end product.

Scratch resistance improvement

Soft polymers are more sensitive to scratch than some harder plastics.

The use of silicone, at a level of 2% to less than 10%, helps reduce the coefficient of friction and correspondingly improves the scratch resistance.

For example, the scratch resistance of talc-filled TPOs modified with 2–3% silicone from masterbatches is significantly improved and visible whitening is suppressed under conditions that damage the same TPO without silicone. Paintability must be verified but a low silicone level (2.5% for example) does not affect paintability, and weathering resistance increases showing less change in aspect than the control without silicone.

Surface treatments with hard resins are also used.

Odours

Some plastics can develop unpleasant odours during and after processing or after ageing. To avoid or reduce that it is possible:

- to choose odourless grades and additives
- to add deodorants or specific fragrances marketed for polymers
- to add bactericides or preservatives to avoid growth of micro-organisms, fungi and so on during service life.

3.8.2.4 Specific properties: specific grades and specific additives

Fire behaviour

Fire behaviour is very complex for several reasons:

- technically: it is necessary to converge on a difficult balance of fire retardance and low smoke emission with constraints concerning the opacity, toxicity and corrosivity of fumes
- legally: standards, regulations and specifications are complex and evolving and vary according to country and industrial sector
- fire retardants can modify mechanical properties and aesthetics

The first question is to decide between halogen-free and halogen-containing systems. The second concerns the possible use of phosphorus additives. Figure 3.43 schematizes some possible routes in each case.

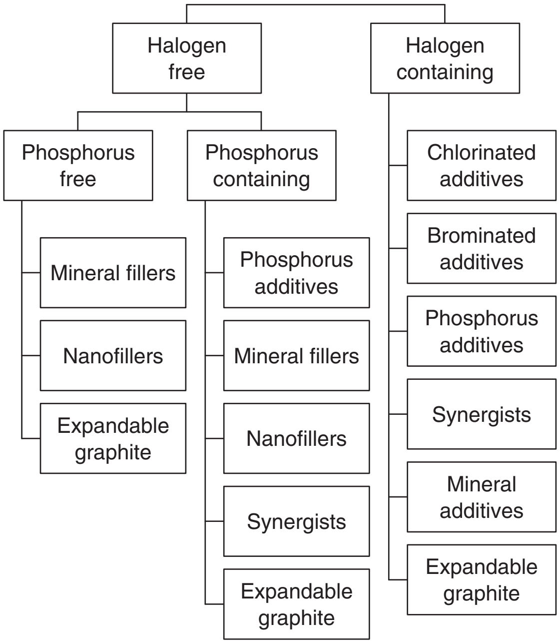


Figure 3.43. Examples of routes for fireproofing

Some fire retardants are detailed:

- Mineral fillers and additives: aluminium trihydrate (ATH), magnesium hydroxide and boron derivates are the best known but tin derivates, ammonium salts, molybdenum derivates and magnesium sulphate heptahydrate are used to varying extents and nanofillers are developing.
- Phosphorus additives: red phosphorus, phosphate esters, ammonium polyphosphate, melamine phosphates, melamine pyrophosphate. Some of them are halogenated.
- Halogenated derivates: brominated organic compounds are the most used, often in combination with antimony trioxide to develop a synergistic effect. However, this generates a lot of smoke and toxic fumes, which is unacceptable for many regulations and standards.
- Brominated polystyrene is marketed as a fire-retardant additive.

Table 3.15 shows some example properties of fireproofed grades. These examples are not exhaustive and indicated limits concern only a few grades. Other data can be found relating to other grades.

Conductive polymers

Two routes are suitable for producing conductive polymers:

- Intrinsic conductive polymers (ICP) obtained by polymerization of conductive macromolecules. This is a difficult route for industrial applications.
- Extrinsic conductive polymers obtained by adding specific additives to naturally insulating polymers. At present, this is the easiest industrial method.

According to the conductivity level, the main additives used are:

- antistatic specialities
- conductive carbon blacks

Table 3.15 Examples of flame-retardant grade properties

	Rigid PVC		
	Control	Limits of ten FR formulations	
Oxygen index (%)	38	39	64
Smoke parameter (arbitrary unit)	164	57	230
Heat stability (arbitrary unit)	36	19	39
Impact strength (arbitrary unit)	14	7	20
	EVA		
	Control	Limits of ten halogen-free FR formulations	
Oxygen index (%)	18	32	39
UL94 fire rating	Fail	V2	V0
Smoke, CO yield (arbitrary unit)	0.028	0.008	0.012
Tensile strength (MPa)	17	9	11
Elongation at break (%)	1470	65	160

- conductive fibres, carbon or steel
- metal powders or flakes.

Antistatic specialities

Non-black antistatics allow surface resistivities roughly in the range of 10^7 to 10^8 ohms per square to be obtained but their action generally depends on the relative humidity. However, new generations are being marketed without this drawback and are efficient at a relative humidity as low as 15%. Some are offered in masterbatches based on polyolefins, polystyrenes, polyesters, acrylics, ABS, polyacetals . . .

Conductive carbon blacks

There are specific grades and masterbatches of carbon blacks especially marketed as additives for conductive plastics. It should be noted that the carbon blacks modify other properties of the polymer, especially its colour.

Conductive fibres

Specific grades of carbon and steel fibres are especially marketed as additives for conductive plastics allowing resistivities of roughly 10^3 ohm.cm to be obtained. The other properties of the final material – colour, modulus, impact strength . . . are modified. Carbon fibres have a large reinforcing effect.

Table 3.16 compares some properties of conductive polypropylenes obtained by adding stainless steel or carbon fibres.

Table 3.16 Conductive polypropylene: stainless steel or carbon fibres

Fibres	Stainless steel	Carbon
Resistivity (ohm.cm)	10^3	10^3
Tensile or flexural strength (MPa)	41	41
Flexural modulus (GPa)	1.4	4.3

Metal powders or flakes

Aluminium, copper, nickel and silver powders or flakes are used to obtain EMI (electromagnetic interference) grades. The other properties – colour, modulus, impact strength . . . are modified.

Table 3.17 shows some examples using aluminium powder for EMI shielding.

Table 3.17 Properties of EMI grades compared to neat polymers

Aluminium level (%)	PA66		PPE	
	0	40	0	40
Specific gravity (g/cm^3)	1.1	1.5	1.1	1.5
Elastic modulus (GPa)	2.3	5	2.5	5.2
Tensile strength (MPa)	60	41	55	45
Elongation at break (%)	200	4	30	3
CTE (10^{-5}/°C)	10	2.2	5	1.1
HDT 1.82 MPa (°C)	85	190	110	110

Additives for antifriction polymers

The most up-to-date additives for antifriction compounds are:

- specific fillers: MoS_2, graphite
- polymers: PTFE and silicone are efficient for providing antifriction properties but wear resistance falls.

More rarely used are:

- carbon or aramid fibres to simultaneously enhance mechanical properties and coefficient of friction and decrease the wear
- ceramics such as boron nitride or silicon carbide.

To enhance mechanical properties and decrease wear, glass fibres are added to polymers but they are abrasive and attack the opposing surface. According to the circumstances they can also increase the coefficient of friction.

Carbon fibres are more satisfactory, simultaneously bringing a lower friction coefficient and lower wear.

Table 3.18 shows the effects of several lubricating fillers on the friction properties of polyamides 6 or 66 possibly reinforced with glass or carbon fibres.

Silicon carbide is marketed as a surface enhancer (see Table 3.19). At levels of less than 10% it significantly improves the coefficient of friction and the wear resistance.

Polymers with high thermal conductivity

General-purpose polymers, being thermal insulators, cannot dissipate heat generated by mechanical work or by electronic devices and so on. If the temperature rises, the mechanical properties of the polymer decrease and ageing speeds up. Eventually, the temperature can reach the melting point.

To ease the dissipation of thermal flow, it is worthwhile to use dissipative additives such as ceramics, metal powders or carbon fibres that have a high thermal conductivity.

To provide some idea, thermal conductivities are roughly in the range of:

- 0.2–0.3 for neat polymers such as PP, PA, PPS . . .
- 25–300 for ceramics

Table 3.18 Effects of several lubricating fillers on the friction properties of polyamides

Tribological filler		Polymer	Coefficient of friction		Wear (arbitrary unit)
Type	Level (%)		Static	Dynamic	
Neat and glass fibre reinforced polyamides					
None, control	0	Neat PA	0.22	0.3	4
MoS_2	5	PA6 30 GF	0.3	0.3	2.2
		PA66 30 GF	0.3	0.3	2.8
PTFE	15	PA6	0.18	0.11	120
		PA66	0.17	0.11	100
		PA66 30 GF	0.26	0.1	2
PTFE/silicone oil	13/2	PA66	0.1	0.11	120
		PA6 30 GF	0.19	0.13	2
		PA66 30 GF	0.17	0.1	2.3
Carbon fibres					
Carbon fibres	10	PA66 10 CF	0.22		
	20	PA6 20 CF	0.22		
		PA66 20 CF	0.2		
	30	PA6 30 CF	0.2		
		PA66 30 CF	0.19		
Carbon fibres and tribological fillers					
CF/PTFE	15/20	PA66 15CF/20PTFE	0.11	0.08	1.5
CF/PTFE/silicone oil	15/13/2	PA66 15CF/13PTFE/ 2 silicone oil	0.12	0.08	0.8

Table 3.19 Examples of some polymer characteristics

Polymer	Thermal conductivity (W/m.K)	Tensile strength (MPa)
Polypropylene		
Neat	0.2	34
Ceramic	1.2	17
Polyamide		
Neat	0.2	93
Ceramic	1	93
Aluminium	1	41
PPS		
Neat	0.3	79
Ceramic	1.2	52
Carbon fibre	2.2–7	139

- 60–400 for copper or aluminium
- 10–170 for carbon fibres.

The possible limitations are:

- the cost, for example, boron nitride powder prices are in the range of €60/kg up to €150/kg.
- the toxicity of, for example, beryllium oxide powders when inhaled.

The increase in the polymer thermal conductivity is far from the predicted values resulting from a mixing law and actual data are low, for example:

- 1–1.2 W/m.K for structural plastics
- 2–7 W/m.K for carbon fibre reinforced thermoplastics according to the direction of testing
- 14 W/m.K for non-structural polymers.

Table 3.19 displays some example properties for polymers filled with ceramic, aluminium or carbon fibre. Note:

- ceramics also provide electrical insulation with generally some mechanical performance decay
- carbon fibres also provide high electrical conductivity with high mechanical performances
- aluminium provides medium electrical conductivity with some mechanical performance decay.

Magnetic polymers

General-purpose plastics are not magnetic and cannot be used to produce magnets that generate permanent magnetic or electromagnetic fields for diverse applications, from domestic to high-performance devices: DC micromotors, telephones, coupling devices, toys, hardware, ore screening . . .

However, magnetic additives such as ferrites or rare earths can be added to plastics to produce polymer magnets.

The two main families of magnetic additives used for polymer magnets are ferrites and rare earths, which have very different characteristics.

Anisotropic powders of ferrites have excellent cost/performance ratio, limited service temperatures, and low electrical resistance.

Rare earths have higher magnetic performances, service temperatures, electrical resistance and costs.

Table 3.20 shows property examples of plastic magnets based on ferrites or rare earths.

Table 3.20 Property examples of plastic magnets

Magnetic additive	Ferrite	Rare earth
Induction (kG)	1.5–2.7	4–8
Maximum energy product (MGOe)	0.5–1.7	3–12
Density (g/cm^3)	3.5–3.7	5–6
Tensile strength (MPa)	60–80	
HDT (°C)	100–120	
Service temperature (°C)		Up to 110

3.8.2.5 The cost cutters

It is possible to cut costs by incorporating cheap fillers such as calcium carbonate, talc, kaolin, feldspar, wollastonite, silica . . . or by using recyclates and, to a certain extent, by foaming, which leads to an increase of the volume for the same weight of resin and other expansive ingredients.

Non-black fillers

The main non-black fillers are, for example: calcium carbonates, broadly used in PVC; talcs, broadly used in polypropylene; titanium dioxide used as a white pigment; clays or kaolins;

ATH used in flame-retardant compounds; precipitated silicates; micas, wollastonite or calcium metasilicate; barium sulphate, used for its opacity to X-rays and high density; lithopone; quartz used in flour form.

The cost savings are very different per weight and per volume. For two fillers with the same price, 10% of the polymer price, but of very different densities, 2 and 5 respectively, cost savings are:

- 30% per weight in both cases
- 16% per volume for the light filler and only 5% for the heavy one.

As already seen, the use of mineral fillers not only has economic advantages but also technical advantages (see Table 3.21 showing the performance indices of mineral-filled polyamide) such as:

- lower shrinkage
- lower water absorption for hygroscopic polymers
- higher rigidity
- higher HDT
- lower coefficient of thermal expansion.

Table 3.21 Performance indices of mineral-filled polyamide linked to the same performances of neat PA

	Performances of 30% mineral-filled PA divided by neat PA performances
Density	1.2
Shrinkage	0.4
Water absorption after 24 h	0.6
Tensile stress at yield	0.8
Tensile strength	0.8
Elongation at break	0.3
Tensile modulus	2
Flexural modulus	2
HDT A	2
Coefficient of thermal expansion	0.5

There are also some drawbacks such as:

- higher density
- lower strength and elongation at break.

Use of recycled plastics

Suitably recycled plastics can have properties that are good enough for many applications, with a noticeable economic advantage. Table 3.22 compares properties of virgin and recycled polyamides. These data are examples only and cannot be considered as representative.

As some properties are affected by recycling, the designer must be vigilant, notably concerning ultimate mechanical performances such as tensile and impact strengths.

Some regulations can restrict the use of recyclates.

Miscellaneous opportunities

Choosing a reinforced plastic or one from a more-sophisticated polymer family to provide higher performance can be used to cut overall costs by reducing wall thickness and thus reducing material weight and material cost and enhancing the processing.

Table 3.22 Performance examples of virgin and recycled PA 6

	Virgin neat PA 6	Recycled neat PA 6	Variation (%)
Density	1.13	1.13	=
Shrinkage	1.6	1.6	=
Water absorption saturation	9.4	9.5	=
Rockwell R hardness	119	119	=
Tensile stress at yield	85	80	−6
Tensile strain at yield	5	3.5	−30
Tensile modulus	3.3	3.2	=
Flexural modulus	3	2.8	−7
Notched Izod, −30°C	5	4	−20
Notched Izod, 23°C	5.5	4.5	−18
HDT B	184	175	−5
HDT A	67	60	−10
Coefficient of thermal expansion (10^{-5}/K)	7.5	7.5	=
	33% GF PA 6 virgin	33% GF PA 6 recycled	Variation (%)
Density	1.39	1.38	=
Shrinkage	0.2–0.9	0.2–1	=
Water absorption saturation	6.7	6.6	=
Rockwell R hardness	121	121	=
Tensile stress at break	200	165	−17
Tensile strain at break	3	3	=
Tensile modulus	10.7	9.5	−11
Flexural modulus	9.4	9.3	=
Notched Izod, −30°C	11	8	−27
Notched Izod, 23°C	15	12	−20
HDT B	218	215	=
HDT A	203	208	=

Use of limited blowing leads to structural foams with reduced weight and, therefore, reduction of raw material cost, but the designer must verify that the overall processing cost does not overrun that saved on material and that mechanical properties are good enough. Table 3.23 compares performance examples of structural foam and dense polyetherimide. Drops in tensile strength and modulus are more important than the density change but the declines in flexural modulus and HDT are favourable and the coefficient of thermal expansion of the foam is significantly lower.

Table 3.23 Performance examples of structural foam and dense polyetherimide

	Dense	Structural foam	Variation (%)
Density	1.27	0.9	−29
Tensile stress at break	90	40	−56
Tensile strain at break	60	4	−93
Tensile modulus	3	1.8	−40
Flexural modulus	3.3	2.9	−12
HDT B	210	195	−7
HDT A	200	175	−12
Coefficient of thermal expansion (10^{-5}/K)	5.6	4	−29

Chapter 4

Detailed accounts of thermoplastic resins

For easier reading, certain elements of earlier chapters are repeated in the opening remarks on each material family and in the sections on 'Applications'. However, for the latter, the reader should refer to Chapter 2 for the most complete and up-to-date information.

Unless otherwise specified, the units used in the property tables at the end of each account are:

Specific mass or density	g/cm^3
Shrinkage	%
Absorption of water	% after 24 h of immersion
Tensile strength	MPa
Elongation at break	%
Tensile modulus	GPa
Flexural strength	MPa
Flexural modulus	GPa
Compression strength	MPa
Notched impact strength ASTM D256	J/m
HDT B (0.46 MPa)	°C
HDT A (1.8 MPa)	°C
Continuous use temperature (unstressed)	°C
Glass transition temperature	°C
Brittle point	°C
Thermal conductivity	W/m.K
Specific heat	cal/g/°C [1 cal = 4.19 J]
Coefficient of thermal expansion	10^{-5}/°C
Volume resistivity	ohm.cm
Loss factor	10^{-4}
Dielectric strength	kV/mm
Arc resistance	s

The data are examples that cannot be generalized and cannot be used for design purposes.

4.1 Polyethylene or polythene (PE)

Albeit having a simple chemical formula, $-(CH_2-CH_2)_n-$, polyethylene is a broad family with versatile properties that depend on which of the three main polymerization processes is used:

- Free radical vinyl polymerization, the oldest process, leads to branched low density polyethylene (LDPE). Macromolecules have numerous short branches, which reduce the melting point, tensile strength and crystallinity. Polymers are relatively flexible because of the high volume of the branched molecule and the low crystallinity.
- Ziegler-Natta polymerization leads to linear unbranched polyethylene, the so-called high density polyethylene (HDPE), which is denser, tougher and more crystalline. By copolymerization with other alkenes it is possible to obtain linear low density polyethylene (LLDPE) with better mechanical properties than LDPE. Blends of LLDPE and LDPE are used to combine the good final mechanical properties of LLDPE and the strength of LDPE in the molten state.
- Metallocene catalysis polymerization is the most recent technique, growing fast to produce a consistent, uniform distribution of molecular weight resulting in enhanced toughness, impact and puncture strengths, better cold behaviour and optical properties. These advantages allow the downgauging or enhancement of performances for the same weight of polymer. Metallocene catalysis allows the production of all densities, from ultra-low density to ultra-high molecular weight polyethylenes (UHMWPE).

In addition to their structural diversity, polyethylenes can be crosslinked.

Polyethylenes can be classified versus density and molecular weight:

- ultra-low and very low density, ULDPE and VLDPE
- low density, LDPE and LLDPE
- medium density, MDPE
- high density, HDPE
- high molecular weight, HMWPE
- ultra-high molecular weight, UHMWPE.

Regardless of molecular weight, polyethylene can be classified into five density categories:

- 0.890 to 0.909 or 0.915
- 0.910 to 0.925
- 0.926 to 0.940
- 0.941 to 0.959
- 0.960 and higher.

Regardless of density, polyethylenes have molecular weights of the order of:

- LDPE & HDPE: from a few thousands to 300 000 depending on the end use
- high molecular weight, HMWPE: approximately 200 000 to 500 000
- ultra-high molecular weight, UHMWPE: approximately 3 000 000 and higher.

Considering the versatility of polyethylenes, each polyethylene subfamily has, of course, its favoured application sectors:

- HDPE is used for 86% of all polyethylene goods having applications that are structural to a greater or lesser degree
- LDPE and LLDPE are used for 86% of all polyethylene films.

Expressed in another way:

- 75% of HDPE is converted into parts having a structural function to a greater or lesser degree
- 75% to 80% of LDPE and LLDPE are converted into films.

For films, Table 4.1 proposes an arbitrary classification of the polyethylene subfamilies (where m indicates metallocene catalysis).

Table 4.1 Films: arbitrary classification of the polyethylene subfamilies

Function	Mechanical	Optical	Organo-leptic	Vapour barrier	Sealability	Processability
mVLDPE	1	1	1	2	1	3
mLLDPE	1	2	1	2	2	3
LLDPE	2	2	2	2	2	3
LDPE	3	2	1	2	2	1
HDPE	3	3	2	1	3	2

1 – generally the best adapted to the function
2 – intermediate behaviour
3 – generally less adapted to the function

The same basic monomer generates a lot of common properties and, unless otherwise specified, we will not make a distinction between the various subfamilies. Only the foams will be given special attention as they present particular properties due to their morphology:

- decreased mechanical properties due to the low quantity of polymer and the high proportion of gas
- weaker chemical resistance due to the highly divided state of the polymer. The thin cell walls immediately absorb liquids and gases.

4.1.1 General properties

Advantages

General advantages are low price, attractive price/property ratios, easy transformation, chemical inertness, impact resistance, low absorption of water, low density (HDPE included), good electrical insulator, low coefficient of friction, suitability for food contact, ease of welding, good machinability for rigid grades; good resistance against high-energy radiation, physiological inertness, versatility of processing methods except for UHMWPE.

- LDPE: good mechanical properties, flexibility, impact resistance at ambient temperature; good insulating material even in a wet medium; chemically inert.
- HDPE: same properties as LDPE but more rigid; better thermal and creep behaviour; lower coefficient of friction and higher pressure strength, allowing antifriction applications with higher PV (pressure*velocity) factor; more transparent.
- UHMWPE: better mechanical properties, lower coefficient of friction and higher pressure strength allowing antifriction applications with higher PV factor.
- Linear PE: same properties as the equivalent branched PE with an improvement in the mechanical properties, thermal and creep behaviour, and resistance to stress cracking.
- Metallocene: enhanced toughness, impact and puncture strengths, better cold behaviour and optical properties.
- Crosslinked PE: more resistant to temperature, creep and cracking.

Drawbacks

General drawbacks are the innate sensitivity to heat, UV, light and weathering (but stabilized grades are marketed), stress cracking, and creep; low rigidity, significant shrinkage, limited transparency. Due to the surface tension, gluing, painting and printing are difficult without surface treatments. Composed only of carbon and hydrogen, polyethylenes are naturally flammable but FR grades are marketed.

Processing is difficult for UHMWPE due to the high molecular weight.

Polyethylene is sensitive to pro-oxidant metals such as copper, manganese or cobalt, which must be avoided as inserts.

Special grades

They can be classified according to the type of processing, specific properties, targeted applications:

- Extrusion, injection, compression, blown film, blow moulding, rotational moulding, foam, coating, powdering, co-extrusion, for thin or thick parts, for crosslinking, electrowelding . . .
- Stabilized against heat, UV, light or weathering; antistatic, conductive, reinforced, food contact, physiologically inert, fireproofed, transparent, resistant to stress cracking, low warpage, high fluidity . . .
- For films, sheets, tubes, wire and cable coatings, fibres, mass production of household requisites, bottle racks, bins, containers, pallets, tubes, prostheses, antifriction parts . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide a rough idea. They are generally of the order of €1 per kilogram.

Processing

All molten-state processing methods are usable: extrusion, injection, compression, blown film, blow moulding, rotational moulding, thermoforming, foam, coating, powdering, co-extrusion, fluidized bed, machining for high hardness grades, welding. Special grades can be crosslinked after shaping.

Applications

(See Chapter 2 for further information.)

Although varying according to country, consumption is approximately divided into:

- 40–45% HDPE
- 30–35% LLDPE
- 20–25% LDPE.

Applications vary according to the polyethylene type.

LDPE and LLDPE are mainly used for:

- films for packaging: food, non-food, shrink, stretch . . .
- films for other applications
- sheets
- extrusion coating
- injection moulding
- blow moulding
- pipes and conduits.

HDPE is mainly used for:

- blow moulding of:
  - household chemical bottles
  - industrial drums
  - liquid food bottles
  - drugs, cosmetics and toiletries
- injection moulding of:
  - crates and totes
  - food and beverage containers
  - housewares
  - industrial and shipping pails
- films for food packaging and retail bags
- sheets
- pipes and conduits
- rotomoulding.

Among other applications, let us quote, for example:

- films for agricultural, industrial or general-purpose uses
- fuel tanks for the automotive industry
- moulded basins, bottles, stoppers, toys, hollow parts, small electric equipment, pallets, street furniture, seats
- large-sized objects: cisterns, tanks, septic tanks, hulls of boats, canoes, buoys, sailboards, barrels, drums . . .
- gas, water or sewer pipes, sheaths
- crosslinked foams, extruded and moulded parts
- UHMWPE: gears, bearings, antifriction parts for light loads, prostheses

- foams: densities from 25 kg/m^3 up to 330 kg/m^3, semi-rigid to flexible, with insulating and damping properties for packaging, building insulation, panels and sandwich structures, multi-layer composites for damping (helmets, for example).

4.1.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 90°C for LDPE up to 110–120°C for HDPE and 130°C for crosslinked polyethylenes if the softening or melting temperatures are higher. For example, the sealing temperature of a given grade of VLDPE is 83°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . . They can be of the order of:

- 50–90°C for LDPE
- 50–120°C for HDPE.

As examples:

- for a given grade of LDPE, the short-term modulus retention at 80°C is 40% of the value at 20°C. For two grades of HDPE (see Figure 4.1), the short-term retention of stress at yield is in the range of 35% to 42% at 80°C
- HDTs under 1.8 MPa are:
  - ○ from 30–40°C for LDPE
  - ○ to 45–60°C for HDPE.

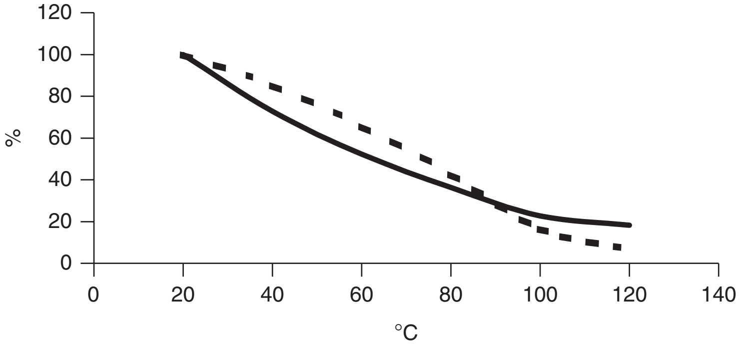


Figure 4.1. HDPE examples of stress at yield retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. For a heat-sensitive characteristic such as elongation at break, the values for a given polyethylene after ageing at 120°C are roughly:

- 60% after 10 days and 40% after 17 days for a grade without a stabilizer
- 80–100% after 10 days and 60–90% after 17 days for several grades with various stabilizers, versus 120–160% initial elongation at break with or without a stabilizer.

The UL temperature indices of specific grades can be 50°C for electrical and mechanical properties including impact.

At low temperatures, the behaviour can be acceptable down to −60°C or even less, down to −110°C according to grades and the mechanical constraints experienced. Figure 4.2 displays examples of stress at yield retention for polyethylenes at subzero temperatures.

Despite a high increase in rigidity UHMWPE can be used down to −269°C.

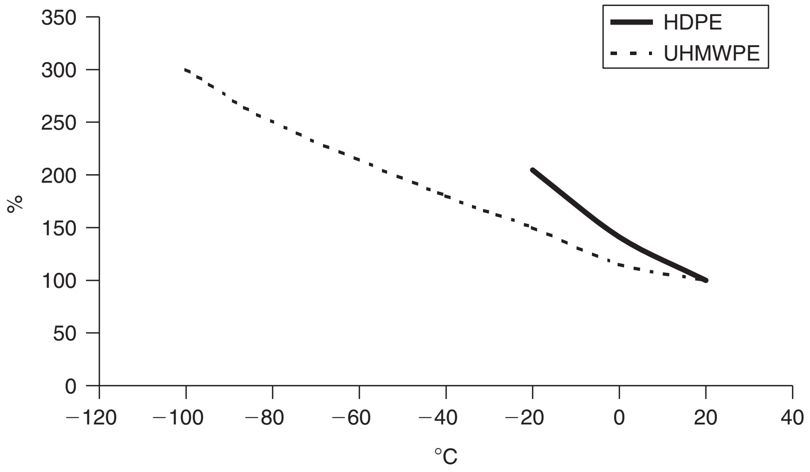


Figure 4.2. HDPE & UHMWPE examples of stress at yield retention (%) versus sub-zero temperatures (°C)

The brittle points are generally of the order of −70°C.

The glass transition temperature of PE by DSC measurements is −110°C. The glass transition temperatures by DMTA measurements can be higher, depending on the frequency.

These results relate to some grades only and cannot be generalized.

4.1.3 Optical properties

Polyethylenes are whitish and translucent to opaque according to the density and grade.

The refractive index varies with the density and type of polyethylene, for example:

- 1.51 for an LDPE
- 1.52 for an MDPE
- 1.54 for an HDPE.

For films, haze can be 5–6% for specific grades.

These results relate to some grades only and cannot be generalized.

4.1.4 Mechanical properties

The mechanical properties are generally fair with high elongations at break but much more limited strains at yield. Moduli and hardnesses are rather weak and impact strength is high to excellent. The abrasion resistance of polyethylene depends on the roughness, type and morphology of the antagonist sliding surface. Wear resistance is sufficient for antifriction applications under moderate pressure and low PV.

Some grades can have weaker characteristics.

Crystallinity and molecular orientation improve the mechanical properties but are harmful to notched impact resistance.

Friction

High density and UHMW polyethylenes are used to make antifriction parts. The coefficients of friction are low but the moduli, hardnesses and softening temperatures are weak, which limits the loads and PV factors.

Table 4.2 gives some PV examples ranging from 0.04 up to 0.07 MPa.m/s. All these values are weak but certain sources quote very different data.

These results relate to a few grades only and cannot be generalized.

Table 4.2 UHMWPE: examples of tribological properties

PV (MPa.m/s)	Pressure, P (MPa)	Velocity, V (m/s)	Coefficient of friction
0.07	0.9	0.08	0.1–0.2
0.07	0.7	0.1	0.1–0.2
0.07	0.23	0.3	0.1–0.2
0.07	0.14	0.5	0.2–0.3
0.06	0.08	0.8	0.2–0.3
0.05	0.05	1	0.2–0.3
0.04	0.025	1.7	>0.2

Dimensional stability

Shrinkage, coefficient of thermal expansion, crystallinity and creep are rather high, but alterations through moisture exposure are slight.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For a given HDPE sample it is evaluated at 0.46, but this is an example only that cannot be generalized.

Creep

Neat thermoplastic polyethylenes have low moduli that involve high strains for moderate loading. Consequently, creep moduli are also low, the more so as the temperature rises, as we can see in Figures 4.3 ((a) and (b)) where creep moduli are displayed as a function of time, load and temperature.

In Figure 4.3(a) we can see a broad difference between two grades tested under a light load (2–3 MPa). The third grade tested under 8.75 MPa is probably more creep resistant.

Figure 4.3(b) displays the fast decrease of creep moduli when the temperature rises moderately. Designers must be vigilant when computing the wall thickness of a part to be used at ambient temperatures (40°C) during warm weather.

Finally, Figure 4.3(c) shows that glass fibre reinforcement is an efficient means to attain more suitable creep moduli.

These results relate to a few grades only and cannot be generalized.

Relaxation

Figure 4.4 ((a) and (b)) displays the same relaxation data, first against a linear time scale, showing the fast drop in stress at the start of test, and second against a logarithmic time scale showing a regular decrease of stress.

These results relate to a few grades only and cannot be generalized.

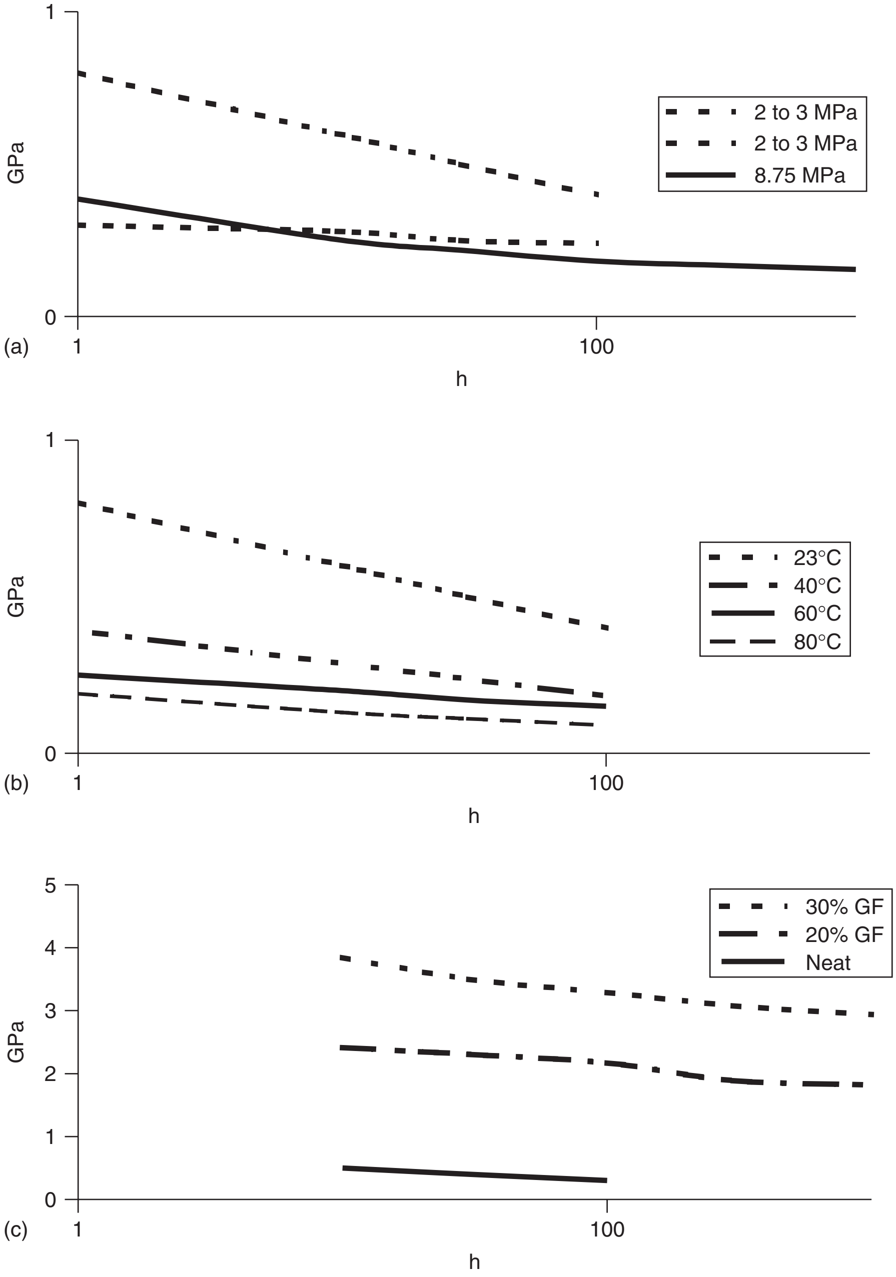


Figure 4.3. *(a) HDPE & UHMWPE examples of creep modulus (GPa) versus time (h) for various loading (MPa); (b) HDPE & UHMWPE examples of creep modulus (GPa) versus time (h) for various temperatures (°C); (c) HDPE examples of creep modulus (GPa) versus time (h) for various reinforcements*

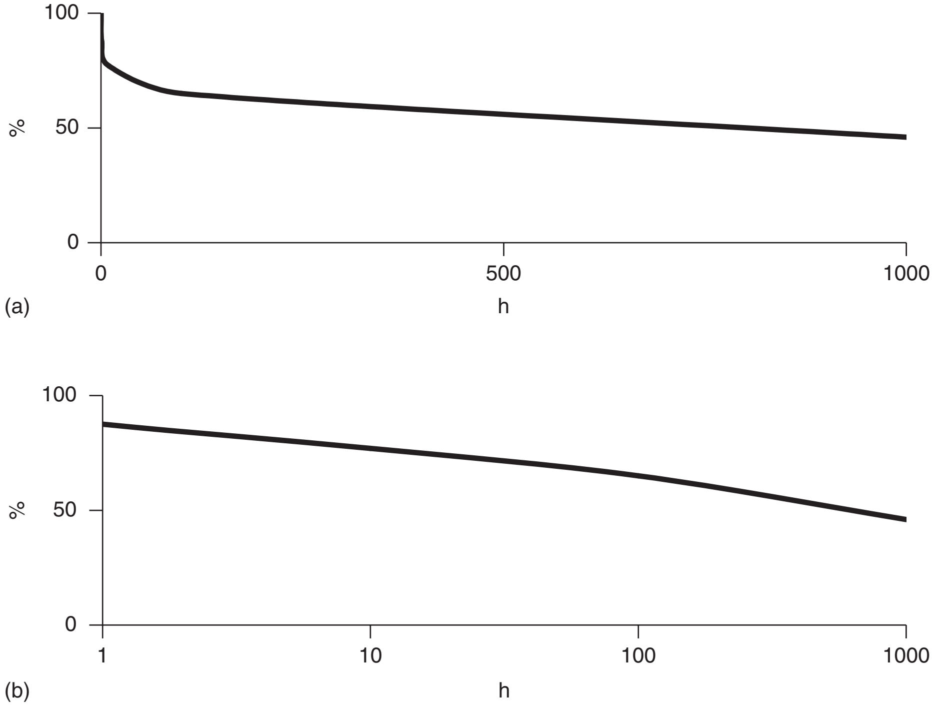


Figure 4.4. Stress relaxation of HDPE, examples of stress retention (%) versus time (h) under 2% strain at 20°C

4.1.5 Ageing

Dynamic fatigue

The dynamic fatigue can be fair or good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the low modulus.

For a given grade of HDPE, Figure 4.5 displays an example of an SN or Wöhler's curve concerning flexural tests with maximum stress of $\pm\sigma$ and average stress of 0.

Weathering

Polyethylene resists hydrolysis well but is naturally sensitive to light and UV. It must be protected by addition of anti-UV and other protective agents or by 2–3% of an adequate carbon black. In such cases, after weathering of test bars for several years in various climates, the retention of tensile strength is generally good but the elongation at break retention can be as low as 10%. These results are examples only and they cannot be generalized.

High-energy radiation

In the absence of oxygen, polyethylene is crosslinked by exposure to high-energy ionizing radiation. The degree of reticulation depends only on the radiation dose. The reticulation brings in particular a better resistance to stress cracking but too high a dose involves a

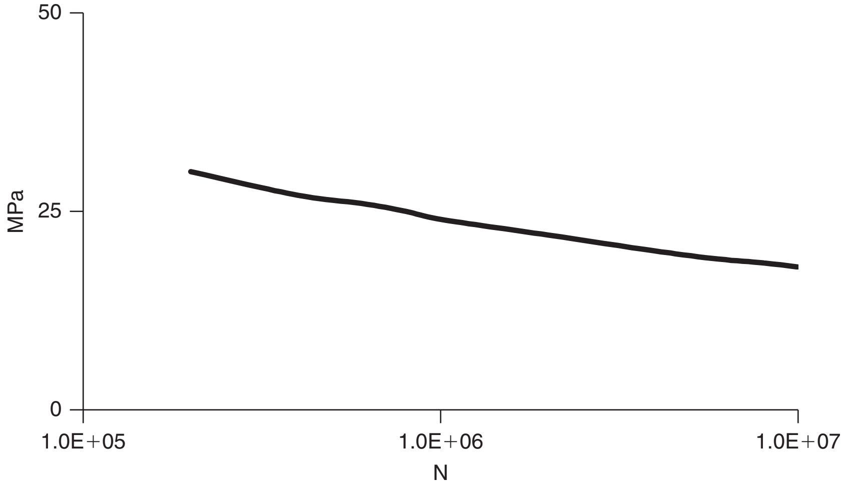


Figure 4.5. SN curve of HDPE, examples of maximum stress (MPa) versus number of cycles at rupture (N)

reduction in elongation at break and impact resistance. For a dose greater than 100 kJ/kg (10 Mrad), the variations become measurable; 1 MJ/kg reduces elongation at break to a few percent of its initial value, but the stress at yield remains practically unchanged.

In the presence of oxygen, for example in air, there are simultaneous crosslinking and degradation reactions. The action of the high-energy radiation depends in a complex way on the power, dose and wall thickness of the polyethylene. A short-duration irradiation to a strong dose on a broad wall thickness has the same effect as an irradiation in the absence of oxygen that does not have sufficient time to diffuse in depth. On the other hand, a long-duration irradiation (months or years) to a low dose involves a considerable reduction in the impact resistance because oxygen has a long enough time to diffuse in depth. Thus, a dose of 10–20 kJ/kg (1–2 mRad) per mm thickness reduces elongation at break to 10% of its initial value. These results are examples only and cannot be generalized.

Behaviour at high frequencies

Polyethylenes have very weak loss factors, about $1\text{–}10 \times 10^{-4}$ and do not heat up under high-frequency current. They cannot be welded by this technique.

Chemicals

Polyethylenes absorb little water and are not very sensitive to it but have some propensity to stress cracking in the presence of soaps, alcohols, detergents . . .

Suitable grades are usable in contact with food and are used for food packaging, milk bottles for example.

Chemical resistance is generally good up to 60°C but polyethylenes are attacked by oxidizing acids, chlorinated solvents, certain oxidants, aromatic hydrocarbons.

Copper, manganese and cobalt are oxidation catalysts and must be avoided, in particular for inserts.

Crystallinity increases the impermeability and, consequently, chemical resistance.

Generally, HDPE is slightly more resistant than LDPE.

Table 4.3 displays some results concerning general assessments of behaviour after prolonged immersion in a range of chemicals at ambient temperature for given grades, which are not necessarily representative of all the polyethylenes. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.3 Polyethylene: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	
		HDPE	LDPE
Acetic acid	10–60	S	S
Acetic acid	>96	S	l
Acetic aldehyde	100	S	l
Acetic anhydride	100	S	l
Acetone	100	l	l
Acetonitrile	100	l	l
Acetophenone	100	S	l
Acetyl chloride	100	l	l
Adipic acid	Saturated	S	S
Allylic alcohol	96	S	l
Alum	Solution	S	S
Aluminium chloride	Solution	S	S
Aluminium fluoride	Saturated	S	S
Aluminium sulfate	Unknown	S	S
Ammonia gas	100	S	S
Ammonia liquid	100	S	l
Ammonium chloride	Solution	S	S
Ammonium fluoride	Solution	S	S
Ammonium hydroxide	30	S	S
Ammonium hydroxide	Dilute	S	S
Ammonium nitrate	Unknown	S	S
Ammonium sulfate	50	S	S
Ammonium sulfide	Solution	S	S
Amyl acetate	100	S	n
Amyl alcohol	100	S	l
Aniline	100	S	n
Antimony chloride	10–90	S	S
Aqua regia	Unknown	n	n
Aromatic hydrocarbons	100	n	n
Arsenic acid	Unknown	S	S
ASTM1 oil	100	S	S
ASTM2 oil	100	S	S
ASTM3 oil	100	S	l
Barium carbonate	Saturated	S	S
Barium chloride	Saturated	S	S
Barium hydroxide	Saturated	S	S
Barium sulfate	Saturated	S	S
Beer	Unknown	S	S
Benzaldehyde	100	S	l
Benzene	100	l	n
Benzoic acid	Saturated	S	S
Benzyl chloride	100	l	l
Benzyl alcohol	100	S	S
Borax	Saturated	S	S
Boric acid	Unknown	S	S
Bromine (dry gas)	100	n	n
Bromine (liquid)	100	n	n
Bromine water	Solution	n	n
Butanol	100	S	S
Butanone	100	S	l
Butyl acetate	100	S	l
Butylamine	Unknown	n	l
Butylchloride	100	n	n
Butyric acid	100	S	l
Butyric acid	Unknown	S	S
Calcium chloride	Unknown	S	S
Calcium hydroxide	Saturated	S	S
Calcium hypochlorite	Solution	S	S
Carbon sulfide	100	l	n
Carbon tetrachloride	100	l	n
Castor oil	100	S	S
Cellosolve	100	n	l
Cellosolve acetate	100	n	l
Chlorinated hydrocarbons	100	n	n
Chlorinated solvents	100	n	n
Chlorine (dry gas)	100	l	n
Chlorine dioxide	Unknown	l	l
Chlorine water	Unknown	l	n
Chloroacetic acid	Unknown	l	n
Chlorobenzene	100	l	l
Chlorobenzene mono	100	l	n
Chloroform	100	n	n
Chlorosulfonic acid	Unknown	n	n
Chromic acid	Unknown	S	S
Citric acid	10 to saturated	S	S
Copper sulfate	Unknown	S	S
Cresol	100	S	l
Cyclohexane	100	S	l
Cyclohexanol	100	S	l
Cyclohexanone	100	S	l
Decaline	100	S	l
Dextrin	Solution	S	S
Dichloroethane	100	l	n
Dichloroethylene	100	l to n	l
Diethylamine	100	l	l
Diethyleneglycol	100	S	S
Diethylether	100	l	n
Dimethylamine	100	l	n

Table 4.3 (Continued)

Chemical	Concentration (%)	Estimated behaviour	
		HDPE	LDPE
Dimethylformamide	100	S	l
Dimethylhydrazine	100	S	S
Dioctylphthalate	100	S	l
Dioxan	100	S	l
Ethanol	40	S	S
Ethanol	96	S	l
Ethanol	Unknown	S	S
Ethylacetate	100	S	l
Ethylchloride	100	l	l
Ethylene glycol	100	S	S
Ethylenebromide	100	n	l
Ethylhexanol	100	S	S
Fluorine	100	n	l
Fluosilicic acid	Unknown	S	S
Formaldehyde	35	S	S
Formic acid	10–100	S	S
Freon 113	100	l	l
Freon 13b1	100	S	S
Freon 22	100	S	S
Freon 32	100	S	S
Furfural	100	S	S
Furfuryl alcohol	100	S	l
Glucose	Dilute	S	S
Glycerol	100	S	S
Glycollic acid	33	S	S
Heptane	100	S	n
Hexane	100	l	l
Hydrazine	100	S	S
Hydrobromic acid	48–100	S	S
Hydrochloric acid	10–36	S	S
Hydrofluoric acid	4–60	S	S
Hydrogen	100	S	S
Hydrogen peroxide	30–90	S	S
Hydrogen sulfide	Unknown	S	S
Hydrogen sulfide gas	Unknown	S	S
Iron(III) chloride	Unknown	S	S
Iron sulfate	Saturated	S	S
Isobutanol	100	S	S
Isooctane (Fuel A)	100	S	l
Isopropanol	100	S	S
Kerosene	100	S	l
Lactic acid	90	S	S
Lead acetate	10	S	S
Linseed oil	100	S	S
Liquid paraffin	100	l to S	l
Magnesium carbonate	Saturated	S	S
Magnesium chloride	Unknown	S	S
Magnesium hydroxide	Unknown	S	S
Maleic acid	Saturated	S	S
Manganese sulfate	Unknown	S	S
Mercury	100	S	S
Mercury chloride	Unknown	S	S
Mercury(II) nitrate	Solution	S	S
Methane chloride	100	l	l
Methanol	100	S	S
Methylbromide	100	l	n
Methylchloride	100	l	l
Methylene chloride	100	l	n
Methylethylketone	100	S	l
Methylglycol	Unknown	S	S
Milk	100	S	S
Mineral oil	100	S	l
Molasses	Unknown	S	S
Monoethanolamine	Unknown	l	l
Monoethyleneglycol	100	S	S
Naphtha	Unknown	S	l
Nickel chloride	Unknown	S	S
Nickel nitrate	Saturated	S	S
Nitric acid	10–25	S	S
Nitric acid	50	l	l
Nitric acid	75	n	l
Nitric acid	100	n	n
Nitrobenzene	100	l	l
Nonanol	100	S	S
Oleic acid	100	S	l
Oleic acid	Unknown	S	S
Olive oil	100	S	S
Oxalic acid	Saturated	S	S
Ozone	Unknown	l	n
Pentanol	100	S	l
Pentylacetate	100	S	n
Perchloroethylene	100	l	n
Petrol aliphatic	100	S	l
Petroleum	100	S	l
Phenol	Unknown	S	S
Phenol	Solution	S	l
Phosphoric acid	50–95	S	S
Picric acid	Solution	S	S
Potassium bromate	Unknown	S	S
Potassium carbonate	Saturated	S	S
Potassium chlorate	Saturated	S	S
Potassium chromate	Saturated	S	S
Potassium cyanide	Unknown	S	S
Potassium dichromate	Saturated	S	S
Potassium ferrocyanide	Saturated	S	S
Potassium fluoride	Unknown	S	S
Potassium hydroxide	10–45	S	S
Potassium hypochlorite	Solution	S	S
Potassium nitrate	Saturated	S	S
Potassium perchlorate	10	S	S
Potassium permanganate	20	S	S
Potassium persulfate	10	S	S

(*Continued*)

Table 4.3 (Continued)

Chemical	Concentration (%)	Estimated behaviour		Chemical	Concentration (%)	Estimated behaviour	
		HDPE	LDPE			HDPE	LDPE
Potassium sulfide	Solution	S	S	Tannic acid	Solution	S	S
Potassium sulfate	Unknown	S	S	Tartaric acid	Solution	S	S
Propanol	100	S	S	Tetrachloroethane	100	l	l
Propionic acid	100	S	S	Tetrachloroethylene	100	l	n
Propylene oxide	100	S	S	Tetrahydrofuran	100	l	l
Pyridine	Unknown	S	S	Thionyl chloride	100	n	n
Salicylic acid	Saturated	S	S	Tin chloride	Unknown	S	S
Sea water	100	S	S	Titanium tetrachloride	Unknown	S	S
Silicone oil	100	S	S	Toluene	100	l	n
Silver acetate	Saturated	S	S	Transformer oil	100	S	S
Silver cyanide	Saturated	S	S	Trichloroacetic acid	Unknown	S	S
Silver nitrate	Saturated	S	S	Trichloroethane	100	n	n
Sodium borate	Unknown	S	S	Trichloroethylene	100	l	l
Sodium carbonate	10–50	S	S	Tricresylphosphate	Unknown	S	S
Sodium chlorate	Saturated	S	S	Triethanolamine	Unknown	S	S
Sodium chloride	25	S	S	Triethylamine	Unknown	l	l
Sodium cyanide	Unknown	S	S	Turpentine oil	100	l	l
Sodium fluoride	Saturated	S	S	Urea	Solution	S	S
Sodium hydroxide	10–55	S	S	Urine	Unknown	S	S
Sodium hypochlorite	20	S	S	Vegetable oil	100	S	S
Sodium nitrate	Solution	S	S	Vinegar	Unknown	S	S
Sulfuric anhydride	100	n	n	Vinyl chloride	Unknown	n	n
Sulfurous acid	Solution	S	S	Vinyl acetate	100	S	l
Sulfurous anhydride (gas)	Unknown	S	S	Water	100	S	S
Sulfur dioxide (dry)	100	S	S	White spirit	100	l	l
Sulfur dioxide (gas)	Unknown	S	S	Wine	Unknown	S	S
Sulfuric acid	2–70	S	S	Xylene	100	l	n
Sulfuric acid	96	S	S to l	Yeast	Solution	S	S
Sulfuric acid	Fuming	n	n	Zinc chloride	Unknown	S	S

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: polyethylene has a low permeability, evaluated from 0.9 up to 2.5 compared to the full range of 0.05 up to 400 for all tested plastics.
- Gases: polyethylene has a rather high permeability, evaluated at:
  - air: 750 to 2750 versus a full range of 3 up to 2750 for all tested plastics
  - carbon dioxide: 7000 to 25 000 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 500 to 1700 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 1900 to 5000 versus a full range of <1 up to 11 000 for all tested plastics
  - hydrogen: 6000 to 20 000 versus a full range of 400 up to 20 000 for all tested plastics.

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames, even after the ignition source is removed. Moreover, polyethylene drips while burning.

Oxygen indices are roughly 17 with a poor UL94 rating.

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties. UL94 V0 rating can be reached for some FR grades.

4.1.6 Electrical properties

Polyethylenes are good insulators even in wet environments, with high dielectric resistivities and rigidities, and low loss factors. Special grades are marketed for electrical applications such as the insulation of wires and cables.

4.1.7 Joining, decoration

Welding is easy using thermal processes, possible with ultrasound methods but impossible with the high-frequency technique.

Gluing is difficult, needing pre-treatments such as, for example, chemical etching (sulfochromic acid etching), flame oxidation or hot-air (500°C) treatment, corona discharge, plasma or UV treatments. The exposure must be brief and superficial and the original and aged properties must be tested.

All precautions must be taken concerning health and safety according to local laws and regulations.

Polyethylene can generally be decorated after the same pre-treatments by painting, printing, metallization. Service conditions must be light.

4.1.8 Crosslinked polyethylene

Specific grades of polyethylene can be cured before use to improve some performances. The main processing methods involve:

- heating to promote chemical reaction of curing agents such as silanes or peroxides leading to crosslinking.
- irradiation to promote direct crosslinking.

Heating can be achieved by discontinuous processes, such as heated moulds, ovens, or by continuous processes such as hot tubes for wire curing or hot tunnels.

Irradiation can be achieved by discontinuous processes such as the cobalt bomb, which is more convenient for thick parts, but slow or continuous processes such as the electron beam are more suitable and speedier for thinner parts.

Crosslinking improves resistance to heat, stress cracking and abrasion, and also reduces permanent set after loading, residual monomers and/or oligomers and VOCs (volatile organic compounds). Irradiation is a 'cold' sterilization process.

Of course, there are also some drawbacks, notably the overspend for an additional processing step and the corresponding investments or subcontracting. Irradiation can also damage polyethylene.

Crosslinking creates an irreversible 3D network and makes polyethylene more difficult to recycle.

4.1.9 Foams

Unlike industrial solid polymers, which are processed as carefully as possible to avoid the formation of bubbles, vacuoles etc., alveolar materials result from the desire to introduce, in a controlled way, a certain proportion of voids with the aim of:

- increasing flexibility: very soft seals
- improving the thermal or phonic insulating character: foams for building, automotive . . .
- making damping parts: foams for packaging, automotive and transport safety parts.

The alveolar materials consist of a polymer skeleton surrounding the cells, which may be closed or partially or completely open to neighbouring cells or the outside.

The intrinsic properties come from those of the polyethylene with:

- a reduction in the mechanical properties due to the small quantity of material and the high proportion of gas.
- a reduction in the chemical behaviour due to the highly divided nature of the material. The thin cell walls immediately absorb liquids and gases and are rapidly damaged.

Generally, the properties of polyethylene foams are:

- densities from 25 kg/m^3 up to 330 kg/m^3.
- semi-rigid to flexible
- closed cells
- crosslinked or linear. Often, crosslinking improves the mechanical properties and chemical resistance.

Polyethylene foams (see Table 4.4) have:

- insulating properties
- damping properties
- fair mechanical characteristics according to their density: Figure 4.6 displays an example of tensile strength versus density
- a low absorption and permeability to water or moisture and excellent hydrolysis behaviour
- a naturally low fire resistance that can be improved by a suitable formulation.

Table 4.4 Examples of some polyethylene foam properties

Density (g/cm^3)	0.025	0.050	0.095	0.185
Density (kg/m^3)	25	50	95	185
Thermal conductivity (W/m.K)	0.034	0.035	0.040	0.052
10% compression stress (MPa)	0.012	0.019–0.032	0.020–0.064	0.070–0.160
50% compression stress (MPa)	0.080–0.095	0.109–0.127	0.131–0.192	0.331–0.605
Compression set, 22 h, 25% (%)	13	4–9	3–4	3–5
Tensile strength (MPa)	0.140–0.280	0.440–0.800	0.830–1.630	1.600–3.900
Elongation at break (%)	80–125	140–295	145–360	230–425
Water absorption, 7 days (%)	<1	<1	<1	<1
Service temperatures (°C) Minimum	−80	−80	−80	−80
Maximum	80–100	80–100	80–100	80–100

Examples of applications

Automotive and transport

Damping and protection; air-, water- and dust-proofing, thermal insulation, soundproofing:

- safety padding of instrument panels, door panels or sun visors
- energy-absorbing bumpers

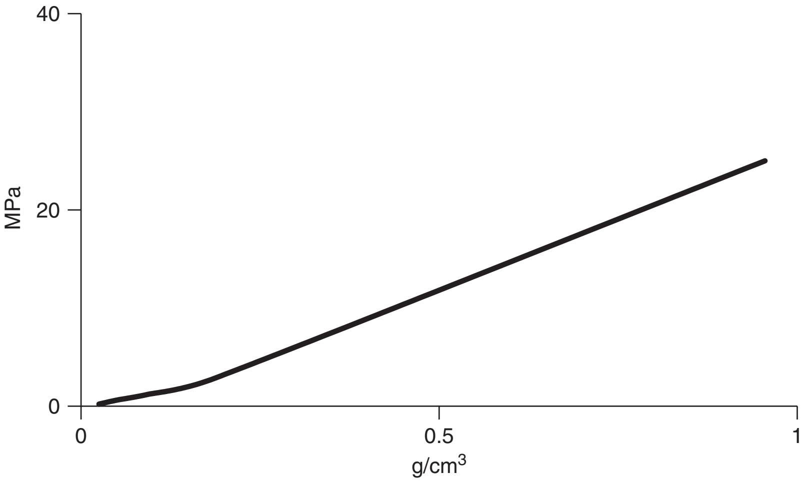


Figure 4.6. Tensile strength versus density for PE foam example

- door fillings
- carpet underlay.

Building and civil engineering

Air-, water- and dust-proofing, heat insulation, soundproofing:

- thermal insulation of roofs, walls, ceilings, floors
- thermal insulation of sandwich panels for industrial construction
- insulation of pipes, pipelines; half-shells for heating piping insulation and air-conditioning
- panels and sandwich structures for protection of oil wellheads.

Packaging

- flakes, chips, sheets, blocks are used for impact protection and damping in the packaging of various products such as cameras, electronic devices . . .
- Antistatic, conductive foams for electronics packaging
- isothermal packaging
- cool bags . . .

Nautical

- life jackets, life suits
- safety padding
- buoys
- floating pipes, insulation of pipelines
- floating cables . . .

Sports and leisure

- gym mats, padding, damping and insulating mats
- stuffing of rucksacks in foam-coated textile
- toys: 2D and 3D puzzles, floating toys . . .

Industry

- machine soundproofing
- impact and vibration damping.

Medical

- electrode pads for electrocardiogram testers
- proofing layers for sanitary towels and disposable nappies.

Miscellaneous

- backing of adhesive tapes
- multilayer joints with PVDC or aluminium for caps
- multilayer composites for damping, sometimes in combination with polypropylene foam. Some helmets, for example, are made of thermoplastic skins and a core of one layer of PE foam with, possibly, a second layer of polypropylene foam.

4.1.10 Industrial fibres

UHMW polyethylene fibres are produced by a gel spinning process from a solution. After stretching, macromolecules of the fibres are highly oriented (95%) and crystallized (85%), resulting in high tenacity and modulus. Due to the high molecular orientation, the coefficient of thermal expansion is highly negative, for example -1.2×10^{-5}.

Table 4.5 compares PE fibres with those of glass and steel. Engineering properties are intermediate between the two but if we take into account the very low density, the specific properties of PE fibres are by far the most attractive.

Table 4.5 Comparative property examples of polyethylene, glass and steel fibres

Fibres	Glass	High strength polyethylene	Steel
Engineering properties			
Density (g/cm^3)	2.5	0.97	7.7
Tensile strength (MPa)	3000	2600–3500	2000
Modulus (GPa)	70	62–124	203
Elongation at break (%)	2.5–5	3–4	2
Melting temperature (°C)	750	144–152	1500
Maximum service temperature (°C)		80–100	
Minimum service temperature (°C)		<-150	
Specific properties: engineering properties/density			
Tensile strength (MPa)	1200	2680–3600	260
Modulus (GPa)	28	64–128	26

These fibres have a soft feel, an excellent abrasion resistance, excellent energy absorption behaviour and a moderate level of cut protection.

Application fields are, for example:

- products for ballistic protection, body armour, riot equipment, police or military vests protecting against rifle bullets, removable protective panels for armoured cars
- full-face helmets for motorbikes with hybrid reinforcement of carbon-polyethylene-glass fibres
- military helmets using composites with PE fibres in different forms and in different matrices, notably thermoplastics
- reinforcement of composites for boat hulls
- cut-resistant gloves, liners inside leather gloves for industrial, military and law enforcement agencies

- reinforcement layers inserted under or into garments to provide slash protection
- ropes for fish-farming, anchorage . . .

4.1.11 Specific ISO standards concerning polyethylenes

Polyethylene (thermoplastics)

ISO 1872-1:1993 Plastics – Polyethylene (PE) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 1872-2:1997 Plastics – Polyethylene (PE) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 1969:2004 Fibre ropes – Polyethylene – 3- and 4-strand ropes

ISO 3458:1976 Assembled joints between fittings and polyethylene (PE) pressure pipes – Test of leakproofness under internal pressure

ISO 3459:1976 Polyethylene (PE) pressure pipes – Joints assembled with mechanical fittings – Internal under-pressure test method and requirement

ISO 3501:1976 Assembled joints between fittings and polyethylene (PE) pressure pipes – Test of resistance to pull out

ISO 3503:1976 Assembled joints between fittings and polyethylene (PE) pressure pipes – Test of leakproofness under internal pressure when subjected to bending

ISO 3663:1976 Polyethylene (PE) pressure pipes and fittings, metric series – Dimensions of flanges

ISO 4059:1978 Polyethylene (PE) pipes – Pressure drop in mechanical pipe-jointing systems – Method of test and requirements

ISO 4427:1996 Polyethylene (PE) pipes for water supply – Specifications

ISO 4437:1997 Buried polyethylene (PE) pipes for the supply of gaseous fuels – Metric series – Specifications

ISO 5834-1:1998 Implants for surgery – Ultra-high molecular weight polyethylene – Part 1: Powder form

ISO 5834-2:1998 Implants for surgery – Ultra-high molecular weight polyethylene – Part 2: Moulded forms

ISO 7214:1998 Cellular plastics – Polyethylene – Methods of test

ISO 8085-1:2001 Polyethylene fittings for use with polyethylene pipes for the supply of gaseous fuels – Metric series – Specifications – Part 1: Fittings for socket fusion using heated tools (available in English only)

ISO 8085-2:2001 Polyethylene fittings for use with polyethylene pipes for the supply of gaseous fuels – Metric series – Specifications – Part 2: Spigot fittings for butt fusion, for socket fusion using heated tools and for use with electrofusion fittings

ISO 8085-3:2001 Polyethylene fittings for use with polyethylene pipes for the supply of gaseous fuels – Metric series – Specifications – Part 3: Electrofusion fittings

ISO 8180:1985 Ductile iron pipes – Polyethylene sleeving

ISO 8283-2:1992 Plastics pipes and fittings – Dimensions of sockets and spigots for discharge systems inside buildings – Part 2: Polyethylene (PE)

ISO 8770:2003 Plastics piping systems for soil and waste discharge (low and high temperature) inside buildings – Polyethylene (PE)

ISO 8772:1991 High-density polyethylene (PE-HD) pipes and fittings for buried drainage and sewerage systems – Specifications

ISO 8779:2001 Polyethylene (PE) pipes for irrigation laterals – Specifications

ISO 8796:2004 Polyethylene PE 32 and PE 40 pipes for irrigation laterals – Susceptibility to environmental stress cracking induced by insert-type fittings – Test method and requirements

ISO 9625:1993 Mechanical joint fittings for use with polyethylene pressure pipes for irrigation purposes

ISO/TR 10837:1991 Determination of the thermal stability of polyethylene (PE) for use in gas pipes and fittings

ISO 10838-1:2000 Mechanical fittings for polyethylene piping systems for the supply of gaseous fuels – Part 1: Metal fittings for pipes of nominal outside diameter less than or equal to 63 mm

ISO 10838-2:2000 Mechanical fittings for polyethylene piping systems for the supply of gaseous fuels – Part 2: Metal fittings for pipes of nominal outside diameter greater than 63 mm

ISO 10838-3:2001 Mechanical fittings for polyethylene piping systems for the supply of gaseous fuels – Part 3: Thermoplastics fittings for pipes of nominal outside diameter less than or equal to 63 mm

ISO/TS 10839:2000 Polyethylene pipes and fittings for the supply of gaseous fuels – Code of practice for design, handling and installation

ISO 10933:1997 Polyethylene (PE) valves for gas distribution systems

ISO 11413:1996 Plastics pipes and fittings – Preparation of test piece assemblies between a polyethylene (PE) pipe and an electrofusion fitting

ISO 11414:1996 Plastics pipes and fittings – Preparation of polyethylene (PE) pipe/pipe or pipe/fitting test piece assemblies by butt fusion

ISO 11542-1:2001 Plastics – Ultra-high-molecular-weight polyethylene (PE-UHMW) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 11542-2:1998 Plastics – Ultra-high-molecular-weight polyethylene (PE-UHMW) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO/TR 11647:1996 Fusion compatibility of polyethylene (PE) pipes and fittings

ISO 12176-1:1998 Plastics pipes and fittings – Equipment for fusion jointing polyethylene systems – Part 1: Butt fusion

ISO 12176-2:2000 Plastics pipes and fittings – Equipment for fusion jointing polyethylene systems – Part 2: Electrofusion

ISO 12176-3:2001 Plastics pipes and fittings – Equipment for fusion jointing polyethylene systems – Part 3: Operator's badge

ISO 12176-4:2003 Plastics pipes and fittings – Equipment for fusion jointing polyethylene systems – Part 4: Traceability coding

ISO 13460:1998 Agricultural irrigation equipment – Plastics saddles for polyethylene pressure pipes

ISO 13480:1997 Polyethylene pipes – Resistance to slow crack growth – Cone test method

ISO 13761:1996 Plastics pipes and fittings – Pressure reduction factors for polyethylene pipeline systems for use at temperatures above 20 degrees C

ISO 13953:2001 Polyethylene (PE) pipes and fittings – Determination of the tensile strength and failure mode of test pieces from a butt-fused joint

ISO 13954:1997 Plastics pipes and fittings – Peel decohesion test for polyethylene (PE) electrofusion assemblies of nominal outside diameter greater than or equal to 90 mm

ISO 13955:1997 Plastics pipes and fittings – Crushing decohesion test for polyethylene (PE) electrofusion assemblies

ISO 13957:1997 Plastics pipes and fittings – Polyethylene (PE) tapping tees – Test method for impact resistance

ISO 14236:2000 Plastics pipes and fittings – Mechanical-joint compression fittings for use with polyethylene pressure pipes in water supply systems

ISO 14616:1997 Plastics – Heatshrinkable films of polyethylene, ethylene copolymers and their mixtures – Determination of shrinkage stress and contraction stress

ISO 14632:1998 Extruded sheets of polyethylene (PE-HD) – Requirements and test methods

ISO 15494:2003 Plastics piping systems for industrial applications – Polybutene (PB), polyethylene (PE) and polypropylene (PP) – Specifications for components and the system – Metric series

ISO 16770:2004 Plastics – Determination of environmental stress cracking (ESC) of polyethylene – Full-notch creep test (FNCT)

Crosslinked polyethylene

ISO 10146:1997 Crosslinked polyethylene (PE-X) pipes – Effect of time and temperature on the expected strength

ISO 10147:1994 Pipes and fittings made of crosslinked polyethylene (PE-X) – Estimation of the degree of crosslinking by determination of the gel content

ISO 14531-1:2002 Plastics pipes and fittings – Crosslinked polyethylene (PE-X) pipe systems for the conveyance of gaseous fuels – Metric series – Specifications – Part 1: Pipes

ISO 14531-2:2004 Plastics pipes and fittings – Crosslinked polyethylene (PE-X) pipe systems for the conveyance of gaseous fuels – Metric series – Specifications – Part 2: Fittings for heat-fusion jointing

ISO 15875-1:2003 Plastics piping systems for hot and cold water installations – Crosslinked polyethylene (PE-X) – Part 1: General

ISO 15875-2:2003 Plastics piping systems for hot and cold water installations – Crosslinked polyethylene (PE-X) – Part 2: Pipes

ISO 15875-3:2003 Plastics piping systems for hot and cold water installations – Crosslinked polyethylene (PE-X) – Part 3: Fittings

ISO 15875-5:2003 Plastics piping systems for hot and cold water installations – Crosslinked polyethylene (PE-X) – Part 5: Fitness for purpose of the system

ISO/TS 15875-7:2003 Plastics piping systems for hot and cold water installations – Crosslinked polyethylene (PE-X) – Part 7: Guidance for the assessment of conformity

4.1.12 Trade name examples

Alathon, Alkathene, Himod, Bormed, Borecene, Borstar, BorPEX, Borcoat, Cestilene, Cestilite, Cestitech, Constat, Elite, Formolene, Fortiflex, Hostalen, Hy-Pact Polymer, Lacqtene, Lennite, Lotrene, Lupolen, Marlex, Neopolen, Novapol, Petrothene, Poly-Eth-Hi-D, Polyfort, Polywax, RotoFlame, Rotothene, Superlink, Ultra-Ethylux, Vestolen . . .

Foams: Alveolit, Alveolen, Alveolux, Ethafoam, Freudenberg, Neopolen E, Ymos . . .

Fibres: Dyneema, Spectra . . .

4.1.13 Property tables

Table 4.6 relates to examples only and cannot be generalized; data cannot be used for design purposes. See also Table 4.5 for foam properties.

Table 4.6 Polyethylenes: examples of properties

	LDPE	HDPE	Linear PE
Miscellaneous properties			
Density (g/cm^3)	0.917–0.940	0.940–0.970	0.915–0.950
Shrinkage (%)	2–4	1.5–4	2–2.5
Absorption of water (%)	0.005–0.015	0.005–0.010	0.005–0.010
Mechanical properties			
Shore hardness, D	40–50	60–70	55–56
Stress at yield (MPa)	10–15	25–30	10–30
Strain at yield (%)		10–15	3–16
Tensile strength (MPa)	10–20	30–40	25–45
Elongation at break (%)	200–600	500–700	300–900
Tensile modulus (GPa)	0.130–0.300	0.500–1.100	0.266–0.525
Flexural modulus (GPa)	0.245–0.235	0.750–1.575	0.280–0.735
Notched impact strength ASTM D256 (J/m)	No break	20–220	54–NB
Thermal properties			
HDT B(0.46 MPa) (°C)	40–50	60–90	
HDT A(1.8 MPa) (°C)	30–40	44–60	
Vicat softening point A (°C)	76–109		96–118
Continuous use temperature (°C)	80–100	80–120	90–110
Glass transition temperature (°C)	−110	−110	−110
Melting temperature (°C)	110–120	130	122–124
Minimum service temperature (°C)	−70	−70 to −100	−70
Thermal conductivity (W/m.K)	0.32–0.35	0.40–0.50	0.35–0.45
Specific heat (cal/g/°C)	0.55	0.55	0.55
Coefficient of thermal expansion (10^{-5}/°C)	10–20	6–15	
Electrical properties			
Volume resistivity (ohm.cm)	10^{16}–10^{18}	10^{16}–10^{18}	10^{16}–10^{18}
Dielectric constant	2.3	2.3	2.3
Loss factor (10^{-4})	3–4	2–20	
Dielectric strength (kV/mm)	16–28	17–45	
Arc resistance (s)	130–160		
Fire behaviour			
Oxygen index	<20	<20	<20
UL94 fire rating	HB	HB	HB

	Coloured HDPE	UHMWPE	30% GF PE
Miscellaneous properties			
Density (g/cm^3)	0.96	0.930–0.950	1.200–1.280
Shrinkage (%)		4.0	0.2–0.6
Absorption of water (%)	0.010	0.005–0.010	0.020–0.060
Mechanical properties			
Shore hardness, D	65	60–70	70–80
Stress at yield (MPa)	28	20–25	52–63
Strain at yield (%)	10		1.5–2.5
Tensile strength (MPa)		39–49	52–63
Elongation at break (%)	>50	200–500	1.5–2.5
Tensile modulus (GPa)	1.35		4.9–6.3
Flexural modulus (GPa)			4.9–5.6
Compressive modulus at 1% (GPa)	0.9		
Notched impact strength ASTM D256 (J/m)		NB	60–80
Thermal properties			
HDT B(0.46 MPa) (°C)		68–82	127–130
HDT A(1.8 MPa) (°C)	44	40–50	121
Vicat softening point VST B50 (°C)	80	80	
Continuous use temperature (°C)	80	100–120	100–120
Glass transition temperature (°C)			−110
Melting temperature (°C)		120–135	120–140

Table 4.6 (Continued)

	Coloured HDPE	UHMWPE	30% GF PE
Minimum service temperature (°C)	−100	−150 to −200	
Thermal conductivity (W/m.K)	0.4		
Coefficient of thermal expansion (10^{-5}/°C)	15	13–20	5
Electrical properties			
Volume resistivity (ohm.cm)	$>10^{14}$	10^{16}–10^{18}	
Dielectric constant	2.4	2.1–3	
Loss factor (10^{-4})	2	2–10	
Dielectric strength (kV/mm)	25–45	25–45	
Fire behaviour			
Oxygen index	<20	<20	
UL94 fire rating	HB	HB	
	HDPE containing reprocessed HDPE	Antistatic HDPE	
Colour	Black/green	Black	
Miscellaneous properties			
Density (g/cm^3)	0.96	0.95	
Absorption of water (%)	0.010	0.05	
Mechanical properties			
Shore hardness, D	65	62	
Stress at yield (MPa)	28	20	
Strain at yield (%)	10	10	
Elongation at break (%)	>50		
Tensile modulus (GPa)	1.350	0.770	
Compressive modulus at 1% (GPa)	0.9	0.5	
Thermal properties			
HDT A(1.8 MPa) (°C)	44	42	
Vicat softening point VST B50 (°C)	80		
Continuous use temperature (°C)	80	80	
Melting temperature (°C)	130–135	130–135	
Minimum service temperature (°C)	−60	−150	
Thermal conductivity (W/m.K)	0.4	0.4	
Coefficient of thermal expansion (10^{-5}/°C)	15	20	
Electrical properties			
Volume resistivity (ohm.cm)	$>10^{14}$	$<10^{6}$	
Dielectric constant	2.4		
Loss factor (10^{-4})	2		
Dielectric strength (kV/mm)	25–45		
Fire behaviour			
Oxygen index	<20	<20	
UL94 fire rating	HB	HB	
	HDPE V0 Halogen free	PE-X Neat and filled	
Miscellaneous properties			
Density (g/cm^3)	0.98	0.915 −1.400	
Shrinkage (%)		0.7–5	
Absorption of water (%)		0.005–0.010	
Mechanical properties			
Shore hardness, D		30–80	
Stress at yield (MPa)	>18		
Tensile strength (MPa)	>18	11–32	
Elongation at break (%)		10–440	
Tensile modulus (GPa)		0.350–3.500	

(*Continued*)

Table 4.6 (Continued)

	HDPE V0 Halogen free	PE-X Neat and filled
Thermal properties		
HDT B(0.46 MPa)		54–107
HDT A(1.8 MPa)		40–63
Continuous use temperature (°C)	90	90–130
Melting temperature (°C)		150–170 before crosslinking
Minimum service temperature (°C)	−200	
Specific heat (cal/g/°C)		0.55
Coefficient of thermal expansion (10^{-5}/°C)		10
Electrical properties		
Volume resistivity (ohm.cm)		10^{16}
Surface resistivity (ohm)	10^{6}	
Dielectric constant		2.2
Loss factor (10^{-4})		4
Dielectric strength (kV/mm)		21
Fire behaviour		
Oxygen index	>28	17
UL94 fire rating	V0	HB

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers and/or black colour are needed
Weak acids	Good behaviour
Strong acids	Good behaviour except oxidizing acids
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Good behaviour up to 60°C except with aromatics, chlorinated solvents, certain oxidants Copper, manganese and cobalt are oxidation catalysts and must be avoided, in particular for inserts
Food contact	Possible for special grades

4.2 Polypropylene (PP)

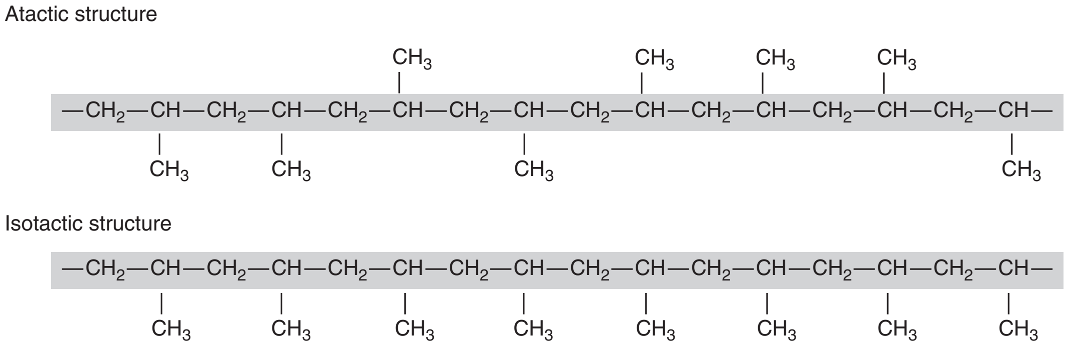
From the simple chemical formula of propylene

$$CH_2{=}CH{-}CH_3$$

are born several subfamilies according to the polymerization process, the use of comonomers, blending with elastomers, and the use of reinforcements:

- **Homopolymers**, by polymerization of propylene alone. Two basic structures can be obtained (Figure 4.7):
  - ○ isotactic with the CH_3 located on only one side of the backbone. This is the only form used for engineering applications
  - ○ atactic with the CH_3 randomly located here and there on either side of the backbone. This form is not used as an engineering material but has some applications such as bitumen modifiers for roofing.

  The homopolymers are rigid but rather brittle.
- **Copolymers**, by polymerization of propylene with another olefin, ethylene being the most used. These copolymers can have:
  - ○ a random structure with the comonomer randomly inserted into the backbone, which induces an amorphous morphology and therefore a better transparency



Atactic structure

$$-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-$$

Isotactic structure

$$-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-$$

Figure 4.7. Atactic and isotactic structures of polypropylene

- ○ a block structure with several comonomer sequences inserted into polypropylene sequences, which favours crystallinity.

The copolymers have better behaviour at low temperature and are more impact resistant but less rigid than the homopolymers. The copolymer blocks present a good balance between rigidity and impact strength that depends on the importance of the blocks and their distribution:

- **modified ethylene-propylene elastomers**, which confer very high impact strengths even at low temperature.
- **reinforcement**: mineral fillers, especially talcs, and glass fibres are used to increase rigidity at ambient and higher temperatures, as well as to decrease creep.

The main polymerization processes are:

- Ziegler-Natta, the oldest process leading to linear and isotactic polypropylene with a low level of atactic structure.
- Metallocene catalysis polymerization, the most recent technique, is growing fast to produce a consistent polypropylene with uniform distribution of molecular weight resulting in enhanced toughness, impact and puncture strengths, better cold behaviour and optical properties. These advantages allow the downgauging or enhancement of performances for the same weight of polymer.

Figure 4.8 ((a), (b), (c), and (d)) displays, in a simplified manner, the alteration of the basic properties of homopolymer (H-PP) when modified with other comonomers (co-PP), with elastomer (impact) or with an inorganic filler: mineral, talc, short or long glass fibres (SGF or LGF).

For mechanical performance properties:

- glass fibres provide a strong reinforcement while mineral fillers act especially and moderately on the modulus
- comonomers and elastomers exclusively increase the impact strength but decrease modulus.

For the heat behaviour:

- glass fibres produce a sizeable increase in HDT A
- mineral fillers have a limited effect
- comonomer and elastomer slightly decrease HDT A.

Despite the apparent similarity in the chemical structure, please note that the tertiary carbons attached to the polypropylene backbone induce a slightly different behaviour from that of polyethylene.

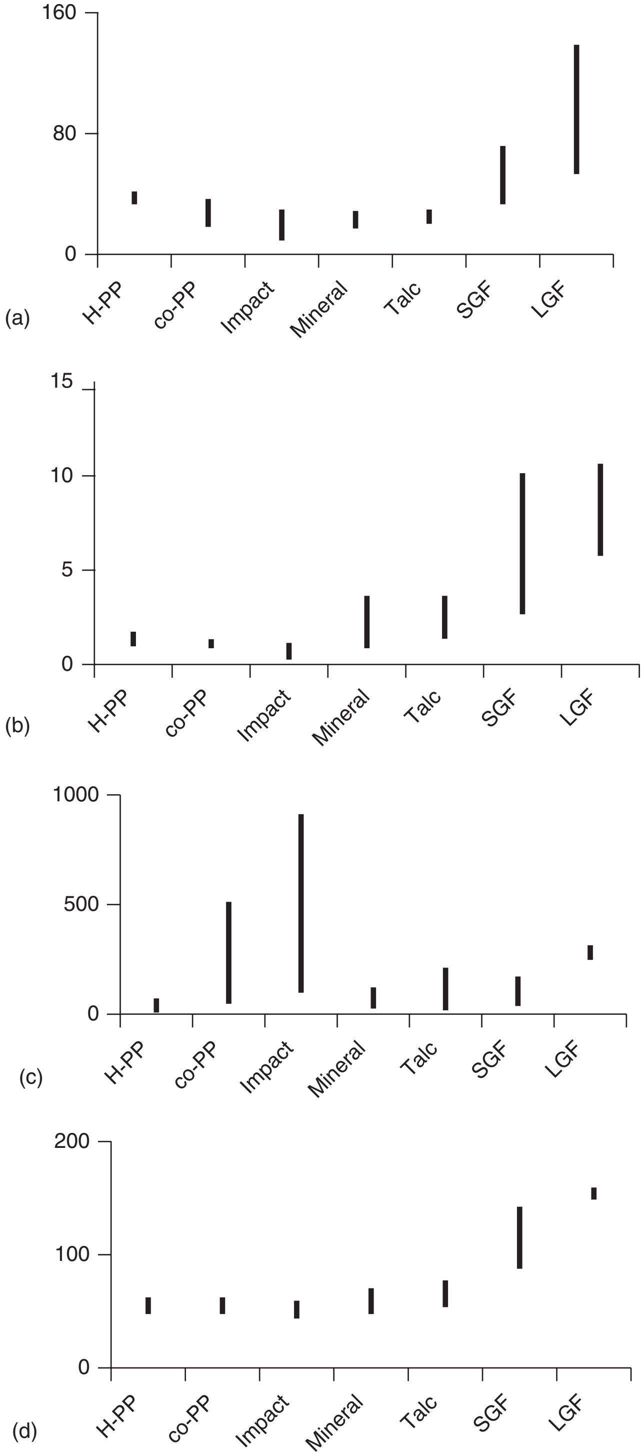


Figure 4.8. (a) PP: stress at yield examples (MPa); (b) PP: modulus examples (GPa); (c) PP: impact strength examples (J/m); (d) PP: HDT A examples (°C)

Because of the versatility of polypropylene, its favoured application sectors are diverse:

- 33% for moulding
- 25% for fibres, filaments and raffias
- 12% for films
- 7% for other extrusion applications
- 23% for unidentified applications.

The same basic propylene monomer induces many common properties and, unless otherwise specified, we will not make a distinction between the various subfamilies. Only the foams will be given special attention as they present particular properties due to their morphology:

- decreased mechanical properties due to the low quantity of polymer and the high proportion of gas
- weaker chemical resistance due to the highly divided state of the polymer. The thin cell walls immediately absorb liquids and gases.

4.2.1 General properties

Advantages

The properties are close to those of polyethylenes, with some differences due to the tertiary carbon linked to the backbone: good mechanical properties at ambient temperature, low price, attractive price/property ratios, easy processing, chemical inertness, weak absorption of water, low density, good electrical insulation even in wet media, feasibility of welding, versatility of processing methods, broad range of available melt flow rates (MFR).

Judiciously selected grades provide: good impact and fatigue resistance, good stiffness and impact balance, suitability for food contact, low extractables, good organoleptic properties, the possibility of autoclave and radiation sterilization in the presence of aqueous solutions . . .

The mineral, talc and, especially, fibreglass-filled grades are more rigid and have better behaviour and lower creep when the temperature rises.

Drawbacks

General drawbacks are the innate sensitivity to heat, low temperature, UV, light and weathering (but stabilized grades are marketed), creep and high-energy radiations; low rigidity, significant shrinkage. Transparency is difficult to achieve and often limited.

The impact resistance is weak for certain homopolymers.

Due to the surface tension, gluing, painting and printing are difficult without surface treatments. Composed only of carbon and hydrogen, polypropylenes are naturally flammable but FR grades are marketed, including halogen-free grades.

Polypropylene is not suitable for crosslinking.

General-purpose polypropylene is sensitive to pro-oxidant metals such as copper, manganese or cobalt, which must be avoided as inserts.

Special grades

They can be classified according to the processing type, specific properties and targeted applications:

- extrusion, injection, compression, cast film, blown film, blow moulding, foam, co-extrusion, for thin or thick parts, for welding . . .

- stabilized against heat, UV, light and weathering, detergents, copper, manganese or cobalt; antistatic; conductive; reinforced; food contact; clean; good organoleptic properties; autoclave and radiation sterilizable; fireproofed; clarified; transparent; low warpage; high fluidity; copper proofed; impact modified; low odour and taste; low extractables; high gloss . . .
- for bumpers, films, sheets, tubes, pipes, fibres, bottle racks, bins, containers, pallets, tubes, clean grades for health care . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide a rough idea. They are generally of the order of €1/kg.

Processing

All molten-state processing methods are usable: extrusion, injection, compression, blown film, blow moulding, thermoforming, foam, co-extrusion, machining for high hardness grades, welding.

Applications

(See Chapter 2 for further information.)

The statistically identified consumptions are roughly:

• fibres	27%
• consumer products	14%
• rigid packaging	11%
• films	9%
• transportation	4%
• sheets	3%
• appliances	2%
• blow moulding	1%.

Polypropylene is a fast-growing family of thermoplastics and the following list of application examples is not exhaustive.

Filaments, fibres and fabrics

Polypropylene filaments, fibres, fabrics, and partially and fully oriented yarns perform well in industrial and textile applications such as cordage, netting, woven bags, indoor and outdoor carpeting, carpet backing, outdoor carpets around swimming pools or miniature golf courses, upholstery, sports apparel, tying and baling twines, strings, strips, cords, nonwovens . . .

Consumer products

Polypropylenes are used to make consumer goods such as:

- storage bins and totes, food wares, thin-walled parts, freezer wares and other applications requiring clarity and stain resistance, trigger sprayers, pails and buckets, trash cans . . .
- luggage, suitcases, vanity cases . . .
- lawn furniture, lawn products, garden furniture, garden tools . . .
- toys . . .

Automotive

Polypropylenes perform well in interior and exterior parts for automotive, under-the-hood and underbody components such as:

- bumpers, bumper fascias, exterior trims, headlight casings and rear light bases, spoilers, step pads, body side mouldings, wheel trims . . .
- interior trim, dashboard, instrument panel inserts, pillar trims, consoles, airbag system parts, door and quarter-panel trims, lift-gate trims . . .
- under-the-hood parts: ventilation and air conditioning units, battery boxes, air ducts, air vents, ventilation nozzles, fan blades, fan bases, fan shrouds, heating device housings, belt covers, corrugated sheaths for wires and cables, windscreen washer parts . . .
- fender liners . . .

Industry

Polypropylenes are cost-effective polymers for casings, caps, frameworks for ventilation, fan blades, air filters, filters and pumps of industrial dishwashers, softeners, washing machines, detergent product vats, parts of pumps for handling chemicals, frames, cable rollers, parts with a film hinge, electrical components, translucent parts, cases, pipes . . .

Packaging

Polypropylenes perform well in:

- blow moulded and sheet thermoformed products for food, personal care, health, medical and labware applications, household chemicals and beauty aid products . . .
- clear or drop impact resistant containers, boxes, hot-filled bottles, dessert pots, horticultural pots, integrated hinge boxes, bottles and other cans up to several litres, caps and closures for beverage and cosmetic applications; medical disposable trays, containers for irrigation, parenteral, haemodialysis solutions . . .
- high clarity parts for medical and food applications . . .

Films

Polypropylenes are used to produce:

- oriented, bi-oriented and cast films and foils for food, non-food and medical packaging, confectioneries, tobacco, clothing packaging, medical pouches, monoblister packaging, film tapes, straps . . .
- film capacitors for military and industrial AC applications
- talc-filled reinforced polypropylene films and foils are beginning to replace PVC for corrugated board, office stationery, labels . . .

Appliances

Polypropylenes are cost-effective polymers for:

- white goods, components for the ‘wet side’ of domestic washing machines, dryers and dishwashers; refrigerator parts, floor care and small appliances, house wares, kitchenware, good clarity parts, jug kettles; toasters and irons parts . . .
- furniture . . .

Healthcare

Clean polypropylenes are used for:

- both packaging and casting cup applications, disposing of sharps, hospital disposables and other bedside applications, safety syringes, pre-filled syringes, general-purpose syringes; autoclave or radiation sterilizable parts in the presence of aqueous solutions, vials and bottles; contact lens casting cups and packaging . . .
- labwares, blood and centrifuge tubes, test tubes, beakers, and pipette tips . . .
- injection-moulded deodorant barrels . . .

4.2.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 90°C up to 130°C if softening temperatures are higher.

The UL temperature indices of specific grades can be 65–120°C for electrical and mechanical properties including impact.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

As examples:

- For a given grade of neat polypropylene, the short-term modulus retention at 80°C is 25% of the value at 20°C and HDT A (1.8 MPa) is of the order of 60°C.
- HDT under 1.8 MPa is of the order of:

○ impact grade	45–60°C
○ comonomer	50–60°C
○ homopolymer	50–65°C
○ mineral filled	50–70°C
○ talc filled	55–75°C
○ low SGF level	90–130°C
○ high SGF level	125–140°C
○ long glass fibres	150–160°C.

Figure 4.9 displays examples of modulus retention versus short-term temperature increase.

For long-term heat ageing, the retention of properties depends on the property and grades considered, notably the heat stabilizers used. Characteristics such as elongation at break and impact strength are especially heat sensitive.

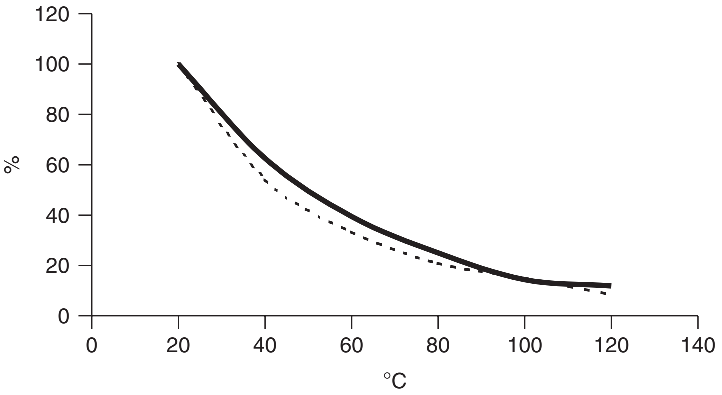


Figure 4.9. Neat PP examples of modulus retention (%) versus temperature (°C)

At low temperatures, general-purpose grades are generally usable down to −10°C but special grades perform well down to −40°C (bumper grades, for example) according to the mechanical constraints experienced.

Figure 4.10 shows two very different examples of impact strength variations versus low temperatures.

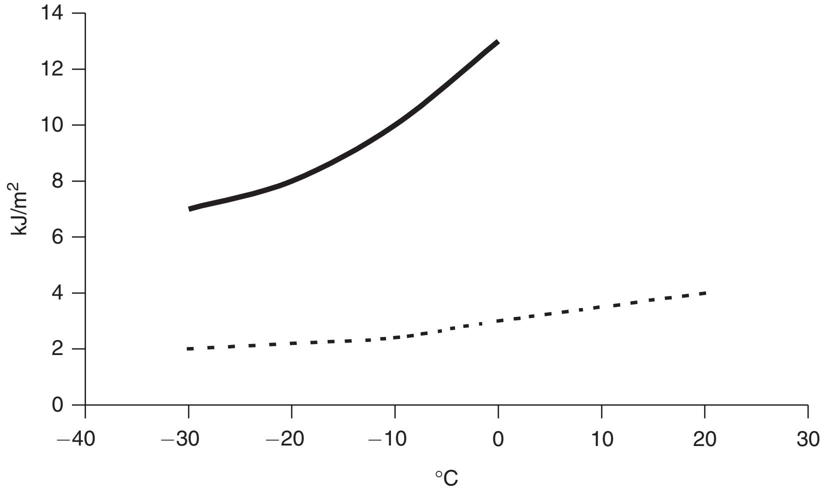


Figure 4.10. Neat PP: examples of Notched Charpy impact (kJ/m²) versus low and sub-zero temperatures (°C)

The glass transition temperatures of polypropylenes by DSC measurements generally range from −10°C to −20°C.

The glass transition temperatures by DTMA measurements can be higher, depending on the frequency.

These results relate to some grades only and cannot be generalized.

4.2.3 Optical properties

General-purpose polypropylenes are naturally whitish, and translucent to opaque according to the grade. Certain grades are especially designed for clarity.

Transmission of light can broadly vary, for example:

- 47% for a high-crystallinity grade
- 89% for a transparent grade
- 93–96% for metallocene grades.

Let us remember that light transmission is of the order of 98% for polystyrene.

For films, haze can be 5–7% for specific grades.

The refractive index varies with the type of polypropylene and can be, for example, in the range of 1.49 to 1.5.

These results relate to some grades only and cannot be generalized.

4.2.4 Mechanical properties

The mechanical properties are generally fair with high elongations at break but much more limited strains at yield. Moduli and hardnesses are higher than those of polyethylene but rather weak, and impact strength is in an intermediate range or even weak for some homopolymers. The abrasion resistance of polypropylene depends on the roughness, type and morphology of the antagonist sliding surface but is limited and polypropylenes are not especially designed for antifriction applications.

Crystallinity and molecular orientation improve the mechanical properties but adversely affect notched impact resistance.

Friction

The coefficients of friction are moderate, from 0.25 up to 0.45 for example, and the moduli, hardnesses and softening temperatures are rather weak, which limits the loads and PV factors. Data can be, for example:

- velocity 0.15 m/s
- pressure 0.5–2.0 MPa
- that is, PV factors of the order of 0.07 to 0.3.

Actually, polypropylenes are not especially used for antifriction applications.

These results relate to a few grades only and cannot be generalized.

Dimensional stability

Shrinkage, coefficient of thermal expansion and creep are rather high depending on crystallinity. The absorption and alteration by moisture exposure are low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For example, the following data are reported:

- 0.4 for a neat grade
- 0.35 for a 40% glass fibre reinforced polypropylene.

Creep

Thermoplastic neat polypropylenes have rather low moduli involving high strains for moderate loading. Consequently:

- Loadings for acceptable times to rupture or onset of yielding are very much lower than engineering strengths, for example:
  - ○ 35 MPa for a 40% glass fibre reinforced polypropylene breaking after 8000 h at ambient temperature.
  - ○ 18 MPa for a 30% glass fibre reinforced polypropylene breaking after 10 000 h at 80°C.
- Creep moduli are also low, the more so as the temperature rises and depending on the presence of comonomer as we can see in Figure 4.11.

From Figure 4.11(a) we note:

- The drop between engineering modulus, roughly 1.2 to 1.6 GPa, and creep modulus, roughly 0.14 to 0.5 after 1000 hr at ambient temperature.
- The broad difference between moduli measured under limited loads, 3.5–8 MPa.

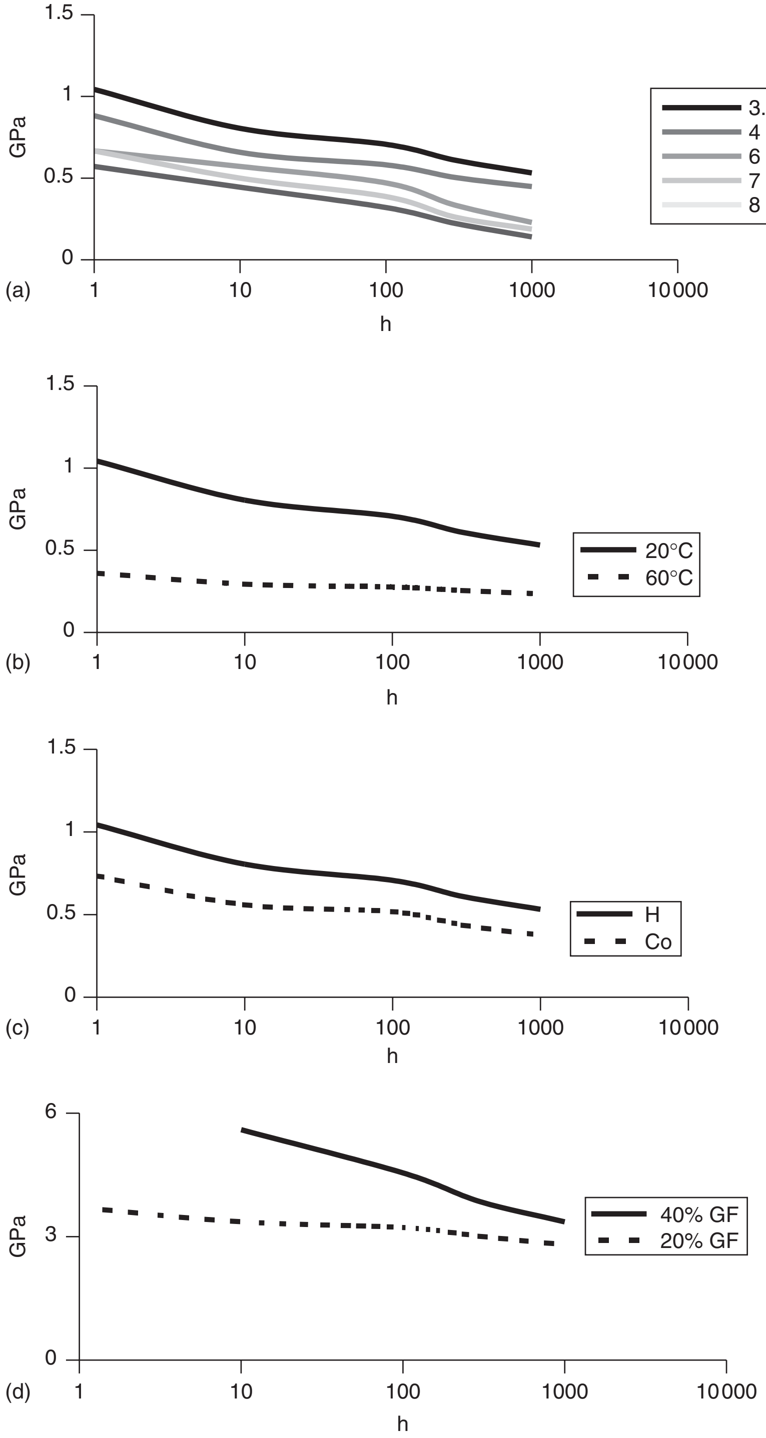


Figure 4.11. *(a) Neat PP creep: examples of creep modulus (GPa) versus time (h) for various loading (3.5 to 8 MPa); (b) Neat PP creep: examples of creep modulus (GPa) versus time (h) at 20°C and 60°C under 3.5 MPa; (c) Neat PP, homo and copolymer: examples of creep modulus (GPa) versus time (h) at 20°C under 3.5 MPa; (d) 20% and 40% GF reinforced PP: examples of creep modulus (GPa) versus time (h) at 20°C under 35 MPa*

Figure 4.11(b) displays the rapid decrease in creep modulus when the temperature rises moderately from ambient to 60°C. Designers must be vigilant when computing the wall thickness for a part to be used at ambient temperatures but exposed to sunlight (60°C) during warm weather.

Figure 4.11(c) shows the difference between a homopolymer (H) with a rather fair creep modulus and a comonomer (Co) with a lower modulus.

Finally, Figure 4.11(d) shows that glass fibre reinforcement is an efficient means to reach more suitable creep moduli. It should be noted that the modulus scale is four times that of the previous diagrams and that the load is ten times higher.

These results relate to a few grades only and cannot be generalized.

Relaxation

Figure 4.12 displays estimated relaxation data as a percentage plotted versus logarithmic time (h), showing a regular decrease of stress. The original times and loads used to calculate these data are very approximate and this diagram is only given to illustrate the principle of relaxation. The data cannot be generalized and cannot be used for designing.

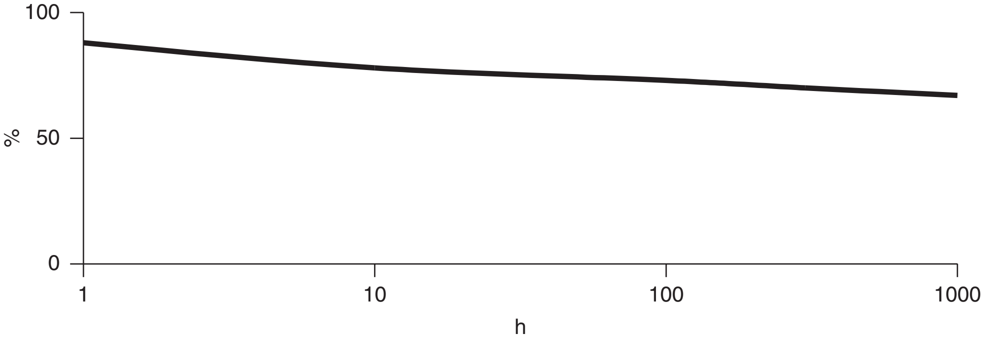


Figure 4.12. Stress relaxation of PP, examples of stress retention (%) versus time (h) under 2% strain at 20°C

4.2.5 Ageing

Dynamic fatigue

The dynamic fatigue can be fair or good for modified grades if care is taken to limit the strains by restricting the stresses to values in keeping with the low modulus.

For a given grade of 20% talc-filled polypropylene, Figure 4.13 displays two examples of SN or Wöhler's curves concerning flexural tests:

- one with maximum stress of ±S and average stress of 0
- the other with minimum stress S and maximum stress 2S.

Weathering

Polypropylene resists hydrolysis well but is naturally sensitive to light and UV. It must be protected by addition of anti-UV and other protective agents or by 2–3% of a suitable carbon black.

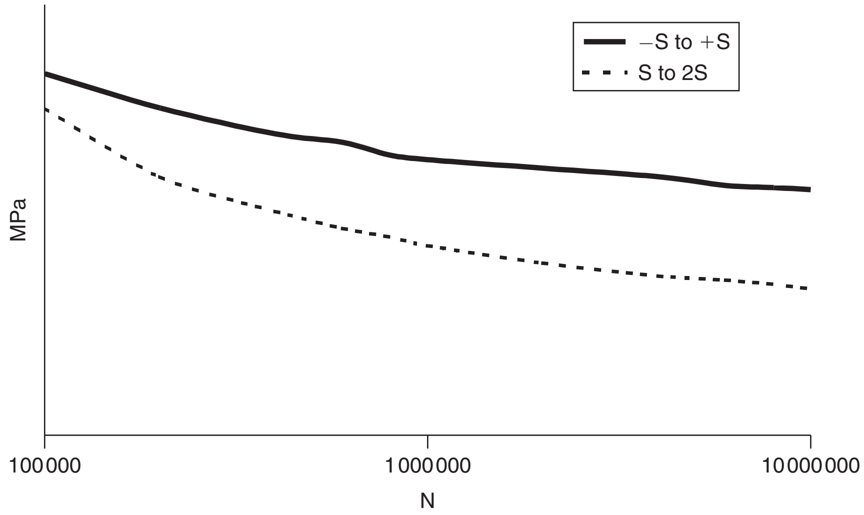


Figure 4.13. SN curves for 20% talc-filled PP: examples of maximum stress S (MPa) versus number of cycles at rupture (N)

After weathering test bars (3 mm thick) for one year in a sunny climate, the retention of properties is, for example:

- 56% for tensile strength, 59% for elongation at break and 62% for impact strength for a natural unprotected grade
- 76% for tensile strength, 78% for elongation at break and 95% for impact strength for a natural UV-protected grade.

These results are examples only and they cannot be generalized.

High-energy radiation

Unlike polyethylene, polypropylene is not crosslinked and deteriorates. The action of high-energy radiation depends in a complex way on the power, dose and wall thickness of polypropylene. Thus, it is often advised to avoid doses greater than 1 kJ/kg (0.1 Mrad). However, special grades are marketed for radiation sterilization but doses of the order of 25 kJ/kg (2.5 Mrad) can lead to a certain brittleness after storage of several months.

These results are examples only and they cannot be generalized.

Behaviour at high frequencies

Polypropylenes have very weak loss factors, about $1–20 \times 10^{-4}$, and do not heat up under high-frequency current. They cannot be welded by this technique.

Chemicals

Neat polypropylenes absorb little water and are not very sensitive to it but can have some propensity to stress cracking in the presence of certain chemicals. Special grades are marketed for washing machines, dishwashers and so on.

Suitable grades are usable in contact with food and are used for food packaging, milk bottles for example.

Chemical resistance is generally good up to 60°C but polypropylenes are attacked by oxidizing acids, chlorinated solvents, certain oxidants, aromatic hydrocarbons.

Copper, manganese and cobalt are oxidation catalysts and must be avoided in particular for inserts.

Crystallinity increases impermeability and, consequently, chemical resistance.

Table 4.7 displays some general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the polypropylenes. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.7 Polypropylene: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10–80	S	Bromine (liquid)	100	n
Acetic acid	>96	S	Bromine water	Solution	n
Acetic aldehyde	100	S	Butane gas	100	S
Acetic anhydride	100	S	Butanol	100	S
Acetone	100	S	Butanone	100	S
Acetonitrile	100	S	Butyl acetate	100	l
Acetophenone	100	l	Butylamine	Unknown	S
Acetyl chloride	100	l	Butylchloride	100	n
Acrylonitrile	100	S	Butylglycol	100	S
Alum	Solution	S	Butylphenol	100	S
Aluminium chloride	Solution	S	Butyric acid	Unknown	S
Aluminium sulfate	Unknown	S	Calcium chloride	Unknown	S
Ammonia	30	S	Calcium hydroxide	Saturated	S
Ammonia gas	100	S	Calcium hypochlorite	Solution	S
Ammonia liquid	100	S	Camphor oil	100	n
Ammonium acetate	Saturated	S	Carbon sulfide	100	l
Ammonium chloride	Solution	S	Carbon tetrachloride	100	l to n
Ammonium fluoride	Solution	S	Castor oil	100	S
Ammonium hydroxide	Dilute to 30	S	Cellosolve	100	S
Ammonium nitrate	Unknown	S	Cellosolve acetate	100	S
Ammonium sulfate	50	S	Chlorinated hydrocarbons	100	n
Amyl acetate	100	l	Chlorinated solvents	100	n
Amyl alcohol	100	S	Chlorine (dry gas)	100	n
Aniline	100	S	Chlorine dioxide	Unknown	l
Antimony chloride	10	S	Chlorine water	Unknown	l
Aqua regia	Unknown	n	Chloroacetic acid	Unknown	S
Aromatic hydrocarbons	100	n	Chlorobenzene	100	l
Arsenic acid	Unknown	S	Chloroform	100	l
ASTM1 oil	100	S	Chlorosulfonic acid	Unknown	n
ASTM3 oil	100	l	Chlorosulfonic acid	100	n
Barium carbonate	Saturated	S	Chromic acid	Unknown	l
Barium chloride	Saturated	S	Chromic acid	50	l
Barium hydroxide	Saturated	S	Chromic acid	10–20	S
Barium sulfate	Saturated	S	Citric acid	10	S
Benzaldehyde	100	l	Copper sulfate	Unknown	S
Benzene	100	l	Cresol	90–100	S
Benzoic acid	Saturated	S	Cyclohexane	100	l
Benzyl chloride	100	l	Cyclohexanol	100	S
Benzyl alcohol	100	S	Cyclohexanone	100	l
Borax	Saturated	S	Decaline	100	n
Boric acid	Unknown	S	Dextrin	Solution	S

Table 4.7 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Dibutylphthalate	100	S	Isobutanol	100	S
Dichloroethane	100	l	Isooctane (Fuel A)	100	l
Dichloroethylene	100	S to l	Isopropanol	100	S
Diethylamine	100	S	Kerosene	100	l
Diethyleneglycol	100	S	Lactic acid	10–90	S
Diethylether	100	l	Lanoline	Unknown	S
Dimethylamine	100	S	Lead acetate	10	S
Dimethylformamide	100	S	Linseed oil	100	S
Dimethylhydrazine	100	S	Liquid paraffin	100	l
Dioctylphthalate	100	S	Magnesium carbonate	Saturated	S
Dioxan	100	l	Magnesium chloride	Unknown	S
Ethanol	Unknown	S	Magnesium hydroxide	Unknown	S
Ethanol	40–96	S	Magnesium sulfate	Unknown	S
Ethanolamine mono	100	S	Malic acid	1	S
Ethanoldiamine	100	S	Manganese sulfate	Unknown	S
Ethylacetate	100	l	Mercury	100	S
Ethylchloride	100	n	Mercury chloride	Unknown	S
Ethylene glycol	Unknown	S	Mercury(II) nitrate	Solution	S
Ethylene glycol	100	S	Methanol	5–100	S
Ethylenechloride	100	l	Methylacetate	100	S
Ethylhexanol	100	S	Methylamine	<32	S
Fluorine	100	n	Methylbromide	100	n
Fluosilicic acid	Unknown	S	Methylbutylketone	100	l
Formaldehyde	37	S	Methylene chloride	100	l
Formic acid	10–100	S	Methylethylketone	100	S
Freon 113	100	S	Methylglycol	Unknown	S
Freon 115	100	S	Milk	100	S
Freon 12	100	S	Mineral oil	100	S
Freon 13b1	100	S	Molasses	Unknown	S
Freon 21	100	S	Monochlorobenzene	100	l
Freon 22	100	S	Monoethyleneglycol	100	S
Freon 32	100	S	Naphtha	Unknown	l
Fruit juice	Unknown	S	Nickel chloride	Unknown	S
Furfural	100	S	Nickel nitrate	Saturated	S
Glucose	Dilute	S	Nitric acid	10–25	S
Glycerol	100	S	Nitric acid	50	l
Glycollic acid	33	S	Nitric acid	65	S to l
Groundnut oil	100	S	Nitric acid	75–100	n
Heptane	100	n	Nitrobenzene	100	S
Hexane	100	l	Nonanol	100	S
Household bleach	Unknown	l	Oleic acid	Unknown	S
Hydrazine	100	S	Oleic acid	100	l
Hydrobromic acid	10–48	S	Oleum @ 10%	Pure	n
Hydrochloric acid	10–36	S	Olive oil	100	S
Hydrofluoric acid	40	l	Oxalic acid	Unknown	S
Hydrofluoric acid	4	S	Oxalic acid	Saturated	S
Hydrogen	100	S	Oxygen	100	S
Hydrogen peroxide	30	S	Ozone	Unknown	l
Hydrogen sulfide	Unknown	S	Pentanol	100	S
Hydrogen sulfide gas	Unknown	S	Pentylacetate	100	l
Iodine (alcoholic solution)	Unknown	S	Perchloric acid	2N	S
Iodine tincture	Unknown	S	Perchloroethylene	100	l
Iron(III) chloride	Unknown	S	Petrol aliphatic	100	n

(*Continued*)

Table 4.7 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Petroleum	100	S	Soya oil	100	S
Petroleum ether (ligroin)	Unknown	l	Strong acids	Concentrated	S
Phenol	Solution	S	Strong bases	Unknown	S
Phenol	5–90	S	Succinic acid	Saturated	S
Phosphoric acid	50–85	S	Sulfamic acid	Solution	S
Picric acid	Solution	S	Sulfurous acid	Solution	S
Potassium bromate	Unknown	S	Sulfurous anhydride (gas)	Unknown	S
Potassium carbonate	Saturated	S	Sulfur dioxide (dry)	100	S
Potassium chlorate	Saturated	S	Sulfur dioxide (gas)	Unknown	S
Potassium chromate	Saturated	S	Sulfuric acid	2–85	S
Potassium cyanide	Unknown	S	Sulfuric acid	96	l
Potassium fluoride	Unknown	S	Sulfuric acid	Fuming	n
Potassium hydroxide	10–45	S	Tartaric acid	Solution	S
Potassium nitrate	Saturated	S	Tetrachloroethane	100	l
Potassium perchlorate	10	S	Tetrachloroethylene	100	l
Potassium permanganate	2N	S	Tetrahydrofuran	100	l
Potassium permanganate	Solution	S	Thionyl chloride	100	n
Potassium permanganate	20	S	Tin chloride	Unknown	S
Potassium persulfate	10	S	Toluene	100	l
Potassium sulfate	Unknown	S	Transformer oil	100	S
Propane (liquid)	100	S	Trichloroacetic acid	Unknown	S
Propanol	100	S	Trichloroacetic acid	10	S
Propionic acid	50–100	S	Trichloroethylene	100	n
Propylene oxide	100	S	Tricresylphosphate	Unknown	S
Sea water	100	S	Triethanolamine	Unknown	S
Silicone oil	Unknown	S	Triethylamine	Unknown	l
Silver nitrate	Saturated	S	Turpentine oil	100	n
Silver nitrate	Unknown	S	Urea	Solution	S
Sodium acetate	Saturated	S	Vinegar	Unknown	S
Sodium bisulfite	Solution	S	Vinyl chloride	Unknown	l
Sodium borate	Unknown	S	Vinyl acetate	100	S
Sodium carbonate	10–50	S	Water	100	S
Sodium chlorate	Saturated	S	Weak acids	Unknown	S
Sodium chloride	25	S	Weak bases	Unknown	S
Sodium cyanide	Unknown	S	Whisky	Unknown	S
Sodium hydroxide	10–55	S	White spirit	100	S
Sodium hypochlorite	2–20	S	Wine	Unknown	S
Sodium nitrate	Solution	S	Xylene	100	n
Sodium perborate	Unknown	S	Zinc chloride	Unknown	S
Sodium sulfite	40	S			

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: polypropylene has a low permeability, roughly evaluated at 2 compared to a full range of 0.05 up to 400 for all tested plastics.

- Gases: polypropylene has a rather high permeability, evaluated at:
  - air: 700 versus a full range of 3 up to 2750 for all tested plastics
  - carbon dioxide: 6000 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 430 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 1900 versus a full range of <1 up to 11 000 for all tested plastics
  - hydrogen: 16 000 versus a full range of 400 up to 20 000 for all tested plastics.

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames, even after the ignition source is removed. Moreover, polypropylene drips while burning.

Oxygen indices are roughly 17 with a poor UL94 rating.

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties. UL94 V0 rating can be reached for some FR grades.

4.2.6 Electrical properties

Polypropylenes are good insulators even in wet environments, with high dielectric resistivities and rigidities, and low loss factors. Special grades are marketed for electrical applications.

4.2.7 Joining, decoration

Welding is easy using thermal processes, possible with ultrasound but impossible by the high-frequency technique.

Gluing is difficult, needing pre-treatments such as, for example, chemical etching (sulfochromic acid etching), flame oxidation or hot-air (500°C) treatment, corona discharge, plasma or UV treatments. The exposure must be brief and superficial and the original and aged properties must be tested.

All precautions must be taken concerning health and safety according to local laws and regulations.

Polypropylene can generally be decorated after the same pre-treatments by painting, printing, metallization. Service conditions must be light.

4.2.8 Foams

Unlike industrial solid polymers, which are processed as carefully as possible to avoid the formation of bubbles, vacuoles etc., alveolar materials result from the desire to introduce, in a controlled way, a certain proportion of voids with the aim of:

- increasing flexibility
- improving the thermal or phonic insulating character: foams for packaging, automotive . . . .
- making damping parts: foams for packaging, automotive and transport safety parts.

The alveolar materials consist of a polymer skeleton surrounding the cells, which may be closed or partially or completely open to neighbouring cells or the outside.

The intrinsic properties come from those of the polypropylene with:

- a reduction in the mechanical properties due to the small quantity of material and the high proportion of gas
- a reduction in the chemical behaviour due to the highly divided nature of the material. The thin cell walls immediately absorb liquids and gases and are rapidly damaged.

Generally, the properties of polypropylene foams are:

- densities from 23 kg/m^3 up to 70 kg/m^3
- closed cells.

Polypropylene foams (see Table 4.8) have:

- insulating properties
- damping properties
- fair mechanical characteristics according to their density. Figure 4.14 displays an example of tensile strength versus density
- a low absorption and permeability to water or moisture and excellent hydrolysis behaviour
- a naturally low fire resistance that can be improved by a suitable formulation.

Table 4.8 Examples of some polypropylene foam properties

Density (g/cm^3)	0.04	0.07
Density (kg/m^3)	40	70
Thermal conductivity (W/m.K)	0.034	0.036
10% compression stress (MPa)	0.022	0.070
50% compression stress (MPa)	0.11–0.13	0.15–0.19
Compression set, 22 h, 25% (%)	10	6–10
Tensile strength (MPa)	0.4–0.7	0.7–1.3
Elongation at break (%)	140–200	200–400
Water absorption, 7 days (%)	<1	<1
Service temperatures (°C) Minimum	−40	−40
Maximum	120–130	120–130

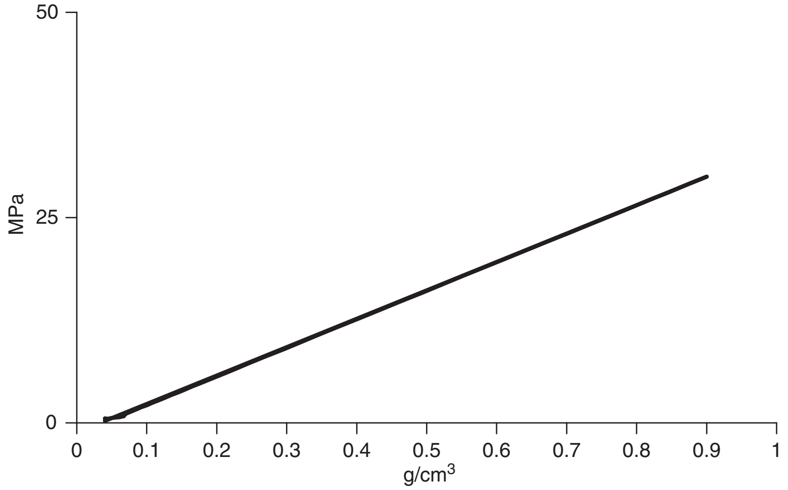


Figure 4.14. Tensile strength examples versus density of Polypropylene foams

Examples of applications

The major application is for the damping cores of car bumpers.

Automotive and transport

Damping and protection; air-, water- and dust-proofing, thermal insulation, soundproofing:

- energy-absorbing bumpers
- door fillings, door panels
- safety padding . . .
- floor filling
- tool boxes . . .

Packaging

Damping and protection; air-, water- and dust-proofing, thermal insulation.

- Reusable packaging or shuttle packaging for heavy parts such as doors, windscreen, rear mirrors . . .
- Packaging of fragile parts: electronics, office automation devices, electric motors . . .
- Damping blocks, intermediate layers . . .
- Functional packaging useful for shipping and installation on site . . .

An interesting development initiated by Neste and Norsk Hydro is a multilayer coating for the insulation of deep-water pipelines. The steel pipe is protected by a layer of solid thermoplastic, a core of polypropylene foam and a coating of solid plastic, all of which are built up by cross head extrusion.

4.2.9 Specific ISO standards concerning polypropylenes

ISO 1346:2004 Fibre ropes – Polypropylene split film, monofilament and multifilament (PP2) and polypropylene high tenacity multifilament (PP3) – 3-, 4- and 8-strand ropes

ISO 1873-1:1995 Plastics – Polypropylene (PP) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 1873-2:1997 Plastics – Polypropylene (PP) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 3213:1996 Polypropylene (PP) pipes – Effect of time and temperature on expected strength

ISO 4577:1983 Plastics – Polypropylene and propylene-copolymers – Determination of thermal oxidative stability in air – Oven method

ISO 7279:1984 Polypropylene (PP) fittings for pipes under pressure – Sockets for fusion using heated tools – Metric series – Dimensions of sockets

ISO 7671:2003 Plastics piping systems for soil and waste discharge (low and high temperature) inside buildings – Polypropylene (PP)

ISO 8242:1989 Polypropylene (PP) valves for pipes under pressure – Basic dimensions – Metric series

ISO 8283-3:1992 Plastics pipes and fittings – Dimensions of sockets and spigots for discharge systems inside buildings – Part 3: Polypropylene (PP)

ISO 8773:1991 Polypropylene (PP) pipes and fittings for buried drainage and sewerage systems – Specifications

ISO 9113:1986 Plastics – Polypropylene (PP) and propylene-copolymer thermoplastics – Determination of isotactic index

ISO 15013:1998 Extruded sheets of polypropylene (PP) – Requirements and test methods

ISO 15494:2003 Plastics piping systems for industrial applications – Polybutene (PB), polyethylene (PE) and polypropylene (PP) – Specifications for components and the system – Metric series

ISO 15874-1:2003 Plastics piping systems for hot and cold water installations – Polypropylene (PP) – Part 1: General

ISO 15874-2:2003 Plastics piping systems for hot and cold water installations – Polypropylene (PP) – Part 2: Pipes

ISO 15874-3:2003 Plastics piping systems for hot and cold water installations – Polypropylene (PP) – Part 3: Fittings

ISO 15874-5:2003 Plastics piping systems for hot and cold water installations – Polypropylene (PP) – Part 5: Fitness for purpose of the system

ISO/TS 15874-7:2003 Plastics piping systems for hot and cold water installations – Polypropylene (PP) – Part 7: Guidance for the assessment of conformity

ISO 17555:2003 Plastics – Film and sheeting – Biaxially oriented polypropylene (PP) films (available in English only)

ISO 17557:2003 Plastics – Film and sheeting – Cast polypropylene (PP) films

4.2.10 Trade name examples

Appryl PP, Capilene, Celstran, Elprop, Exxelor, Fortilene, Hi-prene, HiFax, Hopelen, Hostacom, Hostalen PP, Lacqtène P, Marlex, Metocen, Novolen, Oleplate, Olevac, Pro-Fax, Propathene, Tecnoprene, Topilene, Vestolen P, Yuplene. . . .

Foams: Alveolit, Alveolen, Alveolux, Freudenberg, Neopolen P, Ymos . . .

4.2.11 Property tables

Table 4.9 relates to examples only and cannot be generalized. Data cannot be used for design purposes. See also Table 4.8 for foam properties.

Table 4.9 Polypropylenes: examples of properties

	Homopolymer		Copolymer		Impact modified	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	0.90	0.91	0.90	0.91	0.88	0.91
Shrinkage (%)	1.0	3.0	2.0	3.0	2.0	3.0
Absorption of water (%)	0.01	0.10	0.01	0.10	0.01	0.10
Mechanical properties						
Shore hardness, D	70	83	70	80	45	55
Stress at yield (MPa)	35	40	20	35	11	28
Tensile strength (MPa)	20	40	30	35	23	35
Elongation at break (%)	150	600	200	500	200	700
Tensile modulus (GPa)	1.1	1.6	1.0	1.2	0.4	1.0
Flexural modulus (GPa)	1.2	1.6	1.0	1.4	0.4	1.0
Notched impact strength ASTM D256 (J/m)	20	60	60	500	110	NB
Thermal properties						
HDT B(0.46 MPa) (°C)	100	120	85	104	75	88
HDT A(1.8 MPa) (°C)	50	60	50	60	46	57
Vicat softening point A (°C)	154	154	135	152	135	152
Vicat softening point B (°C)	90	92	45	73	45	73
Continuous use temperature (°C)	120	130	110	130	100	115
Glass transition temperature (°C)	−10	−10	−20	−20	−20	−20
Melting temperature (°C)	168	173	155	173	150	168
Minimum service temperature (°C)	−20	−10	−20	−10	−20	−40
Thermal conductivity (W/m.K)	0.15	0.21	0.15	0.21	0.15	0.21
Specific heat (cal/g/°C)	0.46	0.46	0.46	0.46	0.46	0.46
Coefficient of thermal expansion (10^{-5}/°C)	6	17	7	17	7	17
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{18}	10^{16}	10^{18}	10^{16}	10^{18}
Dielectric constant	2.3	2.3	2.3	2.3	2.3	2.3
Loss factor (10^{-4})	3	5	3	5	3	5
Dielectric strength (kV/mm)	20	28	20	28	20	28
Arc resistance (s)	135	180	135	180	135	180
Fire behaviour						
Oxygen index (%)	17	18	17	18	17	18
UL94 fire rating	HB	HB	HB	HB	HB	HB

Table 4.9 (Continued)

Reinforced PP	10–40% Talc		10–40% Mineral		10–20% Glass Fibre		30–40% Glass Fibre	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties								
Density, (g/cm^3)	0.97	1.25	0.97	1.25	0.97	1.05	1.10	1.23
Shrinkage (%)	0.9	1.4	0.6	1.4	0.3	1.0	0.1	1.0
Absorption of water (%)	0.01	0.03	0.01	0.03	0.01	0.02	0.01	0.02
Mechanical properties								
Shore hardness, D	75	85	70	80	80	85	85	88
Rockwell hardness, M	<10	45	<10	30	30	50	40	50
Stress at yield (MPa)	22	28	19	27	35	56	42	70
Strain at yield (%)					3.0	4.0	2.0	3.0
Tensile strength (MPa)	21	28	18	24	35	56	42	70
Elongation at break (%)	20	30	30	50	3	4	2	3
Tensile modulus (GPa)	1.5	3.5	1	3.5	2.8	4	4	10
Flexural modulus (GPa)	1.5	4	1.4	3.1	2.5	3.5	4	7
Notched impact strength ASTM D256 (J/m)	30	200	38	110	50	145	45	160
Thermal properties								
HDT B(0.46 MPa) (°C)	100	127	85	113	110	140	140	155
HDT A(1.8 MPa) (°C)	56	75	50	68	90	127	125	140
Vicat softening point A (°C)	137	153					150	162
Vicat softening point B (°C)	46	100					96	128
Continuous use temperature (°C)	110	130	110	130	110	130	110	130
Glass transition temperature (°C)	−20	−10	−20	−10	−20	−10	−20	−10
Melting temperature (°C)	160	173	160	173	160	173	160	173
Minimum service temperature (°C)	−20	−5	−20	−5	−40	−5	−30	−5
Thermal conductivity (W/m.K)	0.3	0.4	0.3	0.4	0.2	0.3	0.3	0.3
Coefficient of thermal expansion (10^{-5}/°C)	4	8	3	6	4	7	2	3
Electrical properties								
Volume resistivity (ohm.cm)	10^{16}	10^{17}	10^{16}	10^{17}	10^{16}	10^{17}	10^{16}	10^{17}
Dielectric constant	2.3	2.3	2.3	2.3	2.6	2.6	2.6	2.6
Loss factor (10^{-4})	7	11	7	11	10	20	10	20
Dielectric strength (kV/mm)	30	70	30	70	30	45	30	45
Arc resistance (s)	100	130	100	130	75	100	60	75
Fire behaviour								
Oxygen index (%)	17	18	17	18	17	18	17	18
UL94 fire rating	HB	HB	HB	HB	HB	HB	HB	HB

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers or/and black colour are needed
Weak acids	Good behaviour
Strong acids	Good behaviour except oxidizing acids
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Good behaviour up to 60°C except chlorinated solvents, certain oxidants, aromatic hydrocarbons Copper, manganese and cobalt are oxidation catalysts and must be avoided in particular for inserts
Food contact	Possible for special grades

4.3 Other polyolefins (PO)

4.3.1 Polybutene-1 or polybutylene-1 (PB)

There are two formulae for butene according to the position of the double bond (see Figure 4.15). Only the butene-1 isomer is used to polymerize an engineering material in its isotactic

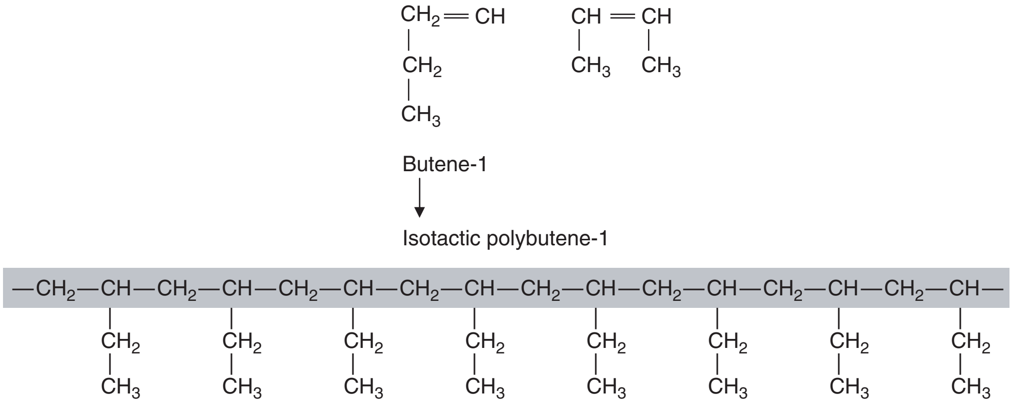


Figure 4.15. Butene and polybutene formulae

form, as shown in Figure 4.15. (The other form of butene leads to polyisobutylene, a low-viscosity polymer, only used as viscosity modifier, for example for oils and chewing gum.)

In the following we will only consider polybutylene-1, simply named polybutene or polybutylene (PB).

Polybutene is a polyolefin differing from polyethylene and polypropylene by the number of carbon atoms in the pendant groups. Polybutene is mainly used for sealing, films and pipes conveying pressurized hot and cold water.

To illustrate the differences in creep behaviour between the main polyolefins, after 1000 h under 8 MPa at room temperature, the elongations are, for example:

- <8% for a PB
- 10% for a PP homopolymer
- 16% for a PP copolymer
- >24% for a PE-X
- ≫24% for a PE.

These results relate to some grades only and cannot be generalized.

There are numerous grades of copolymers with polyethylene having some differing properties.

The incompatibility between polybutene and polyethylene is used to make peelable film seals.

Advantages

Properties are close to those of polyethylenes with some differences: good mechanical properties at ambient temperature, good balance of low stiffness and high toughness, high filler loadings, better creep, stress cracking and heat behaviour than polyethylene, attractive price/property ratios, easy processing, chemically inert, weak absorption of water, low density, good electrical insulation even in wet media, welding feasibility.

Drawbacks

General drawbacks are the innate relative sensitivity to heat and creep, low rigidity, significant shrinkage and poorer low-temperature behaviour than polyethylene.

Due to the surface tension, gluing, painting and printing are difficult without surface treatments. Composed only of carbon and hydrogen, polybutenes are naturally flammable but FR grades are possible, including halogen-free grades.

Grades, processing and applications

Applications and consumption are far lower than for polyethylene and polypropylene. Consequently, there are relatively few grades marketed, corresponding to the major applications such as:

- pipes for cold and hot pressurized water
- films requiring creep resistance . . .
- layers for multilayer films
- blow-moulded tanks for electric domestic heaters
- low melting temperature matrices for masterbatches . . .

All the molten-state processing methods are usable, mainly extrusion, injection, blow moulding, co-extrusion, welding.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 95°C up to 105°C if softening or melting temperatures are higher. For a given grade of neat polybutene, the Vicat softening temperature is of the order of 113°C. For some copolymers, the melting point can be below 100°C.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Characteristics such as elongation at break and impact strength are especially heat sensitive.

Figure 4.16(a) (after data quoted by the Polybutene Piping Systems Association) displays acceptable hoop stress values for 1 year of service for polybutene water pipes.

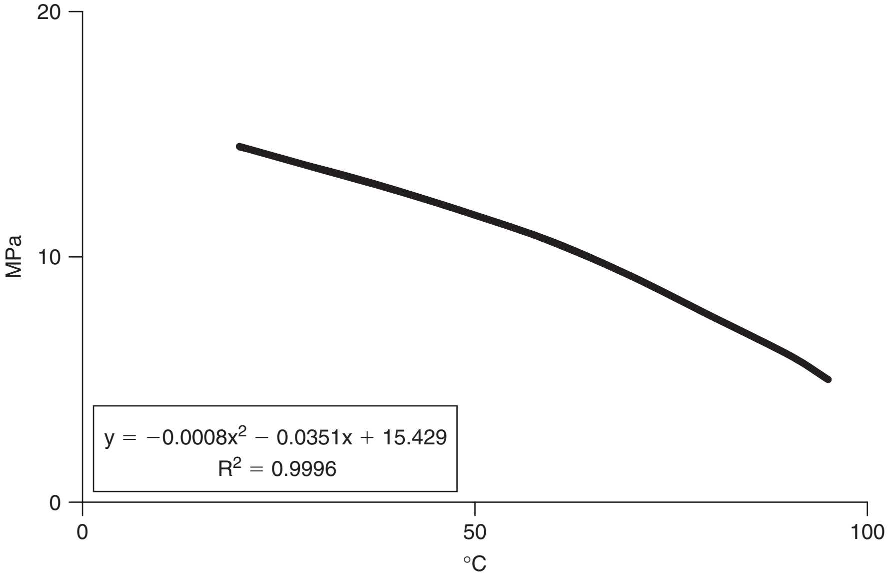


Figure 4.16. (a) PB: Examples of hoop strength at l year versus temperature

Figure 4.16(b) (also from Polybutene Piping Systems Association data) displays the acceptable hoop stress values versus time (years) for polybutene water pipes at 60°C (uppermost curve), 70°C, 80°C and 90°C.

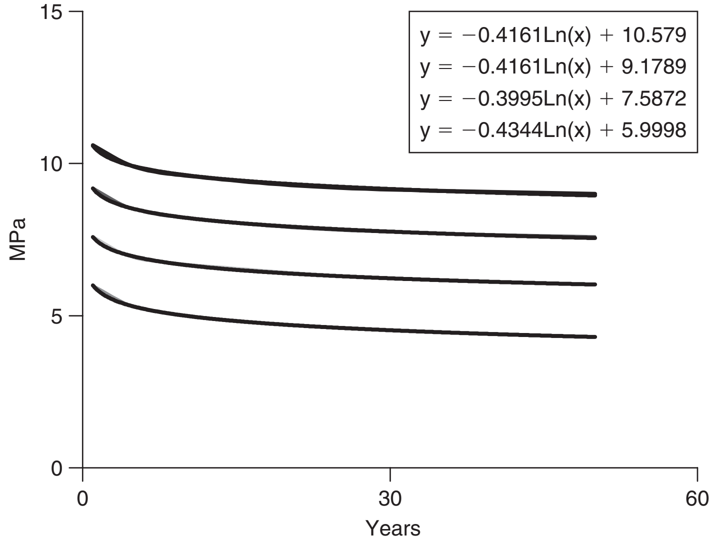


Figure 4.16. (b) PB: Examples of hoop strength at 60, 70, 80 and 90°C versus time in years

The glass transition temperatures of polybutene by DSC measurements are generally about −18°C. Some copolymers have lower brittle points down to −34°C, for example.

The glass temperatures by DTMA measurements can be higher, depending on the frequency.

These results relate to some grades only and cannot be generalized.

Optical properties

General-purpose polybutenes are naturally whitish, and more or less opaque according to the grade and the crystallinity.

Refractive indices are about 1.52.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties are generally fair with high elongations at break but much more limited strains at yield. Moduli and hardnesses are lower than those of polyethylene and impact strength is in a useful range.

Dimensional stability

Shrinkage, coefficient of thermal expansion and creep are rather high depending on crystallinity. The absorption and alteration by moisture exposure are low.

Creep

Thermoplastic neat polybutenes have low moduli involving high strains for moderate loading. Consequently, loading must be limited and creep moduli used for designing must be low, for example:

- The acceptable hoop stresses for pressurized water pipes are roughly:
  - 14 MPa for 15 years of service at ambient temperature
  - 11 MPa for 15 years of service at 50°C
  - 8 MPa for 15 years of service at 70°C
  - 5 MPa for 15 years of service at 90°C.
- Creep moduli are also low, the more so as the temperature rises, for example:
  - 0.2 GPa after 10 h at ambient temperature under a load of 8 MPa
  - 0.1 GPa after 5000 h at ambient temperature under a load of 8 MPa.

These results are only examples and cannot be generalized.

Chemicals

Polybutenes absorb little water and are not very sensitive to it. They are generally fairly resistant to stress cracking.

Suitable grades are usable in contact with food.

Chemical resistance is generally good up to 60°C but, as with the other polyolefins, polybutenes are attacked by oxidizing acids, chlorinated solvents, certain oxidants and aromatic hydrocarbons.

Crystallinity increases impermeability and, consequently, chemical resistance.

Table 4.10 displays general assessments of behaviour after prolonged immersion in a range of chemicals at room temperature for given grades, which are not necessarily representative of all polybutenes. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.10 Polybutenes: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetaldehyde	Unknown	l
Acetic acid	≤80	S
Acetic acid	Glacial	l
Acetic anhydride	Unknown	n
Acetone	Unknown	S
Acetylene	Unknown	l
Adipic acid	Unknown	S
Allyl alcohol	96	S
Aluminium chloride	Unknown	S
Aluminium fluoride	Unknown	S
Aluminium hydroxide	Unknown	S
Aluminium oxychloride	Unknown	S
Aluminium nitrate	Unknown	S
Ammonia gas	Unknown	S
Ammonia liquid	Unknown	S
Ammonium carbonate	Unknown	S
Ammonium chloride	Unknown	S
Ammonium fluoride	25	S
Ammonium hydroxide	28	S
Ammonium metaphosphate	Unknown	S
Ammonium nitrate	Unknown	S
Ammonium persulfate	Unknown	S
Ammonium sulfate	Unknown	S
Amyl acetate	Unknown	S
Amyl alcohol	Unknown	S
Amyl chloride	Unknown	l
Aniline	Unknown	l
Aniline chlorohydrate	Unknown	n
Anthraquinone	Unknown	l
Anthraquinone sulfonic acid	Unknown	l
Antimony trichloride	Unknown	S
Aqua regia	Unknown	n
Arsenic acid	80	S
Asphalt	Unknown	S
Barium carbonate	Unknown	S
Barium chloride	Unknown	S
Barium hydroxide	Unknown	S
Barium sulfate	Unknown	S

(*Continued*)

Table 4.10 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Barium sulfide	Unknown	S
Beer	Unknown	S
Benzaldehyde	Unknown	l
Benzene	Unknown	n
Benzoic acid	Unknown	S
Bismuth carbonate	Unknown	S
Bleach	Unknown	S
Borax	Unknown	S
Boric acid	Unknown	S
Boron trifluoride	Unknown	S
Bromic acid	Unknown	l
Bromine liquid	Unknown	n
Bromine water	Unknown	l
Butanol	Unknown	S
Butyl acetate	Unknown	l
Calcium carbonate	Unknown	S
Calcium chlorate	Unknown	S
Calcium chloride	Unknown	S
Calcium hydroxide	Unknown	S
Calcium hypochlorite	Unknown	S
Calcium nitrate	Unknown	S
Calcium sulfate	Unknown	S
Carbon bisulfide	Unknown	n
Carbon dioxide	Unknown	S
Carbon monoxide	Unknown	S
Carbon tetrachloride	Unknown	n
Casein	Unknown	S
Castor oil	Unknown	S
Caustic potash	Unknown	S
Caustic soda	Unknown	S
Cellosolve	Unknown	S
Chloroacetic acid	Unknown	n
Chloral hydrate	Unknown	n
Chlorine gas (dry)	Unknown	n
Chlorine water	Unknown	n
Chlorobenzene	Unknown	l
Chloroform	Unknown	n
Chlorosulfonic acid	Unknown	S
Chrome alum	Unknown	S
Chromic acid	10–50	S
Citric acid	Unknown	S
Coconut oil	Unknown	S
Copper chloride	Unknown	S
Copper cyanide	Unknown	S
Copper fluoride	2	S
Copper nitrate	Unknown	S
Copper sulfate	Unknown	S
Cotton seed oil	Unknown	S
Cresol	Unknown	n
Cresylic acid	50	n
Crude oil	Unknown	l
Cyclohexanol	Unknown	S
Cyclohexanone	Unknown	n
Dextrin	Unknown	S
Dextrose	Unknown	S
Diazo salts	Unknown	S
Diglycolic acid	Unknown	S
Dimethylamine	Unknown	n
Dioctylphthalate	Unknown	l
Disodium phosphate	Unknown	S
Ethers	Unknown	n
Ethyl acetate	Unknown	l
Ethyl alcohol	Up to 98	S
Ethyl ether	Unknown	l
Ethylene bromide	Unknown	n
Ethylene chlorohydrin	Unknown	n
Ethylene glycol	Unknown	S
Fatty acids	Unknown	S
Ferric chloride	Unknown	S
Ferric nitrate	Unknown	S
Ferric sulfate	Unknown	S
Ferrous chloride	Unknown	S
Ferrous sulfate	Unknown	S
Fluorine gas	Unknown	l
Fluoroboric acid	Unknown	S
Fluosilicic acid	Unknown	S
Formaldehyde	Unknown	S
Formic acid	Unknown	S
Fuel oil	Unknown	n
Gallic acid	Unknown	S
Gas natural	Unknown	S
Gasoline	Unknown	n
Gelatine	Unknown	S
Glucose	Unknown	S
Glycerine or glycerol	Unknown	S
Glycol	Unknown	S
Glycollic acid	30	S
Heptane	Unknown	n
Hexane	Unknown	n
Hexanol	Unknown	S
Hydrobromic acid	20	S
Hydrochloric acid	⩽40	S
Hydrocyanic acid	Unknown	S
Hydrofluoric acid	4–60	S
Hydrofluorosilicic acid	Unknown	S
Hydrogen	Unknown	S
Hydrogen peroxide	30	S
Hydrogen peroxide	50–90	n
Hydrogen phosphide	Unknown	S
Hydrogen sulfide	Unknown	S
Hydroquinone	Unknown	S
Hypochlorous acid	Unknown	S
Iodine alcoholic solution	Unknown	S
Isopropyl alcohol	Unknown	S
Kerosene	Unknown	l
Lactic acid	28	S
Lard oil	Unknown	S
Lead acetate	Unknown	S
Lime sulfur	Unknown	S
Linoleic acid	Unknown	S
Linseed oil	Unknown	S
Magnesium carbonate	Unknown	S
Magnesium chloride	Unknown	S
Magnesium hydroxide	Unknown	S

Table 4.10 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Magnesium nitrate	Unknown	S
Magnesium sulfate	Unknown	S
Maleic acid	Unknown	S
Malic acid	Unknown	S
Mercuric chloride	Unknown	S
Mercuric cyanide	Unknown	S
Mercurous nitrate	Unknown	S
Mercury	Unknown	S
Methyl alcohol	Unknown	S
Methyl chloride	Unknown	n
Methylethylketone	Unknown	S
Methyl sulfuric acid	Unknown	S
Milk	Unknown	S
Mineral oils	Unknown	l
Molasses	Unknown	S
Naphthalene	Unknown	l
Nickel acetate	Unknown	S
Nickel chloride	Unknown	S
Nickel nitrate	Unknown	S
Nicotine acid	Unknown	S
Nitric acid	10	l
Nitric acid	20–70	n
Oils and fats	Unknown	S
Oleum	Unknown	n
Oxalic acid	Unknown	S
Perchloric acid	10	l
Perchloric acid	70	n
Phenol	Unknown	S
Phosphoric acid	⩽75	S
Picric acid	Unknown	S
Potassium acid sulfate	Unknown	S
Potassium bicarbonate	Unknown	S
Potassium borate	1	S
Potassium bromate	10	S
Potassium bromide	Unknown	S
Potassium carbonate	Unknown	S
Potassium chlorate	Unknown	S
Potassium chloride	Unknown	S
Potassium chromate	40	S
Potassium cyanide	Unknown	S
Potassium dichromate	Unknown	S to l
Potassium ferricyanide	Unknown	S
Potassium fluoride	Unknown	S
Potassium hydroxide	10–20	S
Potassium nitrate	Unknown	S
Potassium perborate	Unknown	S
Potassium persulfate	Unknown	S
Potassium sulfate	Unknown	S
Potassium sulfide	Unknown	S
Potassium thiosulfate	Unknown	S
Propyl alcohol	Unknown	S
Salt water	Unknown	S
Selenic acid	Unknown	S
Silicic acid	Unknown	S
Silver cyanide	Unknown	S
Silver plating solutions	Unknown	S
Soaps	Unknown	S
Sodium acetate	Unknown	S
Sodium antimonate	Unknown	S
Sodium arsenite	Unknown	S
Sodium benzoate	Unknown	S
Sodium bicarbonate	Unknown	S
Sodium bisulfate	Unknown	S
Sodium bisulfite	Unknown	S
Sodium bromide	Unknown	S
Sodium carbonate	Unknown	S
Sodium chlorate	Unknown	S
Sodium chloride	Unknown	S
Sodium cyanide	Unknown	S
Sodium dichromate	Unknown	S
Sodium ferricyanide	Unknown	S
Sodium ferrocyanide	Unknown	S
Sodium fluoride	Unknown	S
Sodium hydroxide	10–35	S
Sodium hydroxide	Saturated	S
Sodium hypochlorite	Unknown	S
Sodium nitrate	Unknown	S
Sodium nitrite	Unknown	S
Sodium phosphate	Unknown	S
Sodium sulfide	Unknown	S
Sodium sulfite	Unknown	S
Sodium thiosulfate	Unknown	S
Stannic chloride	Unknown	S
Stannous chloride	Unknown	S
Stearic acid	Unknown	S
Sulfur	Unknown	S
Sulfur dioxide gas (wet)	Unknown	S
Sulfuric acid	⩽50	S
Sulfuric acid	50–90	l
Sulfuric acid	96	n
Sulfurous acid	Unknown	S
Tannic acid	Unknown	S
Tartaric acid	Unknown	S
Tetrahydrofuran	Unknown	l
Toluene	Unknown	n
Trichloroethylene	Unknown	n
Triethanolamine	Unknown	S
Trisodium phosphate	Unknown	S
Turpentine	Unknown	n
Urea	Unknown	S
Urine	Unknown	S
Vinegar	Unknown	S
Water	Unknown	S
Whisky	Unknown	S
Zinc chromate	Unknown	S
Zinc cyanide	Unknown	S
Zinc nitrate	Unknown	S
Zinc sulfate	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Fire resistance

Fire resistance is naturally weak. General-purpose grades burn easily, generating flames, even after removing the ignition source. Moreover, polybutene drips while burning.

Oxygen indices are roughly 17–18 with a poor UL94 rating.

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties.

Electrical properties

Polybutenes are good insulators even in wet environments, with high dielectric resistivities and rigidities, and low loss factors.

Joining, decoration

Welding is easy using thermal processes but impossible by the high-frequency technique.

Gluing is difficult. All precautions must be taken concerning health and safety according to local laws and regulations.

Specific ISO standards concerning polybutenes

ISO 8986-1:1993 Plastics – Polybutene (PB) moulding and extrusion materials – Part 1: Designation system and basis for specifications
ISO 8986-2:1995 Plastics – Polybutene (PB) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties
ISO 12230:1996 Polybutene (PB) pipes – Effect of time and temperature on the expected strength
ISO 15494:2003 Plastics piping systems for industrial applications – Polybutene (PB), polyethylene (PE) and polypropylene (PP) – Specifications for components and the system – Metric series
ISO 15876-1:2003 Plastics piping systems for hot and cold water installations – Polybutylene (PB) – Part 1: General
ISO 15876-2:2003 Plastics piping systems for hot and cold water installations – Polybutylene (PB) – Part 2: Pipes
ISO 15876-3:2003 Plastics piping systems for hot and cold water installations – Polybutylene (PB) – Part 3: Fittings
ISO 15876-5:2003 Plastics piping systems for hot and cold water installations – Polybutylene (PB) – Part 5: Fitness for purpose of the system
ISO/TS 15876-7:2003 Plastics piping systems for hot and cold water installations – Polybutylene (PB) – Part 7: Guidance for the assessment of conformity

Trade name examples

PB-1, Polybutene-1 by Basell, Mitsui Chemicals . . .

Property tables

Table 4.11 relates to examples only. The data cannot be generalized or used for designing.

Table 4.11 Polybutenes: examples of properties

	Polybutene	Copolymers	
	Min.	Min.	Max.
Miscellaneous properties			
Density (g/cm^3)	0.92–0.937	0.895	0.915
Mechanical properties			
Shore hardness, D	53		
Stress at yield (MPa)	18	4	17
Tensile strength (MPa)	36	24	27
Elongation at break (%)	340	>300	
Tensile modulus (GPa)		0.05	0.3
Flexural modulus (GPa)	0.35		
Notched impact strength ISO 180 kJ/m^2 @ 20°C	No break		
@ 0°C	40		
Thermal properties			
Vicat softening point (°C)	113	90	113
Continuous use temperature (°C)	95–105		
Glass transition temperature (°C)	−18	−34	−18
Melting temperature (°C)	126	98	126
Thermal conductivity (W/m.K)	0.19		
Coefficient of thermal expansion (10^{-5}/°C)	13		
Fire behaviour			
Oxygen index (%)	17	17	18
UL94 fire rating	HB	HB	HB

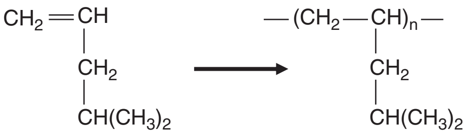
General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Weak acids	Good behaviour
Strong acids	Good behaviour except oxidizing acids
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Good behaviour up to 60°C except aromatics and chlorinated solvents
Food contact	Possible for special grades

4.3.2 Polymethylpentene (PMP)

Using Ziegler-Natta polymerization, methylpentene is converted to polymethylpentene (PMP), as shown in Figure 4.17.

The backbone is identical to those of polyethylene, polypropylene and polybutene but the pendant groups are longer.



$$CH_2{=}CH{-}CH_2{-}CH(CH_3)_2 \longrightarrow {-}(CH_2{-}CH(CH_2{-}CH(CH_3)_2))_n{-}$$

Figure 4.17. Methylpentene and polymethylpentene (PMP) formulae

Advantages

PMP is used for its transparency (visible light and UV), chemical resistance, relatively higher thermal resistance, low density, electrical insulation, harmlessness, suitability for use in microwave ovens, food contact.

Drawbacks

The cost, high for a polyolefin, and the limited number of supply sources curb the development of PMP. Impact strength is rather weak versus some other polyolefins.

Grades, processing and applications

Applications are far fewer than for polyethylene and polypropylene. Consequently there are relatively few grades marketed, corresponding to the major applications such as:

- medical and health care applications: cells for blood tests, syringes, centrifugation tubes, needle hubs, transparent tubes and tubing connectors, nebulizer parts, urine samplers . . .
- small appliances, ovenware, kitchenware, microwave ovenware, tableware, cooking utensils, water tanks for coffee makers or electric irons . . .
- laboratory ware: trays for chemical treatments, floating balls for chemical bath insulation, animal cages . . .
- packaging, films, caps, containers and bottles for cosmetics . . .
- wire and cable insulation . . .
- electric & electronic applications: printed circuits, bobbins, connectors, ink cartridges for printers . . .
- transparent tubes and pipes . . .
- films for food and industrial applications . . .
- backing cartons and release applications . . .

All molten-state processing methods are usable, mainly extrusion, injection, blow moulding, co-extrusion, welding.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 90°C up to 110°C if the softening temperature is higher.

For example:

- For a given grade of neat polymethylpentene, the short-term stress at yield retention at 80°C is roughly 35% of the value at 20°C, and HDT A (1.8 MPa) is of the order of 55°C.
- HDTs under 0.46 MPa are of the order:

○ neat	80–100°C
○ mineral-filled	110°C
○ high SGF level	180–225°C.

Figure 4.18 displays specific examples of stress at yield retention (a) and modulus retention (b) versus short-term temperature variation.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Characteristics such as elongation at break and impact strength are especially heat sensitive.

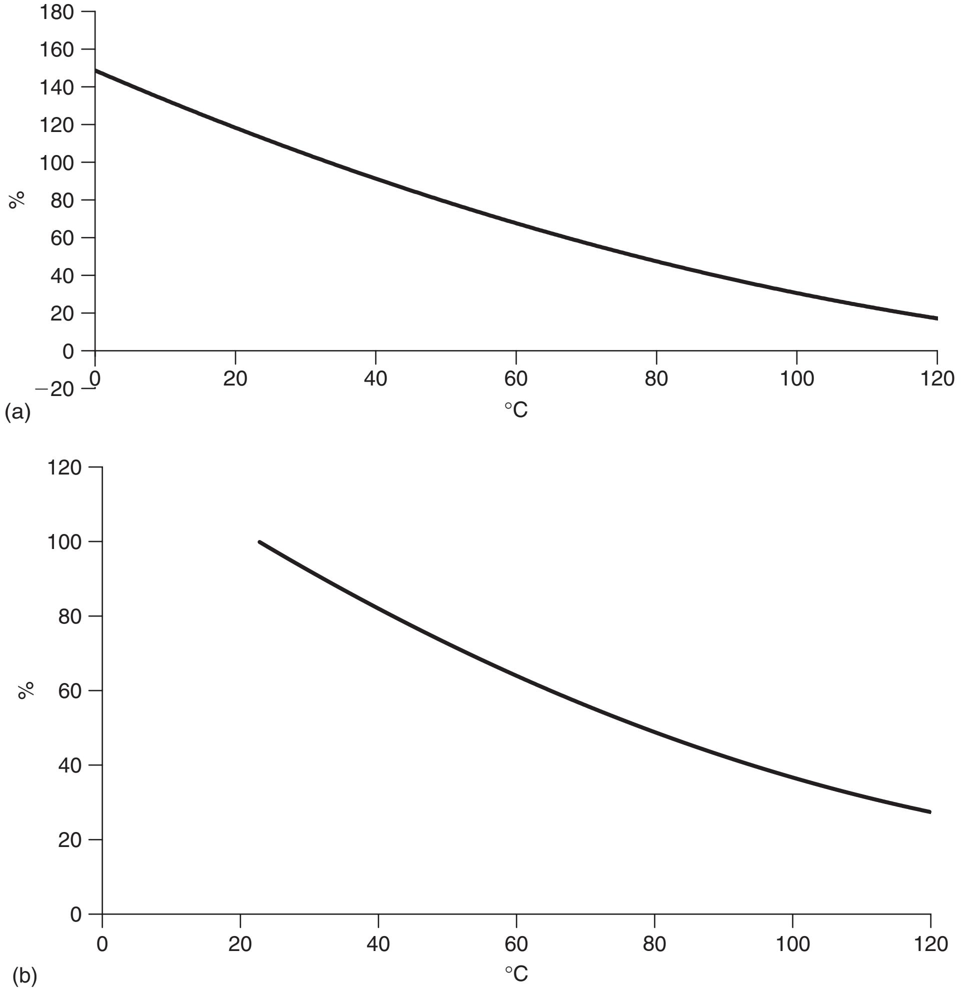


Figure 4.18 (a) Neat PMP examples of stress at yield retention (%) versus temperature (°C) (b) Neat PMP examples of modulus retention (%) versus temperature (°C)

The lifetimes can be, for example, about 1 year at 120–130°C or 5 to 10 years at 100°C, according to the grade. Two examples can be seen in Figure 4.19.

Polymethylpentene is sensitive to pro-oxidant metals such as copper but protective masterbatches are marketed.

The glass transition temperatures of polymethylpentenes by DSC measurements are generally in the room temperature range, from 20°C up to 30°C. The glass temperatures by DTMA measurements can be higher, depending on the frequency.

These results relate to some grades only and cannot be generalized.

Optical properties

Transparency is one of the main advantages of polymethylpentenes and some grades are especially designed for high light transmission, for example 90–92%. Let us remember that transmission data are of the order of 98% for polystyrene.

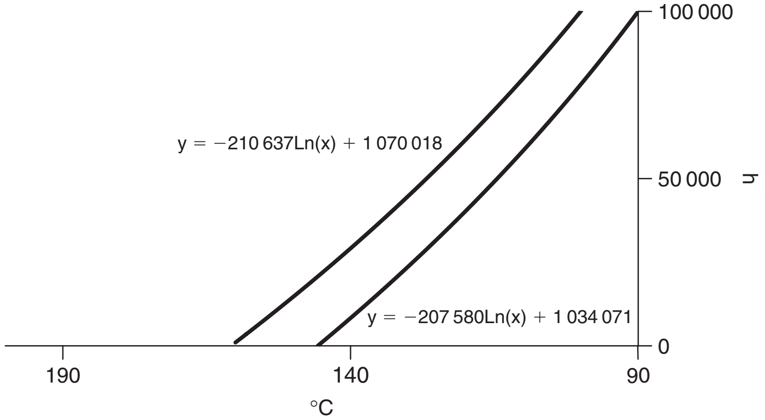


Figure 4.19. Neat PMP examples of lifetime (h) versus temperature (°C)

For films, haze can be 1.2 to 1.5 for specific grades.

The refractive index varies with the type of polymethylpentene, and can be, for example, about 1.463.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties are generally fair, comparable to those of polypropylenes with slightly lower impact strength. Moduli and hardnesses are higher than those of polyethylene but rather weak, and notched impact strengths are much lower than those of polyethylenes.

Dimensional stability

Shrinkage, coefficient of thermal expansion and creep are rather high. Absorption and alteration by moisture exposure are low.

Creep

Thermoplastic neat polymethylpentenes have rather low moduli involving high strains for moderate loading. Consequently:

- loadings for acceptable strains are very much lower than engineering strengths, for example:
  - ○ 5 MPa for a neat PMP stretching by more than 1% after a few months at ambient temperature
- creep moduli also are low, the more so as the temperature rises.

Figure 4.20 displays an example of creep moduli for a neat PMP under a load of 5 MPa.

These results are examples only and cannot be generalized.

Weathering

Polymethylpentene resists hydrolysis well but is naturally sensitive to light and UV. It must be protected by addition of specific anti-UV and other protective agents.

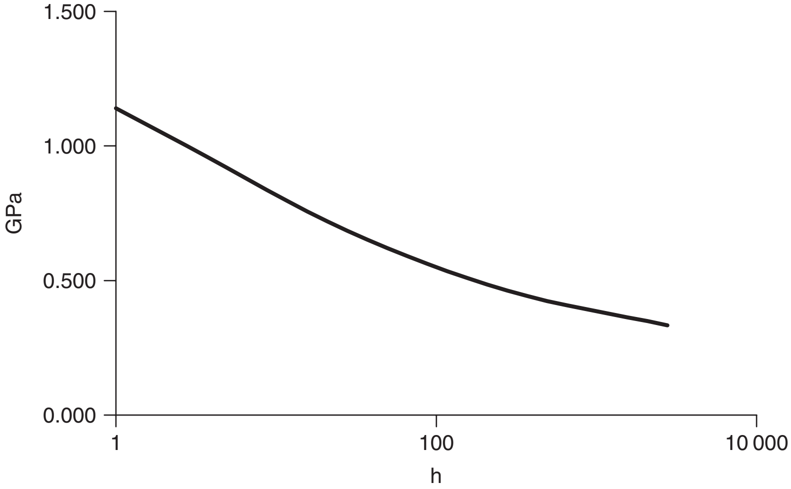


Figure 4.20. Neat PMP creep: examples of creep modulus (GPa) versus time (h) for a 5 MPa loading

High-energy radiation

Specific grades are marketed for radiation sterilization.

Behaviour at high frequencies

Polymethylpentenes have very weak loss factors, about 2×10^{-4}, and do not heat up under high-frequency current. They can be used for microwave ovenware but cannot be welded by the high-frequency technique.

Chemicals

Neat polymethylpentenes absorb little water and are not very sensitive to it.

Compared with other transparent plastics, they can be more resistant to stress cracking for some chemicals and sometimes less resistant for others.

Suitable grades are usable in contact with food and are used for food packaging.

Chemical resistance is generally good but polymethylpentenes are attacked by oxidizing acids, chlorinated solvents, certain oxidants and aromatic hydrocarbons. Resistance to aliphatic hydrocarbons, ketones, gasoline and kerosene is limited.

Copper is an oxidation catalyst and must be avoided, in particular for inserts. However, special grades protected against copper degradation are marketed.

Table 4.12 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all polymethylpentenes. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Permeability

Polymethylpentene is more permeable to gases than some other polyolefins.

Table 4.12 Polymethylpentenes: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S
Acetic acid	>96	l
Acetic aldehyde	100	S
Acetic anhydride	100	S
Acetone	100	l
Acetonitrile	100	S
Acetophenone	100	l
Acetyl chloride	100	l
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonium hydroxide	10	S
Ammonium sulfate	50	S
Amyl acetate	100	n
Amyl alcohol	100	S
Antimony chloride	10	S
Aqua regia	Unknown	n
Arsenic acid	Unknown	S
ASTM1 oil	100	S
ASTM3 oil	100	l
Barium chloride	Saturated	S
Benzaldehyde	100	l
Benzene	100	n
Benzylchloride	100	n
Benzylic alcohol	100	n
Boric acid	Unknown	S
Brake fluid	100	S
Bromine (liquid)	100	n
Butter	100	S
Butyl acetate	100	l
Butylamine	Unknown	S
Butylchloride	100	n
Calcium chloride	Unknown	S
Carbon sulfide	100	n
Carbon tetrachloride	100	n
Castor oil	100	S
Cellosolve	100	S
Cellosolve acetate	100	S
Chlorine (dry gas)	100	l
Chlorine dioxide	Unknown	l
Chlorine water	Unknown	n
Chloroacetic acid	Unknown	S
Chlorobenzene	100	n
Chloroform	100	l
Chlorosulfonic acid	Unknown	n
Chromic acid	Unknown	S
Citric acid	10	S
Colza oil	100	S
Copper sulfate	Unknown	S
Cyclohexanol	100	S
Dichloroethylene	100	l
Diethylamine	100	n
Diethylether	100	n
Dimethylformamide	100	l
Dimethylhydrazine	100	S
Dioctylphthalate	100	S
Dioxan	100	l
Ethanol	Unknown	S
Ethylacetate	100	n
Ethylchloride	100	n
Ethylene glycol	100	S
Fluorine	100	l
Formaldehyde	37	S
Formic acid	85	S
Freon 11	100	l
Freon 113	100	l
Freon 115	100	l
Freon 12	100	l
Freon 13b1	100	l
Freon 21	100	l
Freon 22	100	l
Freon 32	100	l
Furfural	100	l
Glycerol	100	S
Hexane	100	l
Hydrobromic acid	48	S
Hydrochloric acid	36	S
Hydrochloric acid	10	S
Hydrofluoric acid	40	S
Hydrogen peroxide	30	S
Hydrogen sulfide gas	Unknown	S
Iron(III) chloride	Unknown	S
Isooctane (Fuel A)	100	l
Isopropanol	100	S
Kerosene	100	l
Lead acetate	10	S
Linseed oil	100	S
Liquid paraffin	100	l
Magnesium chloride	Unknown	S
Mercury chloride	Unknown	S
Methanol	100	S
Methylethylketone	100	l
Methylisobutylketone	Unknown	l
Mineral oil	100	l
Molasses	Unknown	S
Nickel chloride	Unknown	S
Nitric acid	65–75	l
Nitric acid	10	S
Nitrobenzene	100	l
Olive oil	100	S
Oxalic acid	Unknown	S
Perchloroethylene	100	n
Petrol	100	n
Petroleum	100	l
Phenol	Unknown	S
Phosphoric acid	85	S
Potassium cyanide	Unknown	S
Potassium fluoride	Unknown	S
Potassium hydroxide	45	S

Table 4.12 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Potassium permanganate	1	l	Sulfuric acid	10	S
Potassium permanganate	20	S	Tetrachloroethane	100	l to n
Potassium sulfate	Unknown	S	Tetrahydrofuran	100	l
Propanol	100	S	Tin chloride	Unknown	S
Sea water	100	S	Toluene	100	l to n
Silver nitrate	Unknown	S	Transformer oil	100	S
Sodium borate	Unknown	S	Trichloroacetic acid	Unknown	S
Sodium carbonate	10	S	Trichloroethane	100	n
Sodium chloride	25	S	Trichloroethylene	100	n
Sodium cyanide	Unknown	S	Tricresylphosphate	Unknown	S
Sodium hydroxide	40–55	S	Triethanolamine	Unknown	S
Sodium hydroxide	10	S	Triethylamine	Unknown	l
Sodium hypochlorite	20	S	Turpentine oil	100	l
Sodium nitrate	Solution	S	Vegetable oil	100	l
Sodium oxalate	Unknown	S	Water	100	S
Styrene	100	l	White spirit	100	n
Sulfurous anhydride (gas)	Unknown	S	Wine	Unknown	S
Sulfur dioxide (gas)	Unknown	S	Xylene	100	n
Sulfuric acid	96	l to S	Zinc chloride	Unknown	S
Sulfuric acid	70	S			

S: satisfactory; l: limited; n: not satisfactory

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames, even after the ignition source is removed. Moreover, polymethylpentene drips while burning.

Oxygen indices are roughly 17 with a poor UL94 rating.

Electrical properties

Polymethylpentenes are good insulators even in wet environments, with high dielectric resistivities and rigidities, and low loss factors. General-purpose grades do not heat up in high frequency (HF) or ultra-high frequency (UHF) electric fields. Special grades are marketed for electrical applications such as the insulation of wires and cables.

Joining, decoration

Welding is easy using thermal processes, possible with ultrasound but impossible with the high-frequency technique.

Gluing is difficult. All precautions must be taken concerning health and safety according to local laws and regulations.

Trade name examples

Polymethylpentene TPX.

Property tables

Table 4.13 relates to examples only. The data cannot be generalized or used for designing.

Table 4.13 Polymethylpentene: examples of properties

	Transparent	Low modulus, transparent
Miscellaneous properties		
Density (g/cm^3)	0.833	0.835
Shrinkage (%)	1.7–2.1	1.6–1.9
Absorption of water (%)	0.01	
Mechanical properties		
Shore hardness, D	70–76	60–70
Rockwell hardness, R	80–85	
Stress at yield (MPa)	23–24	15–20
Tensile strength (MPa)	17–25	16–18
Elongation at break (%)	15–25	85–120
Tensile modulus (GPa)	1.1–1.5	0.5–0.8
Flexural modulus (GPa)	1.3–1.5	0.8–1.5
Notched impact strength ASTM D256 (J/m)	49–53	50–150
Thermal properties		
HDT B(0.46 MPa) (°C)	90–100	80–85
HDT A(1.8 MPa) (°C)C	40–55	
Continuous use temperature (°C)	90–110	90–110
Glass transition temperature (°C)	20–30	20–30
Melting temperature (°C)	240	235–240
Minimum service temperature (°C)	−20 to −40	−20 to −40
Thermal conductivity (W/m.K)	0.17	0.17
Specific heat (cal/g/°C)	0.47	0.47
Coefficient of thermal expansion (10^{-5}/°C)	11–12	11–12
Electrical properties		
Volume resistivity (ohm.cm)	$>10^{16}$	$>10^{16}$
Dielectric constant	2.12	2.12
Loss factor (10^{-4})	2	2
Dielectric strength (kV/mm)	65	64
Fire behaviour		
Oxygen index	17	17
UL94 fire rating	HB	HB
	25% Mineral	30% Glass fibres
Miscellaneous properties		
Density (g/cm^3)	1	1.04
Shrinkage (%)	1.5	0.4–0.6
Absorption of water (%)	0.1	0.01
Mechanical properties		
Shore hardness, D	75–80	75–80
Rockwell hardness, R		107
Tensile strength (MPa)	21	34–68
Elongation at break (%)	10	1.5
Tensile modulus (GPa)	3.5	5.2
Flexural modulus (GPa)	2.8	4.1
Notched impact strength ASTM D256 (J/m)	43	64
Thermal properties		
HDT B (0.46 MPa) (°C)	110	177
HDT A (1.8 MPa) (°C)		166
Continuous use temperature (°C)	90–110	90–110
Glass transition temperature (°C)	20–30	20–30
Melting temperature (°C)	240	240
Electrical properties		
Volume resistivity (ohm.cm)	$>10^{16}$	$>10^{16}$
Fire behaviour		
UL94 fire rating	HB	HB

Table 4.13 (Continued)

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilization is needed
Weak acids	Good behaviour
Strong acids	Good behaviour except oxidizing acids
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Good behaviour at room temperature except aromatics and chlorinated solvents and to some extent aliphatic hydrocarbons, ketones, gasolines, kerosene
Food contact	Possible for special grades

4.3.3 Cyclic olefin copolymers or cyclic olefin polymers (COC or COP)

Cyclic olefin copolymers are copolymerized from linear and cyclic (norbornene) olefins (as shown in Figure 4.21) followed by hydrogenation of double bonds.

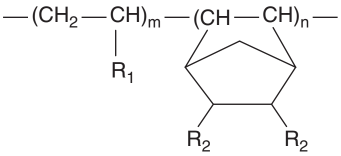


Figure 4.21. PolyCyclic Olefin Copolymers (COC)

The presence of the large cyclic olefin units randomly distributed in the backbone leads to an amorphous copolymer combining high transparency, low birefringence, stiffness, barrier properties and the general characteristics of olefins.

There are several subfamilies that are not differentiated in the following except where special mention is due.

Polycyclic olefin copolymers target optical, medical and electronic applications.

Advantages

General advantages are excellent optical properties combining high transmissibility and low birefringence, excellent balance of optical and mechanical properties, high glass transition temperature, high moduli, chemical inertness, low absorption of water, low density, good electrical insulation, physiological inertness, low levels of impurities, suitability for medical and food applications, low shrinkage and high HDT for a polyolefin, ease of welding, versatility of processing methods, good machinability.

Drawbacks

General drawbacks are the innate sensitivity to UV, light and weathering (but stabilized grades are marketed), and stress cracking. Composed only of carbon and hydrogen, COC are naturally flammable but FR grades are marketed. The high cost, for a polyolefin, and the limited number of supply sources curb its development.

Grades, processing and applications

Applications are far fewer than for polyethylene and polypropylene. Consequently there are relatively few grades classified into two large categories:

- high optical properties for storage media, CD, CD-ROM with low birefringence and high moulding accuracy
- basic or general-purpose grades with various versions differing by modulus and HDT.

The major applications are, for example, without claiming to be exhaustive:

- optical applications: storage media, CD, CD-ROM, DVD, SACD (super audio compact disc); lenses for cameras on mobile phones, digital cameras, compact cameras; CD-players, VTR, office automation equipment such as photocopiers, prisms, mirrors, polygon mirrors, optical films . . .
- medical, laboratory and health care applications: transparent pre-filled syringes, pharmaceutical containers and packages, primary packaging of pharmaceuticals, medical devices, diagnostic disposables, laboratory ware . . .
- electronic: bi-oriented films, metallized films, light guides and diffusion plates for LCDs, semiconductor containers . . .
- packaging: films and packaging with barrier properties, blister packaging, shrink caps, sleeves and stand-up pouches, co-extruded films . . .
- industry, construction and lighting sectors: transparent mouldings, sensors, extensions for automobile headlights and belts, tableware . . .

All molten-state processing methods can be used, mainly extrusion, injection, blow moulding, co-extrusion, welding.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated up to 110°C.

The glass transition temperatures by DSC measurements vary in a broad range from 80°C up to 180°C, which leads to high HDT for a polyolefin, for example HDT B (0.46 MPa) in a range from 75°C to more than 170°C. Consequently, service temperatures are rather high for a polyolefin.

Figure 4.22 displays modulus retention versus temperature for three different grades of COC.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used.

These results relate to some grades only and cannot be generalized.

Optical properties

COC are amorphous and can have excellent optical properties according to the grade, for example:

- light transmissibility commonly in a range from 92 to 93%
- refractive index of 1.53
- very low birefringence
- low haze.

Some grades can be opaque.

These results relate to some grades only and cannot be generalized.

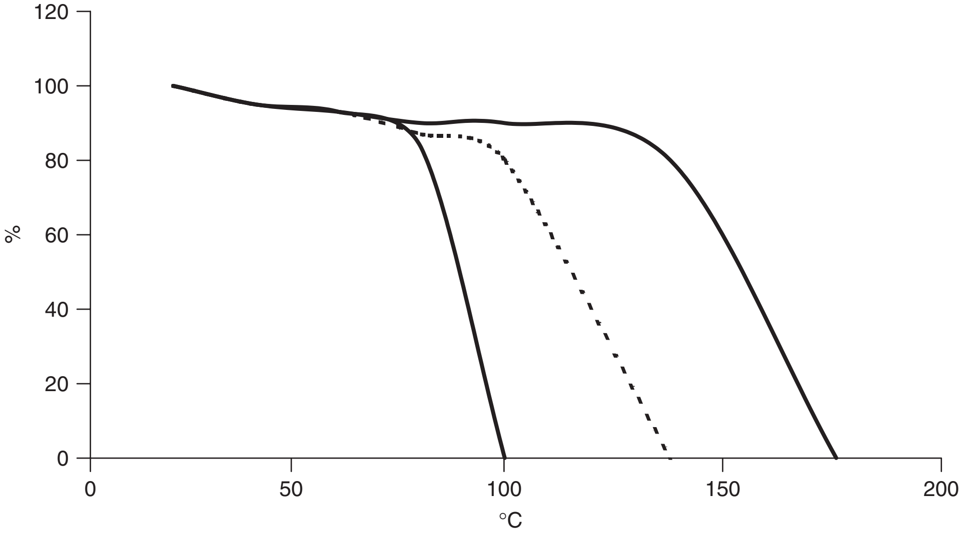


Figure 4.22. *COC examples of modulus retention (%) versus temperature (°C)*

Mechanical properties

The mechanical properties are generally good with high moduli but limited strains at yield except grades for films.

Creep

Thermoplastic neat COCs have fair moduli that involve moderate strains for moderate loading. Consequently, creep moduli (see Figure 4.23(a)) are fair at room temperature. When the temperature rises (Figure 4.23(b)) creep moduli decrease.

Figure 4.23(a) displays an example of creep modulus versus time at room temperature. The load is unfortunately unknown here but we can note the fair behaviour of COC.

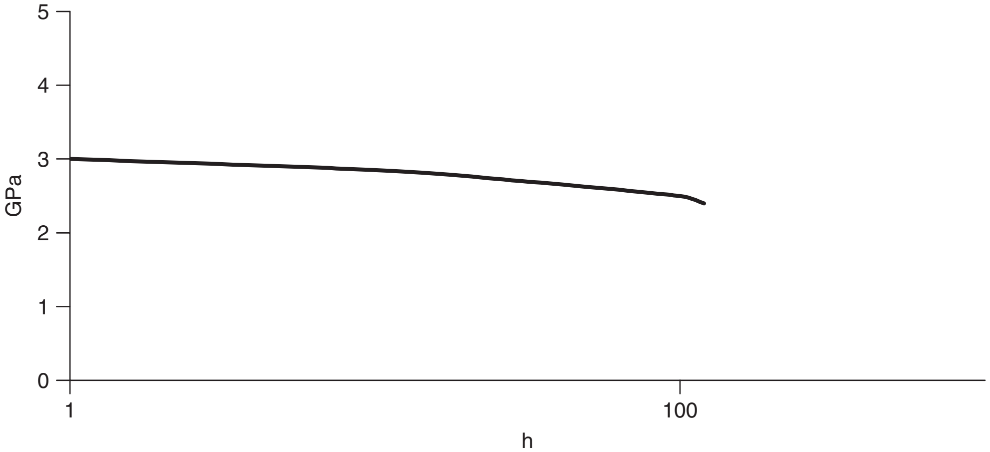


Figure 4.23. *(a) COC examples of creep modulus (GPa) versus time (h) at room temperature*

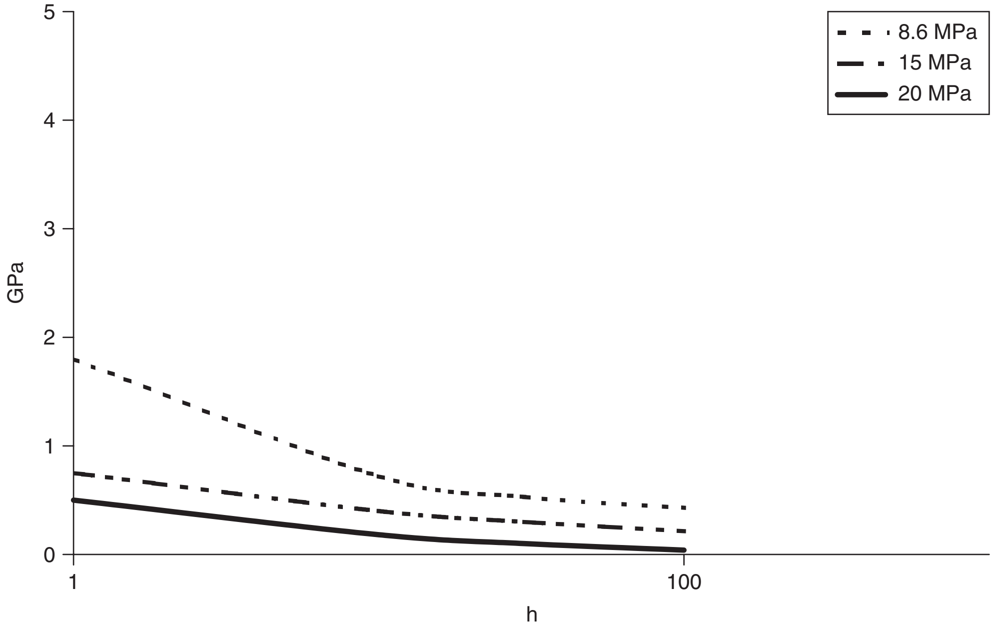


Figure 4.23. (b) COC examples of creep modulus (GPa) versus time (h) at 90°C for various loadings (MPa)

Figure 4.23(b) displays examples of creep modulus (GPa) versus time (h) at 90°C for various loadings (MPa). By comparison with Figure 4.23(a) we can note the fast decrease of creep moduli when the temperature rises to 90°C.

These results relate to a few grades only and cannot be generalized.

Weathering

COC resists hydrolysis well and is naturally sensitive to light and UV.

High-energy radiation

Specific grades are marketed for radiation sterilization.

Behaviour at high frequencies

COC have very weak loss factors, about 2×10^{-4} and do not heat up under a high frequency field. They cannot be welded by this technique.

Chemicals

COCs absorb little water and are not very sensitive to it at room temperature. They can be subject to stress cracking.

Suitable grades that are physiologically inert or approved for food contact are usable for pharmaceutical and food packaging.

Chemical resistance is generally good but COCs are attacked by oxidizing acids, chlorinated solvents, certain oxidants, hydrocarbons, ketones, oils, gasolines, kerosene, ethers.

Table 4.14 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the COCs. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.14 Cyclic olefin copolymers: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S
Acetic acid	>99	S
Acetone	100	S
Ammonium hydroxide	33	S
Aqueous ammonia	10	S
Benzaldehyde	100	l
Butanone	Unknown	S
Caustic soda	50	S
Cyclohexanone	Unknown	n
Dichloroethane	Unknown	n
Dimethylformamide	100	S
Dioctylphthalate	100	n
Ethanol	Unknown	S
Ethyl ether	Unknown	n
Formaldehyde	37	S
Formic acid	10	S
Hair rinse	Unknown	S
Hair shampoo	Unknown	l to S
Hair tonic	Unknown	S
Hexane	100	n
Hydrochloric acid	10	S
Hydrochloric acid	36	S
Hydrochloric acid	Concentrated	S
Hydrofluoric acid	40	S
Hydrogen peroxide	30	S
Isopropanol	100	S
Isopropyl alcohol	Unknown	S
Lemon juice	Unknown	S
Limonene	Unknown	n
Margarine	Unknown	n
Methanol	100	S
Methyl cellosolve	Unknown	S
Methyl methacrylate	Unknown	n
Methylene chloride	Unknown	n
Methylethylketone	100	S
Methylisobutylketone	Unknown	n
Naphtha	Unknown	n
Nitric acid	65	S
Octane	Unknown	n
Oleic acid	Unknown	n
Orange juice	Unknown	S
Pentane	Unknown	n
Phosphoric acid	85	S
Soap	Solution	S
Sodium hydroxide	50	S
Sulfuric acid	Concentrated	n
Sulfuric acid	40	S
Sulfuric acid	10	S
Synthetic neutral detergent	Unknown	S
Tetrahydrofuran	100	n
Toluene	100	n
Vegetable oil	100	n
Xylene	100	n

S: satisfactory; l: limited; n: not satisfactory

Permeability

COC has a low permeability to water vapour, inferior to that of polypropylene.

Fire resistance

Fire resistance is naturally weak with HB UL94 rating.

Electrical properties

COCs are good insulators even in wet environments, with high dielectric resistivities and rigidities, and low loss factors. Special grades are marketed for electrical applications.

Joining, decoration

Welding is possible using thermal processes and by ultrasound but impossible by the high-frequency technique.

Gluing is possible with polyurethane adhesives and solutions of COC. All precautions must be taken concerning health and safety according to local laws and regulations.

Printing and coating need pre-treatment such as corona discharge or plasma treatments. The exposure must be brief and superficial and the original and aged properties must be tested.

COC can generally be metallized without pre-treatment to use in mirrors, reflectors and capacitors.

Trade name examples

Topas, Zeonex, Zeonor.

Property tables

Table 4.15 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.15 Cyclic olefin copolymers: examples of properties

Grades	Basic	Optical	Platable
Optical properties	Transparent	Transparent	Opaque
Miscellaneous properties			
Density (g/cm^3)	1.01	0.95–1.01	1.01
Shrinkage (%)	0.4–0.7		
Absorption of water (%)	<0.01	<0.01	<0.01
Mechanical properties			
Shore hardness, D	78		
Rockwell hardness, M	20		
Tensile strength (MPa)	42–63	45–71	43
Elongation at break (%)	20–140	3–40	100
Tensile modulus (GPa)	2–2.2	2.2–3.1	1.9
Flexural strength (MPa)	55–97	91–104	58
Flexural modulus (GPa)	1.8–2.1	2.1–3.1	1.7
Notched impact strength ASTM D256 (J/m)	18–80	13–24	350
Thermal properties			
HDT A (1.8 MPa) (°C)	68–145	103–123	123
Continuous use temperature (°C)	90–110	110	
Glass transition temperature (°C)	70–162	123–139	138
Coefficient of thermal expansion (10^{-5}/°C)	7	6–9	7
Electrical properties			
Volume resistivity (ohm.cm)	$>10^{16}$	$>10^{16}$	$>10^{16}$
Dielectric constant	2.3	2.3	2.3
Loss factor (10^{-4})	2	2–4	2
Dielectric strength (kV/mm)	40 to >70	40	40
Fire behaviour			
UL94 fire rating	HB	HB	HB
Miscellaneous properties			
Density (g/cm^3)	1.02	1.02	1.02
Shrinkage (%)	0.4–0.7	0.4–0.7	0.4–0.7
Absorption of water (%)	<0.01	<0.01	<0.01

Table 4.15 (Continued)

	Low glass transition	Medium glass transition	High glass transition
Mechanical properties			
Ball indentation hardness, applied load 961 N	130	184	190
Tensile strength (MPa)	66	66	66
Elongation at break (%)	10	3–4	4
Tensile modulus (GPa)	2.6	3.1–3.2	3.2
Notched impact strength Charpy (kJ/m^2)	2.6	1.7–2	2
Thermal properties			
HDT B(0.46 MPa) (°C)	75	130–150	170
Glass transition temperature (°C)	80	140–160	180
Coefficient of thermal expansion (10^{-5}/°C)	7	6–7	6
Electrical properties			
Volume resistivity (ohm.cm)	$>10^{16}$	$>10^{16}$	$>10^{16}$
Dielectric constant	2.35	2.35	2.35
Loss factor (10^{-4})		2	
Fire behaviour			
UL94 fire rating	HB	HB	HB

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Sensitive to UV
Weak acids	Good behaviour
Strong acids	Good behaviour except oxidizing acids
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Good behaviour at room temperature except oxidizing acids, chlorinated solvents, certain oxidants, hydrocarbons, ketones, oils, gasolines, kerosene, ethers

4.4 Polyolefin and non-polyolefin copolymers

4.4.1 Ethylene-vinyl acetate copolymers (EVA, E/VAC, EVAC, VAE, EVM)

In the following, we will generally use the acronyms:

- EVA, which is the most commonly used for ethylene-vinyl acetate copolymers, instead of the standardized acronym E/VAC (ISO 1043). VAE is sometimes used for high VA contents
- VA for vinyl acetate content.

EVM is the standardized acronym for ethylene-vinyl acetate rubbers (ISO 1629).

EVA and VAE (see Figure 4.24) are copolymerized from ethylene and vinyl acetate that is randomly distributed along the backbone. The backbone is identical to that of the polyolefins but the pendant groups are different, with a polar character and a random structure that decreases crystallinity the more so as the vinyl acetate level rises.

The properties depend on the vinyl acetate level, the crystallinity (see Figure 4.25), the branching level, the molecular weight and the polarity.

Figure 4.25 displays examples of crystallinity (%) versus vinyl acetate content (%) for neat EVA. Note the progressive and fast fall in the crystallinity.

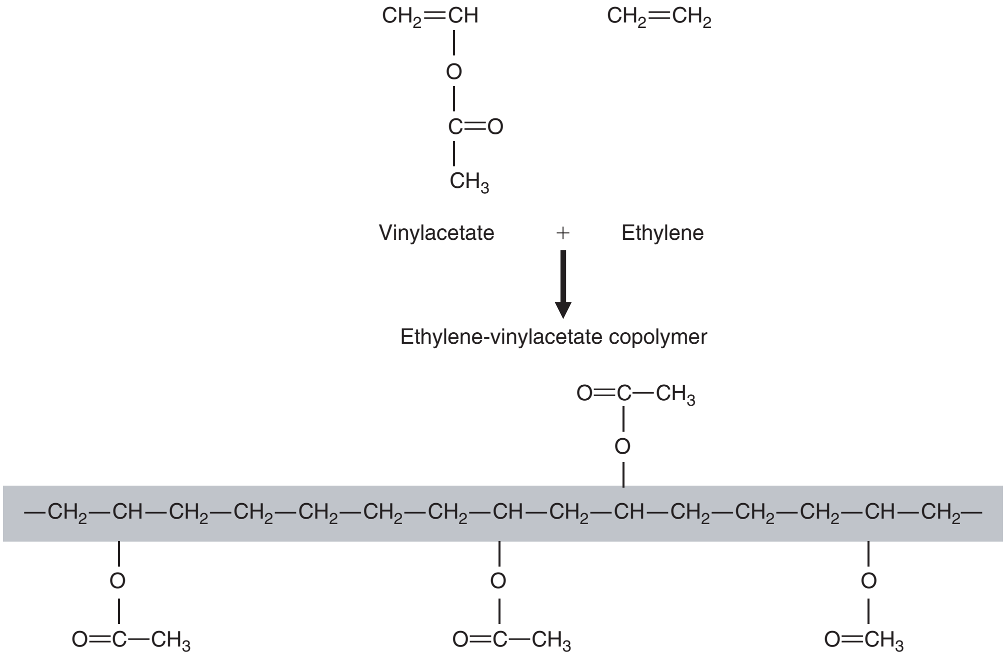


Figure 4.24. Vinyl acetate, ethylene and ethylene-vinylacetate copolymer formulae

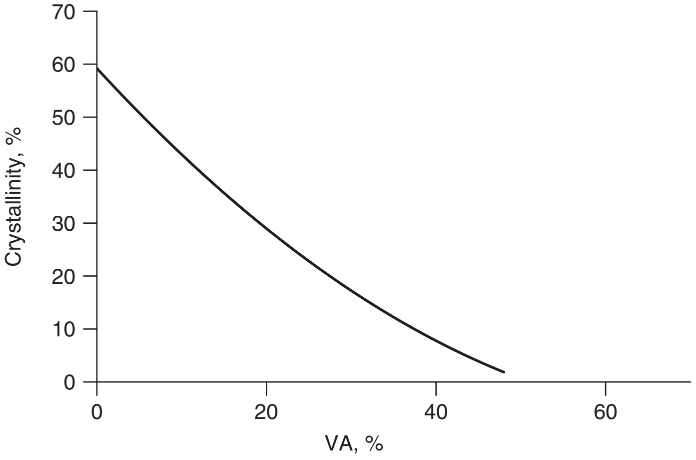


Figure 4.25. Neat EVA: examples of crystallinity (%) versus VA content (%)

Copolymers with low vinyl acetate content (ca. 2–10%) have properties close to those of low-density polyethylene.

When the vinyl acetate content rises, polarity increases, and crystallinity and hardness decrease. For a 40–50% vinyl acetate content, the copolymer is an amorphous resin that is easily crosslinkable.

Resins with high vinyl acetate content (ca. 60–90%) are very often emulsions or dispersions in water used for modification of other polymers, and carriers for plastic and rubber additives. They can also be mixed with fillers and other ingredients, and possibly crosslinked, to make thermoplastic or cured seal sheeting or various parts and goods.

The applications depend on the vinyl acetate level, for example:

- extruded or injected goods: up to 20% VA
- hot-melt adhesives: 20 to 40% VA
- crosslinked goods: higher than 40–45% VA.

Advantages

Increasing vinyl acetate content:

- reduces crystallinity, improving clarity, flexibility, impact strength and resistance to stress cracking
- increases oil resistance
- improves light, UV, ozone and weathering resistance
- improves adhesion to other materials
- decreases melting and sealing temperatures
- improves the possibility of curing by both chemical and radiation methods.

The EVAs make it possible to produce compounds with high filler levels and are compatible with many elastomers, plastics and other materials: SBR, butyl rubber, EPDM, nitrile rubber, Hypalon, thermoplastic elastomers, epoxies, PVC, PVDC, bitumen.

Drawbacks

Increasing vinyl acetate content:

- reduces crystallinity, decreasing stiffness
- decreases heat stability and chemical resistance
- increases permeability to water vapour and gases
- slightly reduces insulating properties even if EVAs are suitable for wire coating.

Grades, processing and applications

Applications are far lower than for polyethylene and polypropylene. Consequently, relatively few grades are marketed, corresponding to the major applications such as:

- films and sheets with high clarity, puncture resistance, impact strength, low heat-seal temperature used for shrink-wrap, heavy-duty shipping sacks, produce bags, bag-in-box, gloves, food and technical packaging films, greenhouse films . . .
- multilayer films with polypropylene, polyester, aluminium foil to provide heat-seals. Typical applications are, for example, frozen food, dry soup, soft drink mix pouches . . .
- pipes, hoses, tubes for home appliances, medical tubing, swimming pool hoses, beverage tubing . . .
- profiles . . .
- electric wire and cable sheathing . . .
- injection of various parts: transparent, filled to a greater or lesser degree, possibly crosslinked or/and foamed in microcellular form to make parts such as, for example, tyres (light uses), kneepads, insulation, footwear, soles, sports and technical items, buoys, flexible toys, ring seals, protective caps, clips, cable binders, infusion bottles, lids, all kinds of closures, bellows, rail pads, O-rings, parts for circuit breakers, buffers and seals, medical products, sound proofing for automotive use . . .
- glues . . .
- foams . . .

All the molten-state processing methods can be used, mainly extrusion, injection, blow moulding, co-extrusion, foaming, welding, crosslinking.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated up to 50–70°C but can be limited by softening or melting. For example, the Vicat softening temperature (see Figure 4.26) can be as low as 35°C and HDTs are generally too low to be measurable.

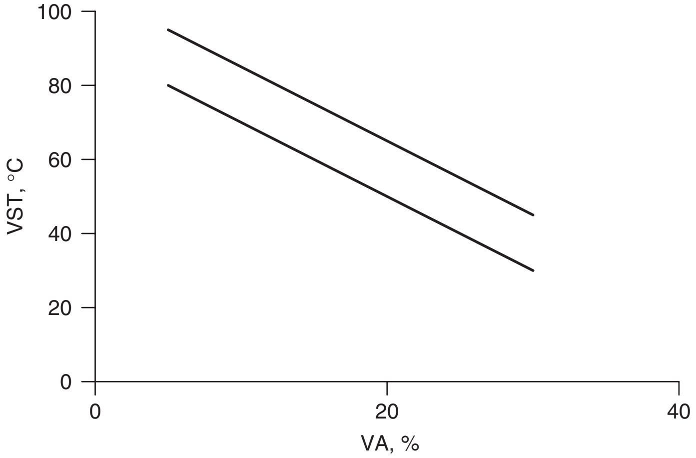


Figure 4.26. Neat EVA: examples of VST (°C) versus VA content (%)

Figure 4.26 displays examples of Vicat softening temperatures (VST) versus VA content. The other important parameter for VST is the melt flow index.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Characteristics such as elongation at break and impact strength are especially heat sensitive. Heat resistance decreases as the VA content rises.

These results relate to some grades only and cannot be generalized.

Optical properties

In the visible light region, the transparency of neat EVAs increases as the VA content rises. The transparency in the near infrared region is weak and favours heat retention for greenhouse films.

Refractive indices are intermediate between those of polyethylenes (ca. 1.52) and polyvinyl acetate (ca. 1.47): for example, 1.48 for an EVA with 40% VA.

Example values of haze for films are 1.5 for one film and 6 for another.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties depend on the examined property, and for a given line of EVAs:

- hardness decreases from more than 90 Shore A (or 40 Sh D) for a low level of VA down to 70 Shore A (or 20 Sh D) for 30% VA
- at the same time, the stress at yield decreases from 7 MPa down to 3 MPa

- shear modulus decreases from 100 MPa down to 5 MPa
- resilience increases from 37% to 55%
- impact strength is in an excellent range
- elongations at break are often greater than 500%.

All these properties vary with the melt flow index for an identical VA content and the above data cannot be generalized.

Dimensional stability

Shrinkage, coefficient of thermal expansion and creep are highly dependent on the VA content. For example, the coefficient of thermal expansion can vary between 20×10^{-5} (low VA) up to 30×10^{-5} (high VA). The absorption of water by moisture exposure slightly increases with VA content but is always limited.

Creep

Thermoplastic neat EVAs have very low moduli involving high strains for moderate loading. Consequently, loading must be limited and creep moduli used for designing must be very low.

Crosslinked EVAs are more resistant to creep but loading must still be low.

Figure 4.27 shows two examples of EVA creep modulus (GPa) versus time (h) at room temperature under 3 MPa. We can note the low level of the creep moduli, very inferior to that of an HDPE example, which is itself among the low-creep-resistant thermoplastics.

These results are only examples and cannot be generalized.

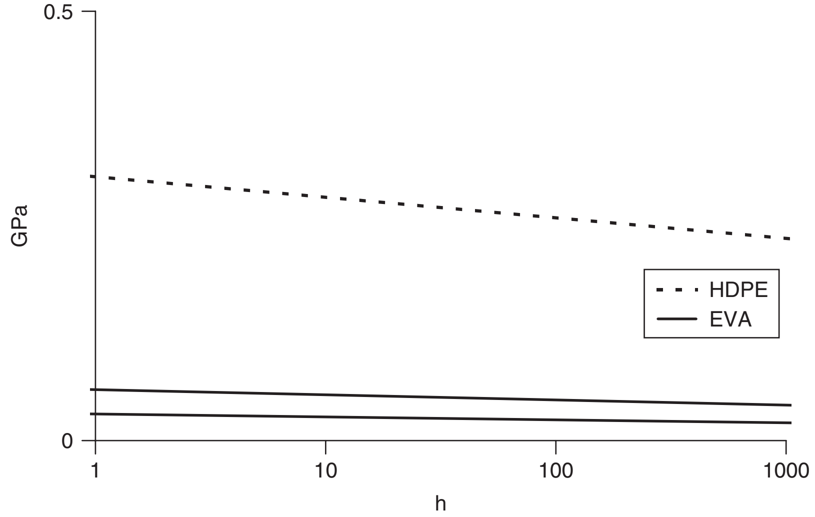


Figure 4.27. EVA and HDPE examples of creep modulus (GPa) versus time (h) at room temperature under 3 MPa

Weathering

EVAs are naturally resistant to light, UV, ozone and weathering and, even more, they can be protected by addition of specific anti-UV and other protective agents. Under identical conditions, lifetimes of films exposed outdoors are 3 years for a protected EVA versus less than 1 year for an LDPE film.

High-energy radiation

Specific grades are crosslinkable by high-energy radiation.

Behaviour at high frequencies

EVAs have higher loss factors, about 200×10^{-4} to near 500×10^{-4}, and heat up under high-frequency current allowing HF welding.

Chemicals

EVAs absorb water the more so as VA content rises, but for a 30% VA the water uptake is acceptable, for example 0.15% for a given grade. EVAs are generally more resistant to stress cracking than comparable LDPE.

Suitable grades are usable in contact with food.

The chemical resistance is generally inferior to that of comparable polyethylenes and decreases when VA rises. EVAs are attacked by concentrated strong acids, halogens, oxidizing acids, chlorinated solvents, certain oxidants, aliphatic and aromatic hydrocarbons, alcohols, ketones, esters, and some others.

Impermeability and, consequently, chemical resistance decrease with decreasing crystallinity.

Table 4.16 displays some general assessments of behaviour after prolonged immersions in a range of chemicals at room temperature for given grades, which are not representative of all the EVAs because of the variation of the chemical resistance as the VA content varies. For example, a given 9% VA grade is resistant to a specific detergent while the 28% VA grade is not. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.16 Ethylene-vinyl acetate copolymers: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S
Acetic acid	>96	n
Acetic aldehyde	40–100	n
Acetic anhydride	100	n
Acetone	100	n
Acrylonitrile	100	n
Adipic acid	Saturated	S
Allylic alcohol	96–100	n
Alum	Solution	S
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonium acetate	Saturated	S
Ammonium chloride	Solution	S
Ammonium hydroxide	30	S
Ammonium nitrate	Unknown	S
Ammonium sulfate	50	S
Amyl acetate	100	n
Amyl chloride	100	n
Amyl alcohol	100	S
Aniline	Saturated to 100	n
Antimony chloride	10–90	S
Aqua regia	Unknown	n
Arsenic acid	20	S
Arsenic acid	Unknown	S
ASTM1 oil	100	l
ASTM2 oil	100	l
ASTM3 oil	100	l
Barium carbonate	Saturated	S
Barium chloride	Saturated	S
Beer	Unknown	S
Benzaldehyde	Dilute to 100	n
Benzene	100	n

Table 4.16 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Benzoic acid	Solution	n
Benzyl chloride	100	n
Benzyl alcohol	100	n
Boric acid	Unknown	S
Bromine (dry gas)	100	n
Bromine (liquid)	100	n
Butanol	100	l
Butter	100	n
Butyl acetate	100	n
Butyric acid	5–100	n
Calcium chloride	Unknown	S
Calcium hypochlorite	Solution	S
Calcium hypochlorite	15	S
Camphor oil	100	n
Carbon sulfide	100	n
Carbon tetrachloride	100	n
Castor oil	100	n
Chlorinated solvents	100	S
Chlorine (dry gas)	100	n
Chlorine (wet)	Unknown	n
Chlorine water	Unknown	n
Chloroacetic acid	Unknown	n
Chlorobenzene	100	n
Chloroform	100	n
Chlorosulfonic acid	100	n
Chlorosulfonic acid	Unknown	n
Chromic acid	50	n
Citric acid	10 to saturated	S
Cognac	Unknown	S
Copper sulfate	Unknown	S
Creosote	Unknown	n
Cresol	100	n
Cyclohexane	100	n
Cyclohexanol	100	n
Cyclohexanone	100	n
Decaline	100	n
Detergent	Unknown	l
Dibutylether	100	n
Dibutylphthalate	100	n
Dichlorobenzene	100	n
Dichloroethane	100	n
Dichloroethylene	100	n
Dichloromethylene	100	n
Dichlorotoluene	100	n
Diethylamine	100	l
Diethylcetone	100	n
Diethyleneglycol	100	S
Diethylether	100	n
Dimethylamine	100	n
Dimethylaniline	100	n
Dimethylformamide	100	n
Dioctylphthalate	100	n
Dioxan	100	n
Esters	100	n
Ethanol	96	l
Ethanol	Unknown	l
Ether	100	n
Ethylacetate	100	n
Ethylbenzene	100	n
Ethylchloride	100	n
Ethylene dibromide	100	n
Ethylene glycol	100	S
Ethylenebromide	100	n
Fluorine	100	n
Fluosilicic acid	Unknown	S
Formaldehyde	Dilute to 37	S
Formic acid	85	S
Furfural	100	n
Furfuryl alcohol	100	n
Glucose	Dilute	S
Glycerol	100	S
Glycol	Unknown	S
Heptane	100	n
Hexane	100	n
Household bleach	Unknown	n
Hydrobromic acid	48–100	n
Hydrochloric acid	10–20	S
Hydrochloric acid	36	l
Hydrofluoric acid	40	S
Hydrogen peroxide	30–90	S
Hydrogen sulfide gas	Unknown	S
Iodine (alcoholic solution)	Unknown	n
Iodine tincture	Unknown	n
Iron(III) chloride	Unknown	S
Isooctane (Fuel A)	100	n
Isopropanol	100	S
Isopropylacetate	100	n
Ketones	100	n
Lactic acid	90	S
Lanoline	Unknown	n
Lead acetate	10	S
Linseed oil	100	n
Liquid paraffin	100	n
Magnesium carbonate	Saturated	S
Magnesium chloride	Unknown	S
Magnesium hydroxide	Unknown	S
Magnesium sulfate	Unknown	S
Maleic acid	Saturated	S
Malic acid	Unknown	S
Manganese sulfate	Unknown	S
Margarine	100	n
Mercury chloride	Unknown	S
Methanol	100	l
Methylbromide	100	n
Methylbutylketone	100	n
Methylchloride	100	n

(*Continued*)

Table 4.16 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Methylene chloride	100	n
Methylethylketone	100	n
Methylisobutylketone	Unknown	n
Mineral oil	100	n
Molasses	Unknown	S
Monochlorobenzene	100	n
Naphtha	Unknown	n
Naphthalene	100	S
Nitric acid	10	S
Nitric acid	⩾50	n
Nitrobenzene	100	n
Oleic acid	Unknown	n
Oleum	Unknown	n
Olive oil	100	n
Oxalic acid	Unknown	l
Ozone	Unknown	n
Perchloroethylene	100	n
Petrol aliphatic or high-octane	100	n
Petroleum	100	n
Phenol	Unknown	n
Phenol	90	n
Phosgene	Unknown	n
Phosphoric acid	50–85	S
Picric acid	Solution	l
Potassium bromate	Unknown	S
Potassium carbonate	Saturated	S
Potassium chlorate	Saturated	S
Potassium chromate	Saturated	S
Potassium cyanide	Unknown	S
Potassium ferrocyanide	Saturated	S
Potassium fluoride	Unknown	S
Potassium hydroxide	45	S
Potassium nitrate	Saturated	S
Potassium permanganate	20	n
Potassium sulfate	Unknown	S
Propionic acid	100	S
Pyridine	100	n
Sea water	100	S
Silicic acid	Unknown	S
Silicone oil	100	l to n
Silver nitrate	Unknown	S
Sodium borate	Unknown	S
Sodium carbonate	10	S
Sodium chloride	25	S
Sodium cyanide	Unknown	n
Sodium hydroxide	10–55	S
Sodium hypochlorite	20	l
Sodium hypochlorite	13	n
Sodium nitrate	Solution	S
Sodium peroxide	Unknown	n
Stearic acid	Saturated	S
Styrene	100	n
Sugar	Solution	S
Sulfurous anhydride (gas)	Unknown	l
Sulfur dioxide (gas)	Unknown	l
Sulfuric acid	10	S
Sulfuric acid	70	l
Sulfuric acid	98, fuming	n
Tannic acid	Solution	S
Tartaric acid	Solution	S
Tetrabromomethane	100	n
Tetrachloroethane	100	n
Tetrachloroethylene	100	n
Tetrahydrofuran	100	n
Thionyl chloride	100	n
Tin chloride	Unknown	S
Toluene	100	n
Transformer oil	100	n
Trichlorobenzene	Unknown	n
Trichloroethane	100	n
Trichloroethylene	100	n
Tricresylphosphate	Unknown	n
Triethanolamine	Unknown	n
Trinitrotoluene	Unknown	n
Trioctylphosphate	Unknown	n
Turpentine oil	100	n
Urea	Solution	S
Uric acid	Unknown	S
Urine	Unknown	S
Vegetable oil	100	n
Vinyl acetate	100	n
Water	100	S
White spirit	100	n
Wine	Unknown	S
Xylene	100	n
Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: EVA has a fair permeability, evaluated from 4 up to 20 compared with a full range of 0.05 up to 400 for all tested plastics.
- Gases: EVA has a high permeability, evaluated at:
- ○ carbon dioxide: 9000 to 50 000 versus a full range of 30 up to 59 000 for all tested plastics
- ○ nitrogen: 800 to 3500 versus a full range of 1 up to 3500 for all tested plastics
- ○ oxygen: 1700 to 11 000 versus a full range of <1 up to 11 000 for all tested plastics.

Permeability increases with the VA content. Between 10% and 30% VA, coefficients of permeability are multiplied by:

- 3.6 for nitrogen
- 3.5 for oxygen
- 3.2 for carbon dioxide
- 8 for water vapour.

Fire resistance

Fire resistance is naturally weak. General-purpose grades burn easily, generating flames, even after the ignition source is removed. Moreover, EVA drips while burning.

Oxygen indices are roughly 18–20 with a poor UL94 rating (HB).

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties.

Electrical properties

The polarity of EVAs leads to an increase in loss factors and dielectric constants but the insulating properties allow their use for wire coating. For example, between 10% and 30% VA:

- loss factors increase from 100×10^{-4} up to 300×10^{-4}
- dielectric constants increase from 2.7 to 3.7.

EVAs heat up in HF and microwave fields.

Joining, decoration

Welding is easy using thermal processes and possible by the high-frequency technique if the VA content is above 13%. Ultrasonic welding is suitable for thin parts.

Gluing is less difficult than for polyethylene. All precautions must be taken concerning health and safety according to local laws and regulations.

Decoration, printing: thanks to the polarity the adhesion is better but a pre-treatment such as corona discharge is necessary.

Specific ISO standards concerning EVAs

ISO 4613-1:1993 Plastics – Ethylene/vinyl acetate (E/VAC) moulding and extrusion materials – Part 1: Designation and specification

ISO 4613-2:1995 Plastics – Ethylene/vinyl acetate (E/VAC) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 8985:1998 Plastics – Ethylene/vinyl acetate copolymer (EVAC) thermoplastics – Determination of vinyl acetate content

Crosslinked EVA

Specific EVA grades are crosslinkable using peroxides, silanes or high-energy radiation, which improves some performances. Often crosslinking is combined with filler loading and/or foaming, which broadens the range of properties. The main processing methods involve:

- heating to promote chemical reactions of curing agents such as silanes or peroxides leading to crosslinking
- irradiation to promote direct crosslinking.

Heating can be achieved by discontinuous processes, such as heated moulds or ovens, or by continuous processes such as hot tubes for wire curing or hot tunnels.

Irradiation can be achieved by discontinuous processes such as the cobalt bomb, which are more convenient for thick parts but slow, or continuous processes such as electron beam, which are more suitable for thinner parts and speedier.

Crosslinking improves resistance to heat, stress cracking, abrasion, and also reduces permanent set after loading, residual monomers and/or oligomers and VOCs. Irradiation is a ‘cold’ sterilization process.

Of course, there are also some drawbacks, notably the overspend for an additional processing step and the corresponding investments or subcontracting. Irradiation can damage EVA. Crosslinking creates an irreversible 3D network and makes EVA more difficult to recycle.

Foams

Unlike industrial solid polymers, which are processed as carefully as possible to avoid the formation of bubbles, vacuoles etc., alveolar materials result from the desire to introduce, in a controlled way, a certain proportion of voids with the aim of:

- increasing flexibility: very soft seals
- improving the thermal or phonic insulating character
- obtaining very low densities (buoys and other floatation devices)
- making damping parts: foams for packaging, automotive and transport safety parts.

The alveolar materials consist of a polymer skeleton surrounding the cells, which may be closed or partially or completely open to neighbouring cells or the outside.

The intrinsic properties come from those of the EVA with:

- a reduction in the mechanical properties due to the small quantity of material and the high proportion of gas
- a reduction in the chemical behaviour due to the highly divided nature of the material. The thin cell walls immediately absorb liquids and gases and are rapidly damaged.

Foaming can be achieved by chemical or physical blowing agents.

EVM rubbers

By weight, EVM rubbers account for less than 1% of worldwide rubber consumption. They are chosen for their continuous use temperatures, which range from 80°C up to 120°C, their good weathering resistance (UV, ozone), their average oil behaviour, the possibility of incorporating large amounts of fillers, notably halogen-free fireproofing fillers, the possibilities of foaming and an attractive cost. On the other hand, chemical resistance can be limited.

Characteristics can be adapted by optimization of the formulations: heat or light stabilizers, fire retardants, conductive agents . . .

The main applications concern, for example, without claiming to be exhaustive:

- coating of wires and cables, in particular halogen-free fire-retardant grades
- tyres for wheels of prams, little wagons, baby walkers, toys . . .
- soles
- knuckle pads and other protections
- foams.

Trade name examples

Airflex, Alcudia, AmscoRes, Elvace, Elvax, Escorene, Evatane, Levapren, Meva, Mowilith, Riblene, Sumikaflex, Vinivil, Vinnapas, Wacker VAE . . .

Property tables

Table 4.17 relates to examples only and cannot be generalized. Data cannot be used for design purposes.

Table 4.17 EVAs: examples of properties

Neat EVAs	Low VA	Medium VA	High VA
VA (%)	11–13	24–28	32–35
Miscellaneous properties			
Density (g/cm^3)	0.93	0.95	0.96
Shrinkage (%)	1–2	0.6–2	0.4–2
Absorption of water (%)	0.05	0.12	0.17
Mechanical properties			
Shore hardness, D	35–40	24	<20
Shore hardness, A	94	62–85	40–65
Tensile strength (MPa)	17–26	3–26	7–11
Elongation at break (%)	750–850	800–1000	900–1400
Flexural modulus @ 23°C (GPa)	0.06–0.08	0.01–0.03	<0.007
Flexural modulus @ 49°C (GPa)	0.03–0.04	0.007–0.02	<0.006
Flexural modulus @ −20°C (GPa)	0.26–0.37	0.06–0.09	
Shear modulus @ 23°C (GPa)	0.04	0.008	<0.005
Shear modulus @ 40°C (GPa)	0.02	<0.005	
Shear modulus @ −20°C (GPa)	0.35	0.2	0.15
Notched impact strength ISO 180 kJ/m^2, 20°C	NB	NB	NB
Thermal properties			
Vicat softening temperature (°C)	65–79	40–55	<36
Continuous use temperature (°C)	50	50	50
Melting temperature (°C)	97	64–77	60–65
Thermal conductivity (W/m.K)	0.33	0.26	
Coefficient of thermal expansion (10^{-5}/°C)	21	26	30
Electrical properties			
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{16}
Dielectric constant	2.8	3.4	4
Loss factor (10^{-4})	100	250	500
Dielectric strength (kV/mm)	27	27	25
Fire behaviour			
Oxygen index (%)	19	19	20
UL94 fire rating	HB	HB	HB

(*Continued*)

Table 4.17 (Continued)

Neat EVAs and VAE	EVA (very high VA)	VAE	VAE
VA (%)	45–46	60	70
Miscellaneous properties			
Density (g/cm^3)	1	1.04	1.07
Mechanical properties			
Shore hardness, D	<5		
Shore hardness, A	30–34	22	20
Tensile strength (MPa)	2–7		
Elongation at break (%)	1300–2100		
Thermal properties			
Vicat softening temperature (°C)	<40		
Melting temperature (°C)	50		
Fire behaviour			
UL94 fire rating	HB	HB	HB
Filled EVAs	**FR (halogen-free)**	**Clay**	**Silica**
VA (%)	18	20	20
Filler amount (phr)	105–150	60	30
Miscellaneous properties			
Density (g/cm^3)		1.25	1.09
Mechanical properties			
Shore hardness, D		58	51
Shore hardness, A		>95	95
Tensile strength (MPa)	9–11	16	10
Elongation at break (%)	65–145	40	500
Tensile modulus (GPa)		0.3	0.12
Shear modulus @ 23°C (GPa)		0.3	0.2
Thermal properties			
Vicat softening temperature (°C)		77	74
Fire behaviour			
Oxygen index (%)	35–39		
UL94 fire rating	V0	HB	HB
EVMs	**Vulcanizate properties**		
VA (%)	40	60	70
Carbon black	50	50	50
Miscellaneous properties			
Density (g/cm^3)			1.2
Mechanical properties			
Shore hardness, D	25	25	25
Shore hardness, A	80	80	79
Tensile strength (MPa)	14	16	14
Elongation at break (%)	125	130	125
Stress @ 100% (GPa)	0.012	0.013	0.013
Compression set 70 h @ 150°C	20	20	22
Thermal properties			
Brittle point (°C)	−36	−29	−14
Air ageing 70 h @ 175°C, property changes:			
Hardness, Shore A points	6	5	8
Stress @ 100% (%)	8	8	14
Tensile strength (%)	−1	−1	5
Elongation @ break (%)	−8	−8	−16
Volume change after 70 h at 100°C in ASTM3 oil	100	45	23
UL94 fire rating	HB	HB	HB
NB: No break			

(*Continued*)

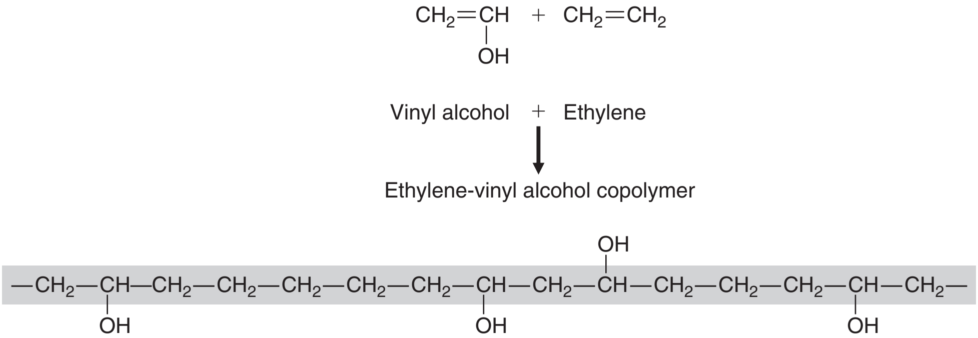
Table 4.17 (Continued)

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.	
Light	Good behaviour enhanced by stabilizers
Weak acids	Good behaviour
Strong acids:	
Low concentration	Good behaviour except oxidizing acids
High concentration	Attacked
Strong bases	Good behaviour
Solvents	EVAs are attacked by concentrated strong acids, halogens, oxidizing acids, chlorinated solvents, certain oxidants, aliphatic and aromatic hydrocarbons, alcohols, ketones, esters, and some others
Food contact	Possible for special grades

4.4.2 Ethylene-vinyl alcohol copolymers (EVOH)

In the following we will generally use VOH as the acronym for the vinyl alcohol level.

EVOHs (see Figure 4.28) are speciality thermoplastics copolymerized from ethylene and vinyl alcohol randomly distributed along the backbone. This is identical to polyolefin backbone but the pendant groups are different with a polar character and a random structure.



$CH_2{=}CH(OH) + CH_2{=}CH_2$

$-CH_2-CH(OH)-CH_2-CH_2-CH_2-CH_2-CH_2-CH(OH)-CH_2-CH(OH)-CH_2-CH_2-CH_2-CH(OH)-CH_2-$

Figure 4.28 Vinyl alcohol, ethylene and ethylene-vinyl alcohol copolymer formulae

The properties depend on the hydroxyl level, the crystallinity, the molecular weight and the polarity.

The main applications derive from the family's gas barrier effects and chemical resistance to fuels in a dry state. High moisture absorption in wet environments is harmful to the impermeability and protective layers of polyethylene or another thermoplastic insensitive to water are often needed.

Advantages

An increasing level of vinyl alcohol:

- decreases oxygen transmission rate
- improves stiffness and mechanical properties
- increases oil resistance.

EVOHs are convenient for food contact, have a good UV behaviour, are sterilizable by radiation and are transparent or translucent.

Drawbacks

The main disadvantage of the EVOHs is their water sensitivity, the more so as the vinyl alcohol content increases. Simultaneously, the barrier effect decreases.

An increase in vinyl alcohol:

- increases hardness and reduces flexibility
- increases melting temperature
- increases density.

The lack of sources – there are only two producers – and the cost curbs the development of EVOH.

Grades, processing and applications

EVOH is a speciality thermoplastic targeting specific applications and consumption is far smaller than for polyethylene and polypropylene. Worldwide production is estimated at 55 000 tonnes including 8000 tonnes consumed in Western Europe, that is to say, less than one thousandth of the total for plastics. Moreover, typical characteristics limit the applications and, consequently, relatively few grades are marketed, corresponding to the major applications:

- co-extruded films: more than 60%
- co-extruded sheets, less than 25%
- bottles: roughly 6%
- pipes, tanks: roughly 2%
- others: 5%.

Applications are induced by the barrier properties to gases and vapours, including oxygen, nitrogen, carbon dioxide, helium, hydrocarbons and fuels, flavours, aromas and various chemicals. The sensitivity to moisture very often requires use in multilayer form to protect EVOH from ambient moisture. Applications can be, for example, without claiming to be exhaustive:

- co-extrusion with polyamides, polypropylene, polyethylene, EVA, thermoplastic polyester, polycarbonate, polystyrene, ionomers for packaging of meat, cheeses, wines, fruit juices, mustards, mayonnaises, fish, pastries, cosmetics, fertilizers, herbicides and chemicals
- films for flexible food packaging
- lids for thermoformed food packages
- pouches for sauces, coffee, tea, soup . . .
- free-standing pouches
- wallpaper
- packaging for organic solvents, agricultural pesticides and all kinds of oils . . .
- barrier layers in automotive plastic fuel tanks
- multilayer pipes with polyethylene or polypropylene for under-floor heating systems in domestic and commercial buildings preventing oxygen from dissolving into the hot water and to avoid metal corrosion of other parts in the heating device.

Table 4.18 displays some suggestions. These general pointers should be verified by consultation with the producer of the selected grades and by specific studies for each case.

Table 4.18 Multilayer examples: suggestions for packaging applications and heating pipes

	Multilayers	Applications
Films	PA/EVOH/LDPE	Packing of meat, cheese
	PA/EVOH/EVA	Packing of wine, water, fruit juices, tomato puree ('bag in box')
	PA/EVOH/ionomer	Packing of fertilizers and herbicides
	PA/EVOH/PA/LDPE	Packing for cooked meat
	PA/EVOH/PA/EVA	Caps for packing in sterilized dishes or under modified atmosphere
	PA/EVOH/PA/ionomer	
	LDPE/EVOH/LDPE	
	LLDPE/EVOH/LLDPE	
	PA/EVOH/PP	
	LDPE/EVOH/OPET	
	LDPE/EVOH/OPP	
	LDPE/EVOH/PC	
	LDPE/EVOH/LDPE/OPET	
	LDPE/EVOH/LDPE/OPP	
	LDPE/EVOH/LDPE/PC	
Bottles	HDPE/EVOH	Packing of oils, industrial solvents, petroleum additives, developers, fertilizers and herbicides
	HDPE/EVOH/HDPE	Cold packing of mustard, nutritional liquids for hospitals
	LDPE/EVOH/LDPE	Hot packing of sauces: ketchup, mayonnaise, barbecue
	PP/EVOH/PP	Packing of marmalades, jams
	PP/EVOH/PC	Packing of cosmetics, pharmaceutical products
Thick sheet for thermoforming	PS/EVOH/PS PS/ EVOH/LDPE	Aseptic and modified-atmosphere packing of soft cheese, fresh vegetables, fish, fresh pastas, fresh pastries, yoghurt, desserts
	PP/EVOH/PP PP/EVOH/PC	Hot packing or sterilization of pre-cooked dishes, marmalades, jams
Flexible tubes	PA/EVOH/LDPE LDPE/EVOH/LDPE LDPE/EVOH	Packing of sauces, mayonnaise, mustard, cosmetics and pharmaceutical products
Rigid tubes	Crosslinked HDPE/EVOH PP/EVOH PB/EVOH	Under-floor heating systems in domestic and commercial buildings

All the molten-state processing methods are usable, mainly extrusion, injection, blow moulding, co-extrusion, welding.

Thermal behaviour

The temperature resistance is sufficient to allow the hot filling of certain foodstuffs.

Glass transition temperatures (45–65°C) and melting points (155–200°C) increase with the vinyl alcohol level.

Optical properties

EVOHs are transparent or translucent.

Refractive indices are intermediate between those of polyethylenes (ca. 1.52) and poly(vinyl alcohol) (ca. 1.5): for example, 1.51 for an EVOH with 50% ethylene.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties depend greatly on the examined property, and for a given line of EVOHs:

- hardness increases from 70 Rockwell M (or 90 Sh D) for a low level of VOH up to 100 Rockwell M (or more than 95 Sh D) for a high VOH content
- at the same time, the tensile stress increases twice as much, from roughly 40 MPa up to nearly 100 MPa
- tensile modulus increases at the same rate, from 2.4 GPa up to near 5 GPa
- elongations at break are often weak.

All these properties are examples and cannot be generalized.

Weathering

EVOH is sufficiently resistant to light and UV to be used in packaging.

High-energy radiation

EVOHs are sterilizable by radiation.

Chemicals

EVOHs absorb water, the more so as the VOH rises, which increases gas permeability and necessitates protection of EVOH by coating with another thermoplastic that is insensitive to moisture.

Suitable grades are usable in contact with food.

The chemical resistance is in general very different from that of polyethylenes, the more so for higher VOH contents.

EVOHs show good resistance to chlorinated solvents, oils, greases, fats, fuels, esters and certain alcohols. They are attacked by acids, bases, certain oxidants, certain alcohols and some other chemicals.

Impermeability and, consequently, chemical resistance decrease with decreasing crystallinity.

Table 4.19 displays some general assessments of behaviour after prolonged immersions in a range of chemicals at room temperature for given grades, which are not representative of all the EVOHs because of the variation of the chemical resistance when the VOH content varies. For example, the assessment after water immersion can vary from ‘limited’ to ‘not satisfactory’ depending on the VOH level. These general indications should be verified

Table 4.19 Ethylene-vinyl alcohol copolymers: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	⩾10	n	Chlorobenzene	100	S
Ammonium hydroxide	⩾10	n	Chloroform	100	S
Battery acid	Unknown	n	Citric acid	Saturated	n
Beer	Unknown	l	Citric acid	10	l
Benzoic acid	Solution	l	Concentrated acids	Concentrated	n
Butyl acetate	100	S	Detergent	Unknown	l
Butyric acid	5	l	Developer (photographic)	Unknown	l
Carbon tetrachloride	100	S	Dichlorobenzene	100	S

Table 4.19 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Dichloroethane	100	S
Dichloroethylene	100	S
Dilute acids	Dilute	n
Ethylacetate	100	S
Fruit juice	Unknown	l
Hydrochloric acid	36	n
Hydrogen peroxide	30	n
Isopropanol	100	S
Kerosene	100	S
Lactic acid	Unknown	l
Methanol	100	n
Methylchloride	100	S
Methylene chloride	100	S
Milk	100	S
Mineral oil	100	S
Monochlorobenzene	100	S
Nitric acid	⩾5	n
Oil of cloves	Unknown	S
Oxalic acid	Dilute	l
Perchloroethylene	100	S
Petrol high-octane	100	S
Petroleum ether (ligroin)	100	S
Phosphoric acid	95	n
Phosphoric acid	<10	l
Potassium hydroxide	10	l
Potassium hydroxide	45	S
Potassium hydroxide	Solution	l
Potassium permanganate	10–20	n
Salicylic acid	Saturated	n
Silicone oil	100	S
Sodium hydroxide	10–25	l
Soya oil	100	S
Strong acids	Unknown	n
Sulfuric acid	⩾10	n
Tartaric acid	Solution	S
Tetrachloroethane	100	S
Tetrachloroethylene	100	S
Trichlorobenzene	Unknown	S
Trichloroethane	100	S
Trichloroethylene	100	S
Turpentine oil	100	S
Urine	Unknown	l
Vinyl acetate	100	S
Water	100	l to n
White spirit	100	S
Wine	Unknown	l

S: satisfactory; l: limited; n: not satisfactory

by consultation with the producer of the selected grades and by tests under operating conditions.

Permeability

Permeability for a given gas depends on the VOH content, the relative humidity, the temperature and the crystallinity, as we can see in Figure 4.29 (a)–(c).

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide an idea and cannot be used for designing any parts or goods.

EVOH has a low permeability to oxygen, evaluated at 0.35 up to 1.8 versus a full range of 0.35 up to 11 000 for all tested plastics.

Table 4.20 displays some examples of permeability at room temperature and for a dry atmosphere.

Specific ISO standards concerning EVOH

ISO 14663-1:1999 Plastics – Ethylene/vinyl alcohol (EVOH) copolymer moulding and extrusion materials – Part 1: Designation system and basis for specifications

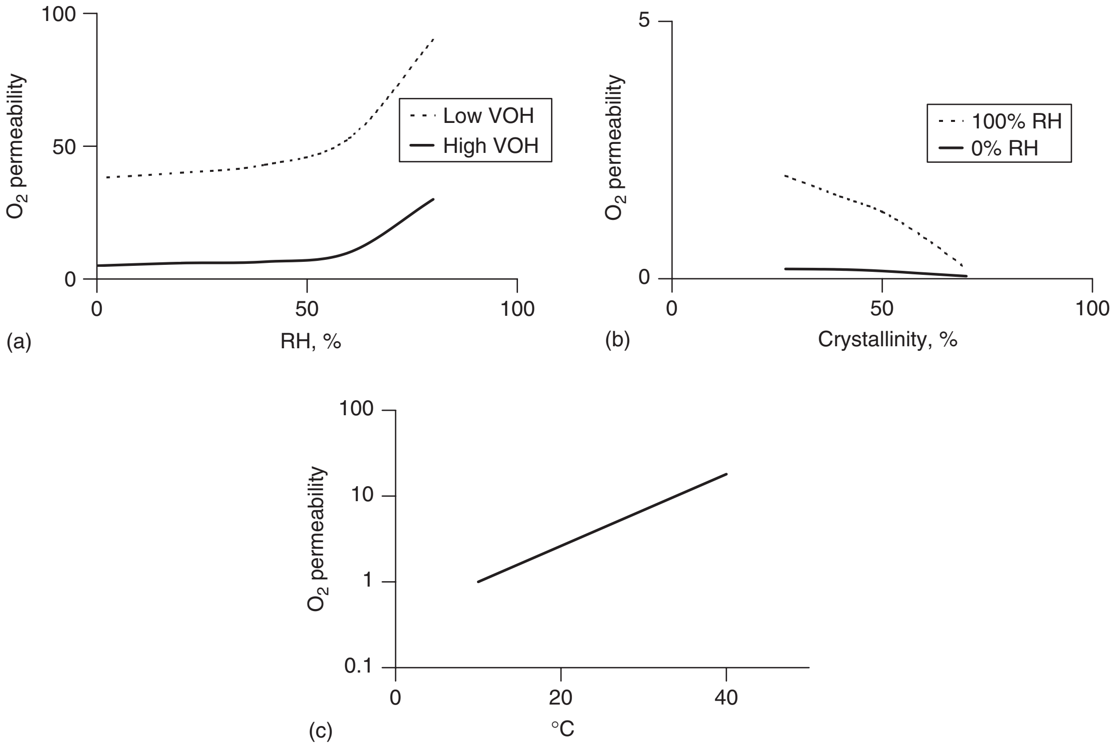


Figure 4.29. (a) EVOH: Examples of oxygen permeability versus hygrometry (%) for low and high VOH content; (b) EVOH: Examples of oxygen permeability versus crystallinity for 0 and 100% hygrometry; (c). EVOH: Example of oxygen permeabilities versus temperatures (°C)

Table 4.20 EVOH: examples of permeability @ 23°C, 0% RH

Chemicals	cm^3.μ/m^2.d.bar
Argon (Ar)	1
Butane (C_4H_{10})	2
Ethylene (C_2H_4)	2
Freon 12	3
Oxygen (O_2)	4
Nitrogen (N_2)	4
Chlorine (Cl_2)	0.4
Carbon monoxide (CO)	5
Sulfur dioxide (SO_2)	6
Methane (CH_4)	8
Carbon dioxide (CO_2)	12
Ammonia (NH_3)	90
Hydrogen (H_2)	450
Helium (He)	2520

ISO 14663-2:1999 Plastics – Ethylene/vinyl alcohol (EVOH) copolymer moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

Trade name examples

Clarene, Eval, Soarnol.

Property tables

Table 4.21 relates to examples only and cannot be generalized. Data cannot be used for design purposes.

Table 4.21 EVOHs: examples of properties

VOH	Very low	Low	Medium	High	Very high
Polyethylene	48	44	38	32	27
Miscellaneous properties					
Density (g/cm^3)	1.12	1.14	1.17	1.17–1.19	1.2
Mechanical properties					
Rockwell hardness, M	70	74	85	90–100	95
Shore hardness, D	90	91	94	>95	>95
Tensile strength (MPa)	26–40	35–57	27–70	34–80	50–98
Elongation at break (%)	14 to >200	17 to >200	15–300	15–150	13–100
Tensile modulus @ 23°C (GPa)	2.3–2.5	2.3–2.7	2.6–3	2.7–4	3–4.7
Flexural modulus @ 23°C (GPa)	2.5–4.8	3–4.8	3–4.8	4–4.8	4.8
Charpy impact strength ISO 179-1 kJ/m^2, 20°C	1	2	2	2	2
Thermal properties					
Glass transition temperature (°C)	49	54	53	57–69	60
Melting temperature (°C)	159	167	172	183	190
Thermal conductivity (W/m.K)		0.30	0.30	0.31	0.33
Specific heat (cal/g/°C)		0.41	0.40	0.37	0.35
Permeability					
Oxygen transmission rate, 20°C, 65% RH (cc.20μ.m^2.day.atm)	3.2	1.5	0.7	0.4–0.6	0.2
Water vapour transmission rate, 40°C, 90% RH (cc.30μ.m^2.day.atm)	20	28	32	34–52	63

4.4.3 Ethylene-methacrylate ionomers (EMA)

EMA ionomers (see Figure 4.30) are speciality thermoplastics copolymerized from ethylene and a small fraction of methacrylic acid, which is then transformed into the salt of sodium, zinc, lithium or another metal randomly distributed along the backbone. The backbone is identical to that of the polyolefins but the pendant groups are different, with a polar and ionic character.

Ionic groups tend to cluster together, building a physical crosslinking that is thermally reversible.

Properties depend on the amount of methacrylic acid, the type and level of metallic ions, the crystallinity, the molecular weight and the polarity.

Advantages

EMA ionomers present a good set of properties: flexibility; tenacity; high tear strength; resistance to greases and many solvents; transparency; gloss; abrasion resistance; good stress cracking and low temperature behaviours; low density; easy coloration; low sealing temperatures; gas permeability similar to LDPE. For specific grades it is possible to develop: soft touch feel; food contact; direct adhesion to epoxy and polyurethane finishes, metal, glass and natural fibres by heat lamination.

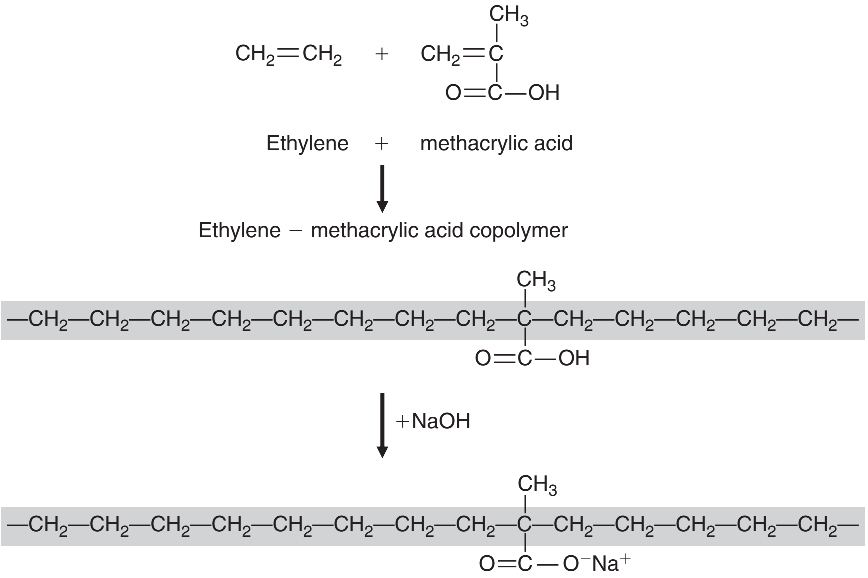


Figure 4.30. Ethylene, methacrylic acid and ethylene-methacrylic acid copolymer formulae

Drawbacks

Applications are curbed by low rigidity, weak HDTs and melting points, a propensity for electrostatic and dust build-up, poor creep resistance, limited resistance to acids, a certain lack of sources, and the cost.

Grades, processing and applications

Applications are far fewer than for polyethylene and polypropylene. Consequently, relatively few grades are marketed, corresponding to the major applications such as, for example:

- films: conventional extrusion/co-extrusion, blown film, cast film and extrusion coating, packaging films and sealants, puncture-resistant films for pouches and blister packs, glass coatings . . .
- packaging: food and non-food, perfume bottle caps, shampoo bottles, various bottles and containers, glass product coatings . . .
- automotive paintless applications:
- ○ moulded-in-colour film laminate technology for bumper fascias
- ○ all-plastic deck lid for 2005 Ford Mustang convertible
- ○ tailgate cap for the 2004 Hummer
- ○ decorative automotive trims . . .
- footwear components: thermoformed shoe inserts, football boot soles, protective pads for shoes and boots . . .
- sporting goods, scratch-resistant golf balls, skittle and bowling pin covers, ski boots . . .
- miscellaneous parts: clothes hangers, watchstraps, tool handles, screwdriver handles, film sandwich for bulletproof glazing, toys (magnifying glass) . . .

Thermal behaviour

The melting points are low, ranging from 72°C up to 96°C, with HDT (0.46 MPa) as low as 40°C to 48°C, which limits the applications when the temperature rises, even in the absence of mechanical loading.

The brittle temperatures are low, for example from −50°C down to −110°C.

Optical properties

Specific grades are transparent and glossy with a haze of, for example, 1.3 up to 27 and a refractive index of the order of 1.51.

These results relate to some grades only and cannot be generalized.

Mechanical properties

Flexibility can meet the range for elastomers with hardness of 80 Shore A. Considering this feature, the mechanical properties are fair:

- impact strengths are in an excellent range even at low temperatures
- elongations at break are high
- puncture resistance of films is good
- abrasion and scuff resistance are in a good range.

The stress at yield and at break are low and EMA ionomers are thermoplastic. Consequently, loading must be limited and creep moduli used for designing must be very low.

Weathering

EMA ionomers must be protected for long exposures to light and UV such as in exterior automotive parts.

Chemicals

Chemical behaviour depends on the precise grade used, which must be carefully tested before the decision is taken to use it.

Table 4.22 displays some general assessments of behaviour after prolonged immersions in a range of chemicals at room temperature for given grades, which are not representative of all the EMA ionomers because of the variation of the chemical resistance when the comonomer and metal contents vary. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Trade name examples

Clarix, Formion, Surlyn

Property tables

Table 4.23 relates to examples only and cannot be generalized.

Table 4.22 EMA ionomers: examples of chemical behaviour

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S	Ethylene bromide	100	n
Acetic acid	>96	n	Fluorine	100	n
Acetic aldehyde	100	l	Fluosilicic acid	Unknown	S
Acetic anhydride	100	S	Formic acid	40–85	S
Aluminium chloride	Solution	S	Freon 113	100	S
Aluminium sulfate	Unknown	S	Furfural	100	n
Ammonium hydroxide	30	S	Glycerol	100	S
Ammonium sulfate	50	S	Hexane	100	l
Amyl acetate	100	n	Hydrobromic acid	48	S
Amyl alcohol	100	l	Hydrochloric acid	10–37	S to l
Aniline	100	l	Hydrogen sulfide gas	Unknown	S
Antimony chloride	10	S	Iron(III) chloride	Unknown	S
Aqua regia	Unknown	n	Isooctane (Fuel A)	100	S
Arsenic acid	Unknown	S	Isopropanol	100	l
ASTM1 oil	100	S	Lactic acid	90	S
ASTM2 oil	100	S	Lead acetate	10	S
ASTM3 oil	100	S	Linseed oil	100	l
Barium chloride	Saturated	S	Liquid paraffin	100	l
Benzaldehyde	100	l	Magnesium chloride	Unknown	S
Benzene	100	l	Mercury chloride	Unknown	S
Boric acid	Unknown	S	Methanol	100	l
Bromine (liquid)	100	n	Methylbromide	100	n
Butanol	100	l	Methylene chloride	100	n
Butyl acetate	100	l	Methylethylketone	100	l
Butyric acid	Unknown	n	Mineral oil	100	S
Calcium chloride	Unknown	S	Molasses	Unknown	S
Carbon sulfide	100	n	Nickel chloride	Unknown	S
Carbon tetrachloride	100	n	Nitric acid	>65	n
Castor oil	100	S	Nitric acid	10	S
Cellosolve	100	l	Nitrobenzene	100	n
Cellosolve acetate	100	l	Oleic acid	Unknown	n
Chlorine (dry gas)	100	n	Oxalic acid	Unknown	S
Chlorine water	Unknown	S	Ozone	Unknown	S
Chlorobenzene	100	n	Perchloroethylene	100	l
Chloroform	100	n	Petroleum	100	l
Chlorosulfonic acid	Unknown	n	Phenol	Unknown	n
Chromic acid	Unknown	S	Picric acid	Solution	n
Citric acid	10	S	Potassium cyanide	Unknown	S
Copper sulfate	Unknown	S	Potassium fluoride	Unknown	S
Cresol	100	n	Potassium hydroxide	45	S
Cyclohexane	100	S	Potassium permanganate	20	S
Cyclohexanol	100	S	Potassium sulfate	Unknown	S
Cyclohexanone	100	l	Propanol	100	l
Dichloroethylene	100	n	Pyridine	Unknown	S
Diethylamine	100	n	Sea water	100	S
Diethyleneglycol	100	S	Silver nitrate	Unknown	S
Diethylether	100	S	Sodium borate	Unknown	S
Dimethylamine	100	n	Sodium carbonate	10	S
Dioctylphthalate	100	l	Sodium chloride	25	S
Ethanol	Unknown	l	Sodium cyanide	Unknown	S
Ethylacetate	100	l	Sodium hydroxide	10–55	S
Ethylchloride	100	n	Sodium hypochlorite	20	S
Ethylene glycol	100	l	Sodium nitrate	Solution	S
Ethylene glycol	Unknown	l	Styrene	100	n

Table 4.22 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Sulfuric acid	10	S	Trichloroethylene	100	n
Sulfuric acid	70–98	n	Tricresylphosphate	Unknown	l
Sulfuric acid	Fuming	n	Turpentine oil	100	l
Sulfurous anhydride (gas)	Unknown	S	Vinyl acetate	100	l
Tetrahydrofuran	100	n	Water	100	S
Thionyl chloride	100	n	White spirit	100	l
Tin chloride	Unknown	S	Wine	Unknown	l
Titanium tetrachloride	Unknown	n	Xylene	100	l
Toluene	100	S	Zinc chloride	Unknown	S
Transformer oil	100	l			

S: satisfactory; l: limited; n: non-satisfactory

Table 4.23 EMA ionomers: examples of properties

Metal	Lithium	Sodium	Zinc
Miscellaneous properties			
Density (g/cm^3)	0.94	0.94–0.96	0.94–0.97
Mechanical properties			
Shore hardness, D	68	25–75	54–72
Shore hardness, A	>95	80 to >95	>95
Stress at yield (MPa)	15–20	3–23	8–16
Tensile strength (MPa)	26	21–39	21–33
Elongation at break (%)	280–290	300–770	200–500
Flexural modulus @ 20°C (GPa)	0.420–0.460	0.019–0.545	0.100–0.440
Flexural modulus @ −20°C (GPa)		0.547–0.717	0.531–0.800
Notched impact strength ASTM D256 (J/m)	NB	610 to NB	365 to NB
Thermal properties			
HDT B (0.46 MPa) (°C)	46	40–45	40–48
Vicat softening point B (°C)	62	48–78	57–79
Brittle point (°C)		−75 to −112	−50 to −112
Melting temperature (°C)	88	72–95	81–96
Thermal conductivity (W/m.K)	0.28–0.32	0.28–0.32	0.28–0.32
Specific heat (cal/g/°C)	0.33–0.64	0.33–0.64	0.33–0.64
Coefficient of thermal expansion (10^{-5}/°C)	10–17	10–17	10–17
Electrical properties			
Volume resistivity (ohm.cm)		10^{16}	10^{16}–10^{18}
Dielectric constant		2.3–2.5	2.2–2.5
Loss factor (10^{-4})		20–110	10–100
Dielectric strength (kV/mm)		31–35	34–43

	3% glass fibre, UV stabilized	10% glass fibre, UV stabilized
Miscellaneous properties		
Density (g/cm^3)	0.96	1.01
Mechanical properties		
Shore hardness, D	60	60
Tensile strength (MPa)	19	22
Elongation at break (%)	375	215
Flexural modulus @ 20°C (GPa)	0.705	0.95
Notched impact strength ISO 180 (kJ/m^2)	40	NB
Thermal properties		
HDT B (0.46 MPa) (°C)	52	64

NB: No break

4.4.4 Ethylene-acid and ethylene-ester copolymers (EBA, EGMA, EMAH, EEA, EAA . . .)

There are various speciality polyethylene copolymers developed from ethylene and acrylic acid, methylacrylate, butylacrylate, ethylacrylate, maleic anhydride, glycidyl methacrylate, acrylic esters, acrylic ester-maleic anhydride . . .

The main applications are not in engineering parts but as:

- adhesive films for co-extrusion or lamination with metals or other thermoplastics such as polyamide, polyethylene, polypropylene, polystyrene, PVDC . . .
- hot melts
- polymer modifiers, impact modifiers, compatibilizing and coupling agents for alloys such as PE/PET, PE/PA . . .
- materials for wires and cables, for example halogen-free FR cables . . .

Some grades are crosslinkable, which increases their resistance to temperature.

All these polymers are very flexible with low melting points, low Vicat softening temperatures, and very low moduli.

Trade name examples

Ebac, Emac, Escor, Lotader, Lotryl.

Table 4.24 displays some examples, which cannot be generalized. Data cannot be used for design purposes.

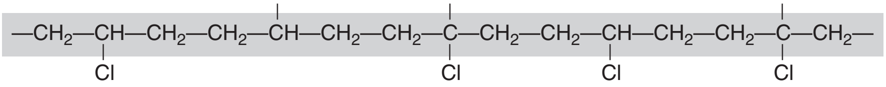
Table 4.24 Ethylene-butylacrylate copolymers and ethylene terpolymers: examples of properties

Copolymer type	Butylacrylate	Acrylic ester and maleic anhydride
Copolymer level	6–37	5–34
Miscellaneous properties		
Density (g/cm^3)	0.94	0.92–0.94
Mechanical properties		
Shore hardness, D	<10–42	14–45
Shore hardness, A	52 to >90	74–95
Tensile strength (MPa)	1–17	6–19
Elongation at break (%)	200–850	
Flexural modulus @ 20°C (GPa)	0.009–0.085	<0.030–0.130
Thermal properties		
Vicat softening point (°C)	48–78	32–93
Melting temperature (°C)	72–95	67–112

4.5 Chlorinated polyethylene (CPE, CM)

CPE is the standardized acronym for thermoplastic chlorinated polyethylene. CM is the standardized acronym for elastomeric chlorinated polyethylene.

Chlorinated polyethylene is produced by chlorination of polyethylene and has the structure shown in Figure 4.31.



$$-CH_2-\underset{Cl}{CH}-CH_2-CH_2-\overset{Cl}{CH}-CH_2-CH_2-\overset{Cl}{\underset{Cl}{C}}-CH_2-CH_2-\underset{Cl}{CH}-CH_2-CH_2-\overset{Cl}{\underset{Cl}{C}}-CH_2-$$

Figure 4.31. Example of chlorinated polyethylene formula

Chlorine content could be as high as 70% by weight but the current grades have a chlorine content in the 25% up to 42% range.

These resins can be used as:

- base thermoplastics for extruded, calendered, solution cast and injection-moulded parts and goods
- elastomers after crosslinking
- modifying resins and additives for other polymers such as PVC, styrene-acrylonitrile, ethylene polymers and copolymers, acrylics . . .

Properties vary with chlorine content, crystallinity and molecular weight.

Applications as primary thermoplastics to produce flexible parts and products are, for example:

- wire and cable jacketing . . .
- extruded profiles: gasketing, tubing . . .
- moulded shapes: pipe fittings . . .
- coated fabrics: extrusion of coated scrim for tarpaulins . . .
- hose for chemical transfer and storage . . .

CM are speciality elastomers that can be crosslinked either by curing agents or irradiation leading to parts with fair flexibility, resistance to heat, oils and fuels, ignition, chemicals, low temperatures and weathering.

Because of their resistance to automotive fluids CM are used for hoses, tubing, air ducts and wire jacketing, tubes and covers for return side power steering hoses, single construction emission and vacuum tubing, hose covers, large diameters and convoluted geometries required for air intake ducts . . .

CPE has been used successfully in under-the-hood wire and cable-coating applications such as flex cord jackets, heater cords, jackets for industrial cables and radiation crosslinkable speciality cables.

As impact modifiers and/or processing aids (permanent plasticizer), they improve economics by increasing filler loading without embrittlement to produce:

- pipes, vinyl siding, window profiles . . .
- semi-flexible and flexible compounds.

Chlorinated polyethylenes present a good set of properties for a highly flexible material: fair to moderate tensile strength, high elongation at break, fair retention of the elongation at break at low temperature. Reinforcement is often needed for high-temperature use.

Due to the chlorine content, oxygen indices are higher than those of the polyethylenes, for example 23 to 25 without fire-retardant additives, but they will act as a combustible material in the event of fire. Combustion products include hydrochloric acid and carbon monoxide, both toxic gases.

Suitable compounds exhibit good property retention after six years of exposure in Arizona, for example:

- 120% for 100% modulus
- 110% for tensile strength
- 90% for elongation at break, which is the most sensitive property to UV and weathering.

Chemical resistance is one of the most attractive properties. It varies with the chlorine content, crystallinity and molecular weight of the CPE resin, with the formulation used for the compound, and with crosslinking, which prevents dissolution.

In general, the resistance to inorganic concentrated salt solutions, strong acids and most bases is good with little or no effect. However, strongly oxidizing or solvating chemicals such as concentrated solutions of nitric acid, chromic acid, chloric and chlorous acids, ammonia and organic amines can chemically attack CPE resins.

The resistance to most paraffinic hydrocarbons is good but aromatic hydrocarbons lead to swelling and can shorten service life.

Chlorinated hydrocarbon solvents and polar solvents such as ketones and ethers may dissolve the CPE resins.

Table 4.25 displays general assessments of behaviour after prolonged immersion in a range of chemicals at room temperature for given grades, which are not representative of all the chlorinated polyethylenes because of the variation of the chemical resistance when the chlorine content varies and the broad possibilities for formulating the compounds: stabilizers, modifying agents, fillers and so on. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.25 Chlorinated polyethylene: examples of chemical behaviour

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S to l	Carbon tetrachloride	100	l to n
Acetic acid	>96	S to l	Castor oil	100	S
Acetic aldehyde	100	l	Cellosolve	100	S
Acetic anhydride	100	l	Cellosolve acetate	100	S
Acetone	100	l to n	Chlorine (dry gas)	100	l
Acetonitrile	100	n	Chlorine water	Unknown	l
Acetophenone	100	S	Chloroacetic acid	Unknown	S
Acetyl chloride	100	n	Chlorobenzene	100	l
Aluminium chloride	Solution	S	Chloroform	100	l
Aluminium sulfate	Unknown	S	Chlorosulfonic acid	Unknown	n
Ammonia	Unknown	n	Chromic acid	Unknown	n
Ammonium hydroxide	30	S to l	Citric acid	10	S
Ammonium sulfate	50	S	Copper sulfate	Unknown	S
Amyl acetate	100	S	Cresol	100	l
Amyl alcohol	100	S	Cyclohexane	100	S to n
Aniline	100	n	Cyclohexanol	100	S
Antimony chloride	10	l	Cyclohexanone	100	S
Aqua regia	Unknown	n	Dichloroethylene	100	n
Arsenic acid	Unknown	S	Diethylamine	100	S
ASTM1 Fuel A	100	S	Diethyleneglycol	100	S
ASTM2 fuel b	100	l	Diethylether	100	S
ASTM3 fuel c	100	l	Dimethylamine	100	S
ASTM1 oil	100	S	Dimethylformamide	100	n
ASTM2 oil	100	S	Dioctylphthalate	100	l
ASTM3 oil	100	S	Dioxan	100	l
Barium chloride	Saturated	S	Ethanol	Unknown	S
Benzaldehyde	100	l	Ethylacetate	100	l to n
Benzene	100	l to n	Ethylchloride	100	S
Benzyl chloride	100	l	Ethylene glycol	100	S
Boric acid	Unknown	S	Ethylenebromide	100	l
Bromine (liquid)	100	n	Fluorine	100	n
Butanol	100	S	Fluosilicic acid	Unknown	S
Butyl acetate	100	l	Formic acid	40–85	S
Butylamine	Unknown	l	Freon 22	100	l
Butylchloride	100	S	Furfural	100	l
Butyric acid	Unknown	S	Glycerol	100	S
Calcium chloride	Unknown	S	Hexane	100	S to l
Carbon sulfide	100	n	Hydrobromic acid	48	S

Table 4.25 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Hydrochloric acid	10–37	S	Potassium permanganate	20	S
Hydrofluoric acid	40	S	Potassium sulfate	Unknown	S
Hydrogen peroxide	90	l	Propylene oxide	100	S
Hydrogen peroxide	30	S	Pyridine	Unknown	l
Hydrogen sulfide gas	Unknown	S	Sea water	100	S
Iron(III) chloride	Unknown	S	Silver nitrate	Unknown	S
Isooctane (Fuel A)	100	S	Sodium borate	Unknown	S
Kerosene	100	l	Sodium carbonate	10	S
Lactic acid	90	S	Sodium chloride	25	S
Lead acetate	10	S	Sodium cyanide	Unknown	S
Linseed oil	100	S	Sodium hydroxide	10–55	S
Liquid paraffin	100	S	Sodium hypochlorite	20	l
Magnesium chloride	Unknown	S	Sodium nitrate	Solution	S
Magnesium sulfate	Unknown	S	Sulfuric acid	10–70	S
Mercury chloride	Unknown	S	Sulfuric acid	96	l
Methanol	100	S	Sulfuric acid	Fuming	n
Methylbromide	100	S	Sulfurous anhydride (gas)	Unknown	l
Methylene chloride	100	n	Tetrachloroethane	100	S to l
Methylethylketone	100	l	Tetrahydrofuran	100	l
Mineral oil	100	S	Thionyl chloride	100	n
Molasses	Unknown	S	Tin chloride	Unknown	S
Monoethanolamine	Unknown	S	Titanium tetrachloride	Unknown	l
Nickel chloride	Unknown	S	Toluene	100	l to n
Nitric acid	10	l	Transformer oil	100	l
Nitric acid	65	l to n	Trichloroethylene	100	l to n
Nitrobenzene	100	l	Tricresylphosphate	Unknown	S
Oleic acid	Unknown	S	Triethanolamine	Unknown	S
Olive oil	100	S	Triethylamine	Unknown	S
Oxalic acid	Unknown	S	Turpentine oil	100	S to l
Perchloroethylene	100	l	Vegetable oil	100	S
Petroleum	100	S	Vinyl chloride	Unknown	l
Phenol	Unknown	l	Vinyl acetate	100	l
Phosphoric acid	50	S	Water	100	S
Picric acid	Solution	l	White spirit	100	S
Potassium cyanide	Unknown	S	Wine	Unknown	S
Potassium fluoride	Unknown	S	Xylene	100	l to n
Potassium hydroxide	45	S	Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Specific ISO standards concerning chlorinated polyethylene copolymers

ISO 6402-1:2002 Plastics – Acrylonitrile-styrene-acrylate (ASA), acrylonitrile-(ethylene-propylene-diene)-styrene (AEPDS) and acrylonitrile-(chlorinated polyethylene)-styrene (ACS) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 6402-2:2003 Plastics – Acrylonitrile-styrene-acrylate (ASA), acrylonitrile-(ethylene-propylene-diene)-styrene (AEPDS) and acrylonitrile-(chlorinated polyethylene)-styrene (ACS) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

Trade name examples

PolyOne CPE, Tyrin.

Property tables

Table 4.26 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.26 Chlorinated polyethylenes: examples of properties

	CPE	CPE	CM	CM
		Jacketing	Black	White
Miscellaneous properties				
Density (g/cm^3)	1.16	1.31		
Shrinkage (%)	3			
Absorption of water (%)	0.01			
Mechanical properties				
Shore hardness, A	60–70	93	65–70	60–70
Shore hardness, D	<10–15	46	10–15	<10–15
Tensile strength (MPa)	6–12	12	15	9–13
Elongation at break (%)	700–800	400	300–400	300–600
Flexural modulus (GPa)	0.002	0.007		
Notched impact strength ASTM D256 (J/m)	NB			
Thermal properties				
HDT B (0.46 MPa) (°C)	35			
HDT A (1.8 MPa) (°C)	25			
Continuous use temperature (°C)	60–80		100–130	100–130
Brittle point (°C)		−35	−60 to −35	
Melting temperature (°C)	150–170			
Minimum service temperature (°C)	−70			
Electrical properties				
Volume resistivity (ohm.cm)	1–5×10^{13}			
Dielectric constant	5–6			
Loss factor (10^{-4})	100–1000			
Dielectric strength (kV/mm)	12			
Fire behaviour				
Oxygen index	22–25	31	25–35	
UL94 fire rating	HB			
Air ageing 168 h @ 125°C				
Shore hardness, A change			+7 to +11	+2 to +16
Tensile strength (% change)			+4 to +16	−34 to −3
Elongation at break (% change)			−35 to −16	−88 to −25
Air ageing 168 h @ 150°C				
Shore hardness, A change			+14 to +21	+11 to +22
Tensile strength (% change)			−47 to −9	−62 to −2
Elongation at break (% change)			−75	−99 to −93

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

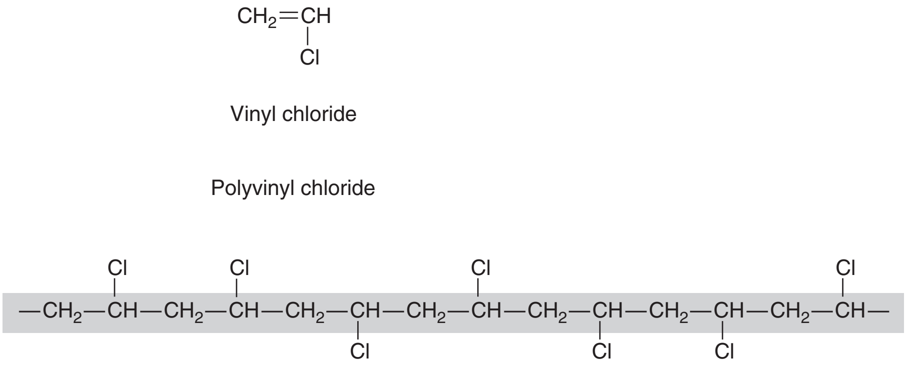
Light	Good behaviour enhanced by stabilizers
Weak acids	Good behaviour
Strong acids	
Low concentration	Good behaviour except oxidizing acids
High concentration	Little effect except oxidizing acids
Oxidizing or solvating chemicals	Strongly oxidizing or solvating chemicals such as concentrated solutions of nitric acid, chromic acid, hydrochloric and hydrochlorous acids, ammonia, organic amines can chemically attack CPE resins
Strong bases	Good behaviour, little or no effect
Solvents	The resistance to most paraffinic hydrocarbons is good but aromatic hydrocarbons lead to swelling and can shorten service life Chlorinated hydrocarbon solvents and polar solvents such as ketones and ethers may dissolve the CPE resins
Food contact	Possible for special grades

4.6 Polyvinyl chloride (PVC)

Several acronyms are used for different PVCs:

- S-PVC for suspension PVC
- E-PVC for emulsion PVC
- M-PVC for mass or bulk PVC
- PVC-U for unplasticized PVC
- PVC-P for plasticized PVC
- PVC-HI for high impact PVC
- PVC-C or CPVC for chlorinated PVC (see Section 4.7).

Pure PVC is the linear homopolymer of vinyl chloride, as we can see in Figure 4.32. The industrial polymers are amorphous with a backbone identical to those of polyethylene, polypropylene and polybutene but the pendant chlorine atoms result in a polar polymer. The theoretical chlorine content is roughly 57%.



Vinyl chloride

Polyvinyl chloride

Figure 4.32. Vinyl chloride, polyvinyl chloride formulae

PVC can be polymerized, possibly with a comonomer (mainly vinyl acetate):

- In an emulsion, the oldest process. The presence of emulsifiers at a greater or lesser level gives a variable haze to the finished articles, eases the processing, decreases the electrostatic build-up, and increases the absorption of water. E-PVC, dispersion PVC or PVC pastes are used to make plastisols and organosols.
- In suspension. This process gives transparent parts, good electrical properties and a weak absorption of water.
- In bulk. PVC is free from additives such as protective emulsifiers, dispersants or colloids, which makes it possible to obtain parts that are even more transparent and glossy than suspension PVC.
- In solution. Today this technique is obsolete.

The property sets of raw PVCs as-polymerized are generally unsuitable for the range of intended applications. It is essential to upgrade and customize the raw polymers by compounding to satisfy the requirements of customers and applications. Numerous additives, fillers, plasticizers, stabilizers etc. are used, allowing the manufacture of a variety of parts and goods from a very rigid to a very soft character.

Albeit starting from a single and simple chemical formula, PVC leads to a myriad of products with very different properties. In general, and where no other indication is given, the following features relate to rigid PVC.

In addition to this diversity, a few PVC products, cables or foams for example, are crosslinked.

PVCs can be classified versus:

- Their molecular weight or degree of polymerization, often expressed as K value or K-wert, inferred from viscosity measurements. Figure 4.33 (a & b) displays some examples of polymerization degrees and molecular weights versus K values. Slightly different data can be found quoted elsewhere because several methods to measure K values exist.
- Rigidity or plasticization: rigid or unplasticized PVC (PVC-U), semi-rigid PVC, flexible or soft PVC.
- The type of processing: in the melt state, in the liquid state (plastisols or organosols), foams. Plastisols have very special mechanical, thermal and chemical properties due to their high flexibility and the use of large amounts of plasticizers. The particular morphology of foams induces:
  - A decrease in the mechanical properties due to the low quantity of polymer and the high proportion of gas.
  - A weaker chemical resistance due to the highly divided state of the polymer. The thin cell walls immediately absorb liquids and gases.

Lastly PVC/PVAc are the most-used copolymers for some speciality application niches. They are appreciated for their lower melt viscosities, higher tolerance to additive fillers, and better cold-draw properties than homopolymers.

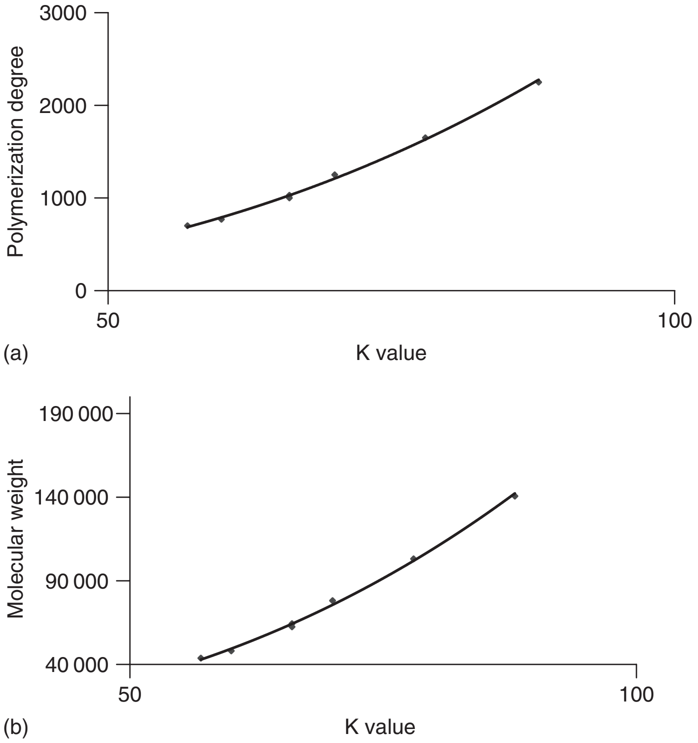


Figure 4.33. (a) PVC: examples of degrees of polymerization versus K values; (b) PVC: examples of molecular weights versus K values

4.6.1 General properties

Advantages

PVC is regarded as perhaps the most versatile thermoplastic resin, due to its ability to accept an extremely wide variety of additives: Plasticizers, stabilizers, fillers, processing aids, impact modifiers, lubricants, foaming agents, biocides, pigments, reinforcements . . .

General advantages depend on the type of compound.

Rigid PVC is appreciated for its rigidity at room temperature, low price, chemical resistance except to certain solvents, dimensional stability, easy welding and joining, resistance to weathering for well-optimized compounds, possibility of transparency, food contact, fireproofing.

Flexible PVC is appreciated for the versatility of its characteristics according to the formulation. Significant quantities of fillers and plasticizers are used to optimize some of the characteristics such as behaviour at low temperatures, fire resistance, flexibility and hardness in the elastomer range, low price, electric insulation, easy welding and joining, possibility of transparency, food contact, fireproofing.

Plastisols allowing the use of particular liquid-state processing techniques: casting, rotomoulding, dipping, coating . . .

Drawbacks

PVC by itself cannot be processed, it must be compounded with at least a stabilizer, a lubricant and, if flexible, a plasticizer.

PVCs are currently handicapped by the ecological problems associated with chlorine and also with some of the plasticizers for the flexible products.

Rigid PVC: inherent sensitivity to UV without protection (but adequate compounds exist); softening and creep when the temperature rises; attack by aromatic or chlorinated hydrocarbons as well as by esters and ketones; impact sensitivity, the more so as the temperature decreases; high density; fume toxicity and corrosivity in the event of fire; less easy to inject; tool corrosion.

Flexible PVC suffers from the same drawbacks as rigid PVC the more so as the amount of plasticizer increases, increasing creep, fire sensitivity (except for FR plasticizers), fume toxicity and corrosivity, and decreasing chemical resistance and thermal ageing resistance.

Special grades

These can be classified according to the type of processing, specific properties, targeted applications:

- extrusion, injection, compression, blown film, thermoforming, calendering, blow moulding, rotational moulding, foam, slush moulding, coating, powdering, co-extrusion, for thin or thick parts, for plastisols. . .
- stabilized against heat, UV, light and weathering; antistatic, conductive, reinforced, food contact, approved for medical applications, fireproofed, transparent, low warpage, high fluidity, low to high K-values, high plasticizer absorption, low fogging, very low fisheye level . . .
- for films, sheets, tubes, wire and cable coatings, fibres, mass-produced goods . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide a rough idea. They are generally of the order of €1/kg.

Processing

All the molten-state processing methods are usable: extrusion, injection, compression, blown film, blow moulding, rotational moulding, thermoforming, foam, coating, powdering, co-extrusion, fluidized bed, machining for high hardness grades, welding. Special grades can be crosslinked after shaping.

Processing methods in the liquid state are also used: casting, rotomoulding, dipping, coating . . .

Applications

(See Chapter 2 for further information.)

Although varying according to the country, consumption is approximately divided into:

- 68% rigid PVC
- 31% flexible PVC
- 1% in other applications.

The main application sector by far is the building & construction sector, which consumes more than two-thirds of all PVC. Then there are multiple applications in packaging, electrical & electronics (EE), home and leisure, medical, automotive, industry . . .

- Building & construction
  - pipes & fittings consume 47% of the PVC total for potable water, sewer, irrigation, drain, rainwater, soil and waste systems, venting, ducting, fire sprinkler piping, chemical and food processing . . . Physical forms are very diverse, from monolayer tubes to corrugated or multilayer pipes, spiral wound, small or large diameter . . .
  - siding consumes 15% of all PVC with gutters, downspouts, boardings . . .
  - windows and doors consume 4% of the PVC total with shutters, architectural glazing systems, conservatory devices . . .
  - fencing, barriers, decking . . .
  - docking, landfill liners, membranes, swimming pool liners . . .
  - internal and external cladding, roofing and ceiling systems . . .
  - flooring and wall covering . . .
- Packaging
  - films and sheets for packaging and thermoforming consume 7% of the total for PVC
  - clear and opaque bottles consume 1% of all PVC
  - food and non-food packaging, various containers for chemicals, clear blisters . . .
  - jar lid gasketing . . .
- Electricity, electronics & appliances
  - wire and cable insulation consumes 4% of the PVC total with construction and automobile wires, electrical cord jacketing, fibre optic sheathing, heat-shrinkable sleeves . . .
  - components in phone systems, power tools, refrigerators, washing machines, air conditioners, computers, keyboards, housings . . .
  - floppy disk jackets . . .
- Home & leisure sector applications consume 7% of the total for PVC
  - garden hoses
  - toys, dolls, fishing lures, fancy goods . . .
  - inflatable covers, structures and devices . . .
  - shoe soles
  - coated fabrics for clothing, leather working, opaque curtains, tarpaulins . . .
  - films and sheets for adhesive tapes, translucent curtains, school and office stationery . . .

  - upholstery, covering, padding . . .
  - patio furniture
  - coated metal racks and shelving . . .
  - credit cards
  - strapping, fibres . . .
- Medical applications consume 4% of all PVC
  - fluid bags and containers for blood, plasmas, intravenous solutions, urine continence . . .
  - blood vessels for artificial kidneys, heart and lung bypass sets . . .
  - tubing, catheters, cannulas, endotracheal tubing, feeding and pressure monitoring tubing . . .
  - artificial skin in emergency burns treatment
  - drip chamber components
  - inflatable splints, prosthetics . . .
  - surgical and examination gloves, inhalation masks, overshoes, protective sheeting and tailored covers, mattress and bedding covers, anti-bump protection bars . . .
  - blisters and dosage packs for pharmaceuticals and medicines, single dose medication packaging, shatter-proof bottles and jars . . .
- The automotive and transportation sector consumes 2% of the PVC total
  - instrument panels and associated mouldings, dashboards, interior door panels and pockets, sun visors, security covers, headlining, floor coverings, floor mats, arm rests, seat coverings . . .
  - exterior side mouldings, protective strips, window trims, body side mouldings . . .
  - underbody anti-abrasion coating, mud flaps, anti-stone damage protection . . .
  - body seam sealing, seals, foamed gaskets . . .

A new and fast-developing application is ‘synthetic wood’ (i.e. WPC) made from rigid PVC heavily filled with wood flour, extruded in wood-like profiles that can be sawn, nailed and screwed just like natural wood.

4.6.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated up to 90°C for a rigid PVC and 80°C or less for a flexible PVC.

Service temperatures are definitely lower under mechanical stress because of modulus decay, strain, creep, relaxation . . . They can be of the order of 50°C up to 80°C according to the HDT and applied stresses.

For example:

- for a flexible PVC, the stress at 60°C is half that at 20°C
- for a given rigid PVC, the tensile strength falls by 50% between 20°C and 60°C and the HDT A (1.8 MPa) is 65°C.

For a given grade of PVC (30% plasticizer), the retention of short-term tensile strength and elongation at break versus temperature is shown in Figure 4.34. The short-term retention of tensile strength falls to roughly 30% at 80°C and, at the same time, the elongation at break retention roughly doubles.

For long-term heat ageing, PVC follows two degradation pathways:

- an oxidative reaction like numerous other polymers, which can be compensated for with antioxidants
- dehydrochlorination, releasing HCl, which needs compounding with very effective protective stabilizers in order to prevent this.

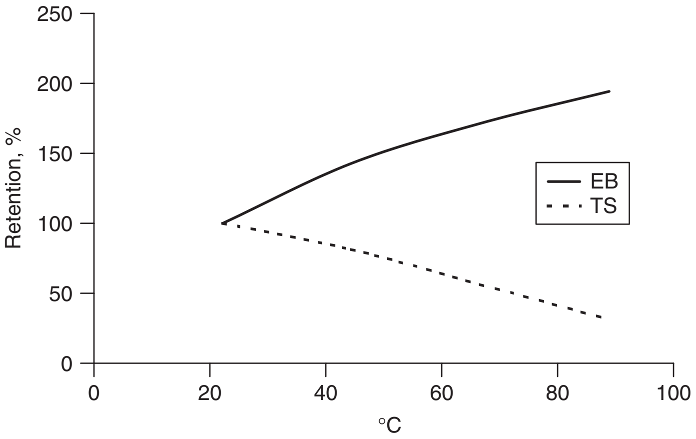


Figure 4.34. PVC examples of retentions of tensile strengths (TS,%) and elongations @ break (EB,%) versus temperature (°C)

The UL temperature indices of specific grades can be:

- 50–90°C for the electrical properties alone
- 50–85°C for electrical and mechanical properties, excluding impact strength
- 50–70°C for electrical and mechanical properties, including impact strength

Rigid PVCs are brittle materials with a minimum service temperature of the order of 0°C to −10°C.

Plasticized PVCs are more resistant and, according to the type and amount of plasticizers, can have a minimum service temperature of the order of −5°C down to −50°C.

The glass transition temperature (T_g) range for rigid PVC by DSC measurements is roughly 60–100°C. After plasticization, the T_g range can be from −5°C down to −50°C.

These results relate to some grades only and cannot be generalized.

4.6.3 Optical properties

PVC can be transparent to opaque according to the grade. The light transmission for the 500–800 nm region can be as high as 85–90% with a haze of 2.5% and a refractive index of about 1.53–1.54.

These results relate to some grades only and cannot be generalized.

4.6.4 Mechanical properties

Rigid PVC is a stiff and brittle material with rather high modulus and tensile strength but low elongation at break and weak impact strength.

After plasticization, the behaviour can be totally different, with very low moduli and tensile strength, high elongation at break and better impact resistance.

The coefficients of friction are rather high, 0.4–0.45 for example, or higher for some plasticized grades.

Dimensional stability

Rigid PVC is an amorphous polymer with low shrinkage, a fair coefficient of thermal expansion for a polymer, limited creep at room temperature, and low water absorption by moisture exposure.

This good dimensional stability can be altered by plasticization to a greater or lesser degree.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For a given sample, it was evaluated at 0.35 for a rigid PVC and significantly higher for a flexible grade. This is an example only that cannot be generalized.

Creep

Rigid PVCs have average moduli, which limits strains and leads to average creep moduli at room temperature. After plasticization, the very low moduli involve high strains for moderate stresses and low creep moduli even at room temperature.

When the temperature rises, creep increases and creep moduli fall.

Figure 4.35(a) displays examples of creep under relatively high stresses (10 to 30 MPa) for rigid PVC at room temperature. We can note that the creep moduli are much higher than those of polyethylene or polypropylene (less than 1 GPa).

Figure 4.35(b) displays examples of creep under relatively high stresses (7 to 14 MPa) at room temperature for impact-modified rigid PVC or PVC-HI. Times are much longer than for the previous graph (20 000 h versus 400). Compared to Figure 4.35(a), the plasticization decreases the creep moduli. However, they are always higher than those of polyethylene or polypropylene (less than 1 GPa) for a same creep time.

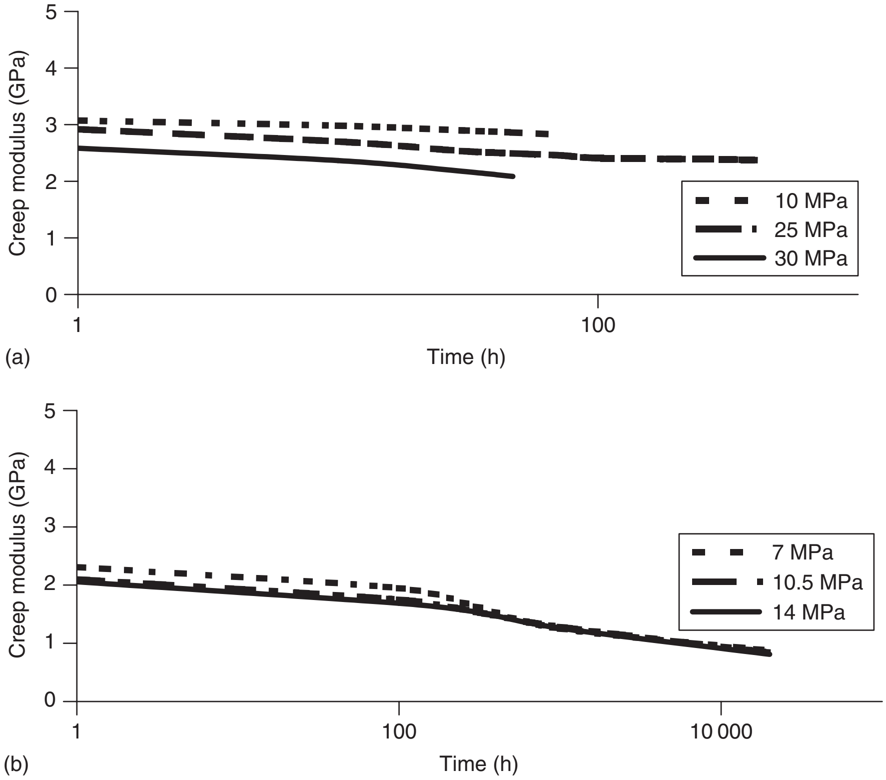


Figure 4.35. (a) Rigid PVC examples of creep modulus (GPa) versus time (h) for various stresses (MPa); (b) PVC-HI examples of creep modulus (GPa) versus time (h) for various stresses (MPa)

Relaxation

Figures 4.36 (a) and (b) display the same relaxation data expressed as stress retention, the first with an algebraic time scale showing the fast drop of stress at the start of test and the second with a logarithmic time scale showing a regular decrease of stress.

These results relate to one grade only and cannot be generalized.

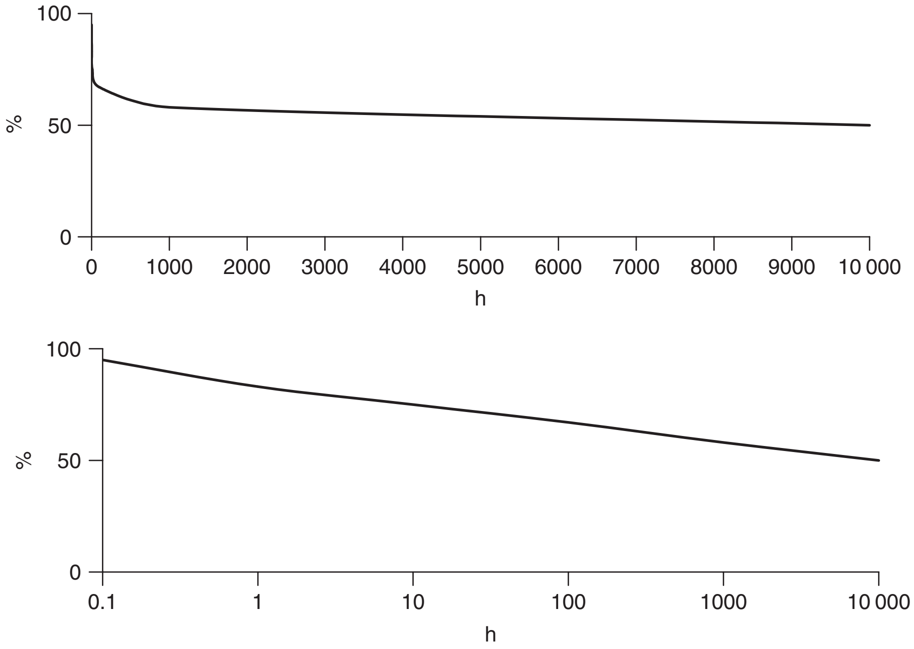


Figure 4.36. (a) Stress relaxation of PVC, examples of stress retention (%) versus time (h) under 0.5% strain at 20°C; (b) Stress relaxation of PVC, examples of stress retention (%) versus time (h) under 0.5% strain at 20°C

4.6.5 Ageing

Dynamic fatigue

The dynamic fatigue can be fair for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the low elongation at break of the rigid PVCs.

For a given grade of PVC, Figure 4.37 displays an example of the SN or Wöhler's curve concerning flexural tests with maximum stress of $\pm\sigma$ and average stress of 0.

Weathering

PVC resists hydrolysis well but is naturally sensitive to light and UV. It must be protected by addition of anti-UV and other protective agents. In these cases, long warranty periods can be allowed, for example ten years and more. For a white, protected, rigid PVC, after natural weathering for 3 years in Michigan, the retention of impact strength is 68% and the yellowness index increases by 5.

These results are examples only and they cannot be generalized.

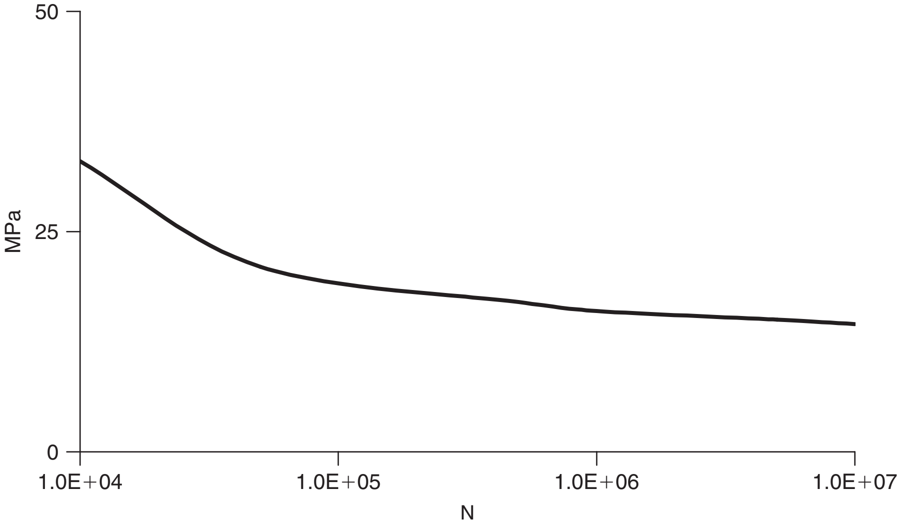


Figure 4.37. SN curve of rigid PVC, examples of maximum stress (MPa) versus number of cycles at rupture (N)

High-energy radiation

PVC behaves well when exposed to high-energy radiation (electron beam, gamma rays) in the absence of oxygen.

In the presence of air, it yellows and releases chlorine even for weak doses of irradiation. It is preferable to avoid sterilization by high-energy radiation.

However, it is possible to crosslink exceptional compounds by high-energy radiation under particular conditions. This method is used, for example, for cable coating and foams.

These results are examples only and they cannot be generalized.

Behaviour at high frequencies

PVCs have high loss factors, about 100×10^{-4}, and heat up under high-frequency current. They can be welded by this technique.

Chemicals

Rigid PVC absorbs little water and is not very sensitive to it.

Appropriate grades are approved for food contact or for medical applications.

Chemical inertia is generally fair up to 60°C.

PVC resists dilute acids, dilute alkalis and aliphatic hydrocarbons well.

PVC is attacked by aromatic hydrocarbons, chlorinated solvents, esters, ethers and ketones.

Resistance to oils, greases and alcohols is variable.

The chemical resistance of flexible PVC can be strongly reduced and the absorption of water can be appreciably higher.

Table 4.27 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the PVCs. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.27 PVC: examples of chemical behaviour at room temperature

Chemicals	Concentration (%)	Estimated behaviour	
		Rigid PVC	Plasticized PVC
Acetic acid	10–96	l	l
Acetic aldehyde	100	n	n
Acetic anhydride	100	n	n
Acetone	100	n	n
Acetonitrile	100	n	n
Acetophenone	100	n	n
Aluminium chloride	Solution	S	S
Aluminium sulfate	Unknown	S	S
Ammonium hydroxide	30	S	S
Ammonium sulfate	50	S	S
Amyl acetate	100	n	n
Amyl alcohol	100	S	S
Aniline	100	n	n
Aqua regia	Unknown	l	n
Arsenic acid	Unknown	S	S
ASTM1 oil	100	S	S
ASTM2 oil	100	S	S
ASTM3 oil	100	S	S
Barium chloride	Saturated	S	S
Benzaldehyde	100	n	n
Benzene	100	n	n
Benzyl alcohol	100	S	S
Boric acid	Unknown	S	S
Bromine (liquid)	100	n	n
Butanol	100	S	S
Butyl acetate	100	n	n
Butyric acid	Unknown	S	S
Calcium chloride	Unknown	S	S
Carbon sulfide	100	n	n
Carbon tetrachloride	100	l	l
Castor oil	100	S	S
Chlorine (dry gas)	100	l	l
Chlorine water	Unknown	l	l
Chloroacetic acid	Unknown	S	n
Chlorobenzene	100	n	n
Chloroform	100	n	n
Chlorosulfonic acid	Unknown	l	n
Chromic acid	Unknown	S	S
Citric acid	10	S	S
Copper sulfate	Unknown	S	S
Cyclohexane	100	S	S
Dichloroethylene	100	n	n
Diethylamine	100	l	n
Diethyleneglycol	100	S	S
Diethylether	100	n	n
Dimethylamine	100	l	l
Dimethylformamide	100	n	n
Dioctylphthalate	100	n	n
Ethanol	Unknown	S	S
Ethylacetate	100	n	n
Ethylchloride	100	n	n
Ethylene glycol	100	S	S
Fluosilicic acid	Unknown	S	S
Formic acid	40–85	S	S
Freon 11	100	l	l
Furfural	100	n	n
Glycerol	100	S	S
Hexane	100	S	S
Hydrazine	100	S to l	n
Hydrobromic acid	48	S	S
Hydrochloric acid	10–36	S	S
Hydrofluoric acid	40	l	l
Hydrogen peroxide	30	S	S
Hydrogen peroxide	90	S to l	n
Hydrogen sulfide gas	Unknown	S	S
Iron(III) chloride	Unknown	S	S
Isopropanol	100	S	S
Lactic acid	90	l	l
Lead acetate	10	S	S
Linseed oil	100	S	S
Liquid paraffin	100	S	S
Magnesium chloride	Unknown	S	S
Mercury chloride	Unknown	S	S
Methanol	100	S	l
Methylbromide	100	n	n
Methylene chloride	100	l	n
Methylethylketone	100	n	n
Mineral oil	100	S	S
Monoethanolamine	Unknown	n	n
Nickel chloride	Unknown	S	S
Nitric acid	10	S	S
Nitric acid	65	S	n
Nitric acid	>75	n	n
Nitrobenzene	100	n	n
Oleic acid	Unknown	S	S
Olive oil	100	S	S
Oxalic acid	Unknown	S	S
Ozone	Unknown	S	S
Perchloroethylene	100	n	n
Petroleum	100	S to l	l
Phenol	Unknown	l	n
Phosphoric acid	85	S	S
Picric acid	Solution	S	S
Potassium cyanide	Unknown	S	S
Potassium fluoride	Unknown	S	S
Potassium hydroxide	45	S	S
Potassium permanganate	20	S	S
Potassium sulfate	Unknown	S	S
Propanol	100	S	S
Pyridine	Unknown	n	n
Sea water	100	S	S
Silver nitrate	Unknown	S	S
Sodium borate	Unknown	S	S

Table 4.27 (Continued)

Chemicals	Concentration (%)	Estimated behaviour	
		Rigid PVC	Plasticized PVC
Sodium carbonate	10	S	S
Sodium chloride	25	S	S
Sodium cyanide	Unknown	S	S
Sodium hydroxide	10–55	S	S
Sodium hypochlorite	20	S	S
Sodium nitrate	Solution	S	S
Sulfamic acid	Solution	S	S
Sulfuric acid	10–70	S	S
Sulfuric acid	96	l to n	n
Sulfuric acid	Fuming	n	n
Sulfurous anhydride (gas)	Unknown	S	S
Thionyl chloride	100	n	n
Tin chloride	Unknown	S	S
Toluene	100	n	n
Transformer oil	100	S	S
Trichloroethane	100	n	n
Trichloroethylene	100	n	n
Tricresylphosphate	Unknown	n	n
Triethylamine	Unknown	S	l
Turpentine oil	100	S	S
Vegetable oil	100	S	S
Water	100	S	S
Xylene	100	n	n
Zinc chloride	Unknown	S	S

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide some idea and cannot be used for designing any parts or goods.

- Water vapour: rigid and flexible PVCs have permeabilities evaluated at 8 and 20, respectively, compared to a full range of 0.05 up to 400 for all tested plastics.
- Gases: rigid and flexible PVCs have permeabilities, evaluated at:
  - air: 28 and 550 versus a full range of 3 up to 2750 for all tested plastics
  - carbon dioxide: 200 and 8500 versus a full range of 30 up to 59 000 all tested plastics
  - nitrogen: 12 and 350 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 87 and 1500 versus a full range of <1 up to 11 000 for all tested plastics.

Fire resistance

Due to the chlorine content, the fire resistance is inherently better than for hydrocarbon polymers. Rigid PVC is self-extinguishing but releases chlorine during combustion. Oxygen indices are about 45 but can decrease with some plasticizers.

Flexible PVC generally burns more easily than rigid PVC, the more so the higher the level of flammable plasticizers. Oxygen indices as low as 20 are quoted. Using fire-retardant plasticizers the oxygen index can reach 40.

4.6.6 Electrical properties

PVCs are good insulators even in a wet environment, with fair dielectric resistivities and rigidities, and rather high loss factors. Resistivity decreases when the temperature rises. PVCs heat up under high-frequency current and microwaves.

Special grades and compounds are marketed for electrical applications such as the insulation of wires and cables.

The transverse resistivity of plasticized PVCs decreases as the plasticizer content increases.

4.6.7 Joining, decoration

Welding is easy by all the processes for rigid PVCs. Sometimes it can be more difficult for flexible PVCs and even impossible by frictional techniques for very soft compounds.

Gluing is easy for rigid PVCs including using solutions of PVC. Sometimes it can be more difficult for flexible PVCs.

All precautions must be taken concerning health and safety according to local laws and regulations.

4.6.8 Foams

Unlike industrial solid polymers, which are processed as carefully as possible to avoid the formation of bubbles, vacuoles etc., alveolar materials result from the desire to introduce, in a controlled way, a certain proportion of voids with the aim of:

- increasing flexibility: very soft seals.
- improving the thermal or phonic insulating character: foams for building, automotive. . .
- making damping parts: foams for packaging, automotive and transport safety parts.

The alveolar materials consist of a polymer skeleton surrounding the cells, which may be closed or partially or completely open to neighbouring cells or the outside.

The intrinsic properties come from those of the polyvinyl chloride with:

- a reduction in the mechanical properties due to the small quantity of material and the high proportion of gas
- a reduction in the chemical behaviour due to the highly divided nature of the material. The thin cell walls immediately absorb liquids and gases and are rapidly damaged.

Generally, the properties of the PVC foams are:

- densities from 30 kg/m^3 up to 700 kg/m^3 for rigid foams and 50 kg/m^3 up to 100 kg/m^3 for flexible foams
- rigid to flexible
- closed or open cells
- crosslinked or linear: often, crosslinking improves the mechanical properties and chemical resistance.

The absorption and the permeability to water or moisture are low for those foams with closed cells and their hydrolysis behaviour is generally fair.

The fire resistance is inherently good and can be improved by an appropriate formulation, but PVC contains a high chlorine level that is released in the event of combustion and can involve corrosion during processing. The thermal behaviour is limited.

PVC foams (see Table 4.28) have:

- insulating properties
- damping properties
- fair mechanical characteristics according to their density
- a low absorption and permeability to water or moisture for closed cell foams and excellent hydrolysis behaviour
- a naturally fair fire resistance that can be improved by an appropriate formulation
- ease of machining with tools used for wood. PVC foams can be glued, welded, stamped and thermoformed.

Table 4.28 Examples of the properties of PVC foams

	Crosslinked PVC foams					
Density (kg/m^3)	30		100		400	
	Property		Property		Property	
	Actual	Specific	Actual	Specific	Actual	Specific
Density (g/cm^3)	0.03		0.1		0.4	
Maximum service temperature (°C)	80		70–80			
Minimal service temperature (°C)	−200		−200		−200	
Compression strength (MPa)	0.220	7.3	1.700	17	11.240	28
Compression modulus (GPa)	0.012	0.4	0.125	1.25	0.500	1.2
Tensile strength (MPa)	0.510	17	3.100	31	12.400	31
Tensile modulus (GPa)	0.020	0.67	0.105	1.05	0.469	1.2
Thermal conductivity (W/m.K)	0.029		0.023		0.059	
Water absorption, 7 days, 40°C (%)	0.11				0.02	
Poisson's ratio			0.32			
Coefficient of thermal expansion (10^{-5}/°C)	4		3.5		2.2	
	Linear PVC foams					
Density (kg/m^3)	60		90		140	
Density (g/cm^3)	0.06		0.09		0.14	
Compression strength (MPa)	0.380	6.3	0.900	10	1.600	11.4
Compression modulus (GPa)	0.030	0.5	0.056	0.6	0.135	1
Tensile strength (MPa)	0.900	15	1.400	15.6	2.400	17
Tensile modulus (GPa)	0.030	0.5	0.050	0.56	0.090	0.6
Thermal conductivity (W/m.K)	0.034		0.037		0.039	

Table 4.28 shows some examples of PVC foam properties. These data cannot be used for designing. A specific property is the ratio of the actual property value divided by the density.

4.6.8.1 Examples of applications

Composites

- Sandwich panels for body structures of refrigerated lorries and similar vehicles; roofs of coaches; structural components; containers for maritime, road, railway and air transport; wagons to carry and store food onboard aircraft; shelters, bodies of military light machines.
- Nautical structural components: hulls, decks, superstructures and partitions of motorboats; vessels for fishing or racing.
- Structural and interior components for aeronautic, automotive and railway equipment: floors, radomes, bodies of buses and coaches (Neoplan), front-end components, drivers' cabs, partition walls, luggage racks in high-speed trains.

Building and civil engineering

Air-, water- and dust-proofing, heat insulation, soundproofing:

- Thermal insulation of roofs, walls, ceilings, floors.
- Thermal insulation of sandwich panels for industrial construction.

Nautical

- Life jackets, life suits.
- Safety padding.
- Buoys.
- Floats for cables and other devices . . .

Sports and leisure

- Gym mats, padding, damping and insulating mats.
- Protective devices for various sports such as hockey, basket, soccer, boxing . . .
- Padding of helmets and seats for babies and children . . .

Industry

- Machine soundproofing.
- Impact and vibration damping.

Miscellaneous

- Panels for showrooms, display units . . .
- Scenery . . .
- Shop fittings . . .
- Insulation of tanks, pipes . . .
- Packaging of fragile goods, warm or cold foods . . .
- Scale models, do-it-yourself . . .

4.6.9 Specific ISO standards concerning PVC

ISO 105-X10 Textiles – Tests for colour fastness – Part X10: Assessment of migration of textile colours into polyvinyl chloride coatings

ISO 264:1976 Unplasticized polyvinyl chloride (PVC) fittings with plain sockets for pipes under pressure – Laying lengths – Metric series

ISO 265-1:1988 Pipes and fittings of plastics materials – Fittings for domestic and industrial waste pipes – Basic dimensions: Metric series – Part 1: Unplasticized poly(vinyl chloride) (PVC-U)

ISO 580:1990 Injection-moulded unplasticized poly(vinyl chloride) (PVC-U) fittings – Oven test – Test method and basic specifications

ISO 727-1:2002 Fittings made from unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C) or acrylonitrile/butadiene/styrene (ABS) with plain sockets for pipes under pressure – Part 1: Metric series

ISO 727-2:2002 Fittings made from unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C) or acrylonitrile/butadiene/styrene (ABS) with plain sockets for pipes under pressure – Part 2: Inch-based series

ISO 1163-1:1995 Plastics – Unplasticized poly(vinyl chloride) (PVC-U) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 1163-2:1995 Plastics – Unplasticized poly(vinyl chloride) (PVC-U) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 1265:1979 Plastics – Polyvinyl chloride resins – Determination of number of impurities and foreign particles

ISO 2035:1974 Unplasticized polyvinyl chloride (PVC) moulded fittings for elastic sealing ring type joints for use under pressure – Pressure-resistance test

ISO 2044:1974 Unplasticized polyvinyl chloride (PVC) injection-moulded solvent-welded socket fittings for use with pressure pipe – Hydraulic internal pressure test

ISO 2045:1988 Single sockets for unplasticized poly(vinyl chloride) (PVC-U) and chlorinated poly(vinyl chloride) (PVC-C) pressure pipes with elastic sealing ring type joints – Minimum depths of engagement

ISO 2048:1990 Double-socket fittings for unplasticized poly(vinyl chloride) (PVC-U) pressure pipes with elastic sealing ring type joints – Minimum depths of engagement

ISO 2507-2:1995 Thermoplastics pipes and fittings – Vicat softening temperature – Part 2: Test conditions for unplasticized poly(vinyl chloride) (PVC-U) or chlorinated poly(vinyl chloride) (PVC-C) pipes and fittings and for high impact resistance poly(vinyl chloride) (PVC-HI) pipes

ISO 2536:1974 Unplasticized polyvinyl chloride (PVC) pressure pipes and fittings, metric series – Dimensions of flanges

ISO 2898-1:1996 Plastics – Plasticized poly(vinyl chloride) (PVC-P) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 2898-2:1997 Plastics – Plasticized poly(vinyl chloride) (PVC-P) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 3114:1977 Unplasticized polyvinyl chloride (PVC) pipes for potable water supply – Extractability of lead and tin – Test method

ISO 3460:1975 Unplasticized polyvinyl chloride (PVC) pressures pipes – Metric series – Dimensions of adapter for backing flange

ISO 3603:1977 Fittings for unplasticized polyvinyl chloride (PVC) pressure pipes with elastic sealing ring type joints – Pressure test for leakproofness

ISO 3604:1976 Fittings for unplasticized polyvinyl chloride (PVC) pressure pipes with elastic sealing ring type joints – Pressure test for leakproofness under conditions of external hydraulic pressure

ISO 3633:2002 Plastics piping systems for soil and waste discharge (low and high temperature) inside buildings – Unplasticized poly(vinyl chloride) (PVC-U)

ISO 4132:1979 Unplasticized polyvinyl chloride (PVC) and metal adaptor fittings for pipes under pressure – Laying lengths and size of threads – Metric series

ISO/TR 4191:1989 Unplasticized polyvinyl chloride (PVC-U) pipes for water supply – Recommended practice for laying

ISO 4422-1:1996 Pipes and fittings made of unplasticized poly(vinyl chloride) (PVC-U) for water supply – Specifications – Part 1: General

ISO 4422-2:1996 Pipes and fittings made of unplasticized poly(vinyl chloride) (PVC-U) for water supply – Specifications – Part 2: Pipes (with or without integral sockets)

ISO 4422-3:1996 Pipes and fittings made of unplasticized poly(vinyl chloride) (PVC-U) for water supply – Specifications – Part 3: Fittings and joints

ISO 4422-4:1997 Pipes and fittings made of unplasticized poly(vinyl chloride) (PVC-U) for water supply – Specifications – Part 4: Valves and ancillary equipment

ISO 4422-5:1997 Pipes and fittings made of unplasticized poly(vinyl chloride) (PVC-U) for water supply – Specifications – Part 5: Fitness for purpose of the system

ISO 4433-3:1997 Thermoplastics pipes – Resistance to liquid chemicals – Classification – Part 3: Unplasticized poly(vinyl chloride) (PVC-U), high-impact poly(vinyl chloride) (PVC-HI) and chlorinated poly(vinyl chloride) (PVC-C) pipes

ISO 4434:1977 Unplasticized polyvinyl chloride (PVC) adaptor fittings for pipes under pressure – Laying length and size of threads – Metric series

ISO 4435:2003 Plastics piping systems for non-pressure underground drainage and sewerage – Unplasticized poly(vinyl chloride) (PVC-U)

ISO 4439:1979 Unplasticized polyvinyl chloride (PVC) pipes and fittings – Determination and specification of density

ISO 4574:1978 Plastics – PVC resins for general use – Determination of hot plasticizer absorption

ISO 4575:1985 Plastics – Polyvinyl chloride pastes – Determination of apparent viscosity using the Severs rheometer

ISO 4612:1999 Plastics – Preparation of PVC pastes for test purposes – Planetary-mixer method

ISO 6259-2:1997 Thermoplastics pipes – Determination of tensile properties – Part 2: Pipes made of unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C) and high-impact poly(vinyl chloride) (PVC-HI)

ISO 6451:1982 Plastics coated fabrics – Polyvinyl chloride coatings – Rapid method for checking fusion

ISO 6455:1983 Unplasticized polyvinyl chloride (PVC) fittings with elastic sealing ring type joints for pipes under pressure – Dimensions of laying lengths – Metric series

ISO 6992:1986 Unplasticized polyvinyl chloride (PVC-U) pipes for drinking water supply – Extractability of cadmium and mercury occurring as impurities

ISO 6993:2001 Buried, high-impact poly(vinyl chloride) (PVC-HI) pipes for the supply of gaseous fuels – Specifications

ISO/TR 7024:1985 Above-ground drainage – Recommended practice and techniques for the installation of unplasticized polyvinyl chloride (PVC-U) sanitary pipework for above-ground systems inside buildings

ISO/TR 7073:1988 Recommended techniques for the installation of unplasticized poly(vinyl chloride) (PVC-U) buried drains and sewers

ISO 7387-1:1983 Adhesives with solvents for assembly of PVC-U pipe elements – Characterization – Part 1: Basic test methods

ISO 7508:1985 Unplasticized polyvinyl chloride (PVC-U) valves for pipes under pressure – Basic dimensions – Metric series

ISO 7617-1:2001 Plastics-coated fabrics for upholstery – Part 1: Specification for PVC-coated knitted fabrics

ISO 7617-2:2003 Plastics-coated fabrics for upholstery – Part 2: Specification for PVC-coated woven fabrics

ISO 8095:1990 PVC-coated fabrics for tarpaulins – Specification

ISO 8096-1:1989 Rubber- or plastics-coated fabrics for water-resistant clothing – Specification – Part 1: PVC-coated fabrics

ISO 8283-1:1991 Plastics pipes and fittings – Dimensions of sockets and spigots for discharge systems inside buildings – Part 1: Unplasticized poly(vinyl chloride) (PVC-U) and chlorinated poly(vinyl chloride) (PVC-C)

ISO 8361-2:1991 Thermoplastics pipes and fittings – Water absorption – Part 2: Test conditions for unplasticized poly(vinyl chloride) (PVC-U) pipes and fittings

ISO 9393-2:1997 Thermoplastics valves – Pressure test methods and requirements – Part 2: Test conditions and basic requirements for PE, PP, PVC-U and PVDF valves

ISO 9852:1995 Unplasticized poly(vinyl chloride) (PVC-U) pipes – Dichloromethane resistance at specified temperature (DCMT) – Test method

ISO 9853:1991 Injection-moulded unplasticized poly(vinyl chloride) (PVC-U) fittings for pressure pipe systems – Crushing test

ISO 11468:1997 Plastics – Preparation of PVC pastes for test purposes – Dissolver method

ISO 12092:2000 Fittings, valves and other piping system components made of unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C), acrylonitrile-butadiene-styrene (ABS) and acrylonitrile-styrene-acrylester (ASA) for pipes underpressure – Resistance to internal pressure – Test method

ISO 13783:1997 Plastics piping systems – Unplasticized poly(vinyl chloride) (PVC-U) end-load-bearing double-socket joints – Test method for leaktightness and strength while subjected to bending and internal pressure

ISO 13844:2000 Plastics piping systems – Elastomeric-sealing-ring-type socket joints of unplasticized poly(vinyl chloride) (PVC-U) for use with PVC-U pipes – Test method for leaktightness under negative pressure

ISO 13845:2000 Plastics piping systems – Elastomeric-sealing-ring-type socket joints for use with unplasticized poly(vinyl chloride) (PVC-U) pipes – Test method for leaktightness under internal pressure and with angular deflection

ISO 15493:2003 Plastics piping systems for industrial applications – Acrylonitrile-butadiene- styrene (ABS), unplasticized poly(vinyl chloride) (PVC-U) and chlorinated poly(vinyl chloride) (PVC-C) – Specifications for components and the system – Metric series

ISO 19220:2004 Plastics piping systems for soil and waste discharge (low and high temperature) inside buildings – Styrene copolymer blends (SAN + PVC)

4.6.10 Trade name examples

Astralon, Exon, Fiberloc, Geon, Hostalit, Igelite, Lucoflex, Lucovyl, Marvinol, Norvinyl, Opalon, Ortodur, Pevikon, Polychlorovinyl, Polytherm, Porodur, Trovidor, Viniplast, Viniplaen, Vinnol, Vinoflex, Yugovinyl.

Foams: Airex, Celuform, Divinycell, Forex, Herex, Klegecell, Vestolit TSE . . .

4.6.11 Property tables

Table 4.29 relates to examples only and cannot be generalized. Data cannot be used for design purposes. See also Table 4.28 for foam properties.

Table 4.29 PVCs: examples of properties

	PVC	PVC-HI	Rigid compounds
Miscellaneous properties			
Density, (g/cm^3)	1.38	1.34	1.35–1.5
Shrinkage (%)			0.1–0.6
Absorption of water (%)			0.04–0.4
Mechanical properties			
Shore hardness, D	84	82	65–90
Rockwell hardness, M	47	39	<10–70
Rockwell hardness, R	115	105	50–120
Stress at yield (MPa)	55	45	35–50
Tensile strength (MPa)	53	33	35–60
Elongation at break (%)	20–40	40–120	2–80
Tensile modulus (GPa)	3	2.2–3	2.4–4
Flexural strength (MPa)	103	67	
Flexural modulus (GPa)	3	3	2.1–3.5
Notched impact strength ASTM D256 (J/m)	54		20–110
Thermal properties			
HDT B (0.46 MPa) (°C)			57–80
HDT A (1.8 MPa) (°C)	70	70	54–75
Vicat softening point B50 (°C)	83	81	
Continuous use temperature (°C)	60	60	50–80

(*Continued*)

Table 4.29 (Continued)

	PVC	PVC-HI	Rigid compounds
Glass transition temperature (°C)			60–100
Minimum service temperature (°C)			−10 to 0
Thermal conductivity (W/m.K)	0.15	0.15	0.16
Specific heat (cal/g/°C)			0.2–0.3
Coefficient of thermal expansion (10^{-5}/°C)	7–9.5	7–9.5	5–18
Electrical properties			
Volume resistivity (ohm.cm)	10^{15}–10^{16}	10^{15}	10^{15}–10^{16}
Dielectric constant	3–4	3–4	3–4
Loss factor (10^{-4})	25–250	25–250	100–200
Dielectric strength (kV/mm)	50	40	10–40
Arc resistance (s)			60–80
Fire behaviour			
Oxygen index	45		
UL94 fire rating	V0		
	10% GF	**30% GF**	**30% GF HI**
Miscellaneous properties			
Density (g/cm^3)	1.43	1.57	1.53
Shrinkage (%)	0–0.1	0–0.1	0–0.1
Mechanical properties			
Shore hardness, D	86	89	87
Rockwell hardness, M	53	65	57
Rockwell hardness, R	118	118	110
Tensile strength (MPa)	73	97	80
Elongation at break (%)	6	2	3.5
Tensile modulus (GPa)	4	9	6.9
Flexural strength (MPa)	123	159	114
Flexural modulus (GPa)	4.5	8.3	6.6
Notched impact strength @ 20°C ASTM D256 (J/m)	43	60	97
Notched impact strength @ −40°C ASTM D256 (J/m)	38	50	70
Thermal properties			
HDT A (1.8 MPa) (°C)	75	76	75
Thermal conductivity (W/m.K)		0.35	
Specific heat (cal/g/°C)		0.25	
Coefficient of thermal expansion (10^{-5}/°C)	3.6	2.2	2.5
Electrical properties			
Volume resistivity (ohm.cm)		10^{15}	
Dielectric constant		3.4	
Fire behaviour			
UL94 fire rating	5 V to V0	5 V to V0	5 V to V0
	Flexible compounds		
	Plasticized	**Plasticized and filled**	
Miscellaneous properties			
Density (g/cm^3)	1.15–1.35	1.30–1.9	
Shrinkage (%)	0.8–5	0.2–1	
Absorption of water (%)	0.15–0.75	0.2–1	
Mechanical properties			
Shore hardness, A	55 to >96	55 to >96	
Shore hardness, D	<10–70	<10–70	
Rockwell hardness, M	<5	<5	
Rockwell hardness, R	<20–67	<20–67	
Tensile strength (MPa)	10–25	7–25	
Elongation at break (%)	200–500	100–400	

Table 4.29 (Continued)

	Flexible compounds	
	Plasticized	Plasticized and filled
Thermal properties		
HDT B(0.46 MPa) (°C)	<56	<56
HDT A(1.8 MPa) (°C)	<53	<53
Continuous use temperature (°C)	50–80	50–80
Glass transition temperature (°C)	−50 to −5	−50 to −5
Minimum service temperature (°C)	−40 to −5	−40 to −5
Thermal conductivity (W/m.K)	0.16	0.16
Specific heat (cal/g/°C)	0.3–0.5	0.3–0.35
Coefficient of thermal expansion (10^{-5}/°C)	7–25	5–20
Electrical properties		
Volume resistivity (ohm.cm)	10^{10}–10^{16}	10^{10}–10^{16}
Dielectric constant	3–5	3–5
Loss factor (10^{-4})	25–1600	25–1600
Dielectric strength (kV/mm)	10–30	10–30
Fire behaviour		
Oxygen index	21–39	21–39

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

The chemical resistance of flexible PVC can be strongly reduced and the absorption of water can be definitely higher.

Light	UV stabilizers are needed
Dilute acids	Good behaviour
Dilute bases	Good behaviour
Strong bases	Good behaviour
Solvents	Good behaviour with aliphatic hydrocarbons Attacked by aromatic hydrocarbons, chlorinated solvents, esters, ethers and ketones Variable resistance to oils, greases, alcohols
Food contact	Possible for special grades

4.7 Chlorinated PVC (PVC-C or CPVC)

Chlorinated polyvinyl chloride is produced by chlorination of polyvinyl chloride. The chlorine content can be as high as 65–70% versus 57% for PVCs. This leads to:

- a higher service temperature
- a better chemical resistance
- a better retention of mechanical performances when the temperature rises.

Some properties vary significantly with the chlorine content and the molecular weights.

4.7.1 General properties

Advantages

PVC-C is appreciated, in comparison with PVC, for its chemical resistance except to certain solvents, its maximum operating temperature, its higher rigidity particularly when the temperature rises, dimensional stability, and fireproofing.

Drawbacks

PVC-C is currently handicapped by the ecological problems concerned with chlorine, the limited number of producers, the cost, the attack by aromatic or chlorinated hydrocarbons as well as by esters and ketones, the impact sensitivity which increases as the temperature decreases, a high density, the fume toxicity and corrosivity in the event of fire.

Special grades

PVC-C is a speciality polymer produced in a limited range of grades with different chlorine contents and additives for:

- extrusion, injection, calendering, co-extrusion, thermoforming
- stabilized against heat, UV, light and weathering; low combustibility
- for pipes and fittings, window profiles, films and sheets, tubes . . .

Costs

The cost is higher than that of PVC.

Processing

All the molten-state methods are usable but extrusion, injection, calendering, thermoforming, welding and co-extrusion are the most used.

Applications

(See Chapter 2 for further information.)

Applications are far less widespread than for PVC, for example:

- Building & construction
  - pipes and fittings for hot and corrosive environments
  - window profiles.
- Anticorrosion
  - components for cooling towers, laboratory sinks, pumps . . .
  - pipes for paper and surface treatment sectors, electroplating plants, photographic, semiconductor and chemical industries . . .

4.7.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated between 90°C and 105°C.

Service temperatures are often lower under mechanical stress because of modulus decay, strain, creep, relaxation . . .

For example:

- the maximum service temperature for a pipe with an operating pressure of 3 bars can be limited to 90°C
- for another piping application, the maximum service temperature is 80°C
- For several grades, the HDTs A (1.8 MPa) are in the range from 85°C up to 106°C.

The UL temperature index of a specific grade is claimed to be 105°C for electrical and mechanical properties including impact strength.

Minimum service temperatures are of the order of 0°C.

These results relate to some grades only and cannot be generalized.

4.7.3 Mechanical properties

PVC-C is a stiff and brittle material with a rather high modulus and tensile strength but low elongation at break and weak impact strength that can be improved by compounding.

Dimensional stability

Rigid PVC-C is an amorphous polymer with low shrinkage, a fair coefficient of thermal expansion for a polymer, limited creep at room temperature, and low water absorption by moisture exposure.

4.7.4 Ageing

Weathering

PVC-C resists hydrolysis well but is naturally sensitive to light and UV. It must be protected by addition of anti-UV and other protective agents. In these cases, PVC-C can be used for long-lasting exterior parts.

Behaviour at high frequencies

PVC-C has a high loss factor, about 250×10^{-4} for example, and heats up under high-frequency current. It is weldable by this technique.

Chemicals

PVC-C absorbs little water and is not very sensitive to it.

PVC-C resists acids, alkalis and aliphatic hydrocarbons well.

PVC-C is attacked by aromatic hydrocarbons, chlorinated solvents, esters, ethers and ketones.

Table 4.30 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the PVC-Cs. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Fire resistance

Due to the chlorine content, the fire resistance is inherently better than for hydrocarbon polymers and PVC but high amounts of chlorine are released during combustion. Oxygen indices are about 50 with UL rating V0 or 5 VA.

Table 4.30 PVC-C: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10 to >96	S	Hydrochloric acid	10–40	S
Acetic anhydride	100	S	Hydrofluoric acid	40	S
Acetone	100	l	Hydrogen peroxide	30	S
Aluminium chloride	Solution	S	Hydrogen sulfide gas	Unknown	S
Aluminium sulfate	Unknown	S	Iron(III) chloride	Unknown	S
Ammonium hydroxide	30	S	Ketones	100	n
Ammonium sulfate	50	S	Lead acetate	10	S
Amyl alcohol	100	S	Linseed oil	100	S
Aromatic hydrocarbons	100	n	Liquid paraffin	100	S
Arsenic acid	Unknown	S	Magnesium chloride	Unknown	S
ASTM1 oil	100	S	Manganese sulfate	Unknown	S
ASTM2 oil	100	S	Mercury chloride	Unknown	S
ASTM3 oil	100	S	Methanol	100	S
Barium chloride	Saturated	S	Mineral oil	100	S
Benzene	100	l	Molasses	Unknown	S
Boric acid	Unknown	S	Nitric acid	50–65	S
Bromine (liquid)	100	n	Nitrobenzene	100	S
Butanol	100	S	Oleic acid	Unknown	S
Butyl acetate	100	n	Oxalic acid	Unknown	S
Calcium chloride	Unknown	S	Petroleum	100	S
Carbon sulfide	100	n	Phenol	Unknown	S
Carbon tetrachloride	100	S	Phosphoric acid	85	S
Cellosolve	100	S	Potassium cyanide	Unknown	S
Cellosolve acetate	100	S	Potassium fluoride	Unknown	S
Chlorinated hydrocarbons	100	n	Potassium hydroxide	45	S
Chlorine water	Unknown	S	Potassium permanganate	20	S
Chloroacetic acid	Unknown	S	Potassium sulfate	Unknown	S
Chlorosulfonic acid	Unknown	n	Propylene oxide	100	l
Chromic acid	Unknown	S	Sea water	100	S
Citric acid	10	S	Silver nitrate	Unknown	S
Colza oil	100	S	Sodium borate	Unknown	S
Copper sulfate	Unknown	S	Sodium carbonate	10	S
Cyclohexane	100	S	Sodium chloride	25	S
Cyclohexanone	100	n	Sodium cyanide	Unknown	S
Dichloroethylene	100	l	Sodium hydroxide	10–55	S
Diethylether	100	n	Sodium hypochlorite	13–20	S
Dioctylphthalate	100	S	Sodium nitrate	Solution	S
Dioxan	100	n	Styrene	100	S
Ethanol	Unknown	S	Sulfur dioxide (gas)	Unknown	S
Ethylacetate	100	n	Sulfuric acid	10–70	S
Ethylchloride	100	n	Sulfuric acid	96	l
Ethylene glycol	100	S	Sulfurous anhydride (gas)	Unknown	S
Ethylenebromide	100	n	Tetrahydrofuran	100	n
Fluosilicic acid	Unknown	S	Thionyl chloride	100	n
Formaldehyde	37	S	Tin chloride	Unknown	S
Formic acid	85	S	Toluene	100	n
Freon 11	100	S	Transformer oil	100	S
Freon 113	100	S	Trichloroacetic acid	Unknown	S
Freon 12	100	S	Turpentine oil	100	S
Freon 13b1	100	S	Vinyl acetate	100	n
Freon 22	100	l	Water	100	S
Furfural	100	n	Wine	Unknown	S
Glycerol	100	S	Xylene	100	n
Hexane	100	S	Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

4.7.5 Electrical properties

PVC-Cs are good insulators with fair dielectric resistivities and rigidities, and rather high loss factors. PVC-C heats up when subjected to high-frequency currents and microwaves.

Special grades and compounds are marketed for electrical applications.

4.7.6 Joining, decoration

Welding is easy by all processes.

Gluing is easy, including using solutions of PVC-C.

All precautions must be taken concerning health and safety according to local laws and regulations.

4.7.7 Specific ISO standards concerning PVC-C

ISO 3514:1976 Chlorinated polyvinyl chloride (CPVC) pipes and fittings – Specification and determination of density

ISO 727-1:2002 Fittings made from unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C) or acrylonitrile/butadiene/styrene (ABS) with plain sockets for pipes under pressure – Part 1: Metric series

ISO 727-2:2002 Ed. 1 Fittings made from unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C) or acrylonitrile/butadiene/styrene (ABS) with plain sockets for pipes under pressure – Part 2: Inch-based series

ISO 2045:1988 Single sockets for unplasticized poly(vinyl chloride) (PVC-U) and chlorinated poly(vinyl chloride) (PVC-C) pressure pipes with elastic sealing ring type joints – Minimum depths of engagement

ISO 2507-2:1995 Thermoplastics pipes and fittings – Vicat softening temperature – Part 2: Test conditions for unplasticized poly(vinyl chloride) (PVC-U) or chlorinated poly(vinyl chloride) (PVC-C) pipes and fittings and for high impact resistance poly(vinyl chloride) (PVC-HI) pipes

ISO 4433-3:1997 Thermoplastics pipes – Resistance to liquid chemicals – Classification – Part 3: Unplasticized poly(vinyl chloride) (PVC-U), high-impact poly(vinyl chloride) (PVC-HI) and chlorinated poly(vinyl chloride) (PVC-C) pipes

ISO 6259-2:1997 Thermoplastics pipes – Determination of tensile properties – Part 2: Pipes made of unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C) and high-impact poly(vinyl chloride) (PVC-HI)

ISO 7675:2003 Plastics piping systems for soil and waste discharge (low and high temperature) inside buildings – Chlorinated poly(vinyl chloride) (PVC-C)

ISO 8283-1:1991 Plastics pipes and fittings – Dimensions of sockets and spigots for discharge systems inside buildings – Part 1: Unplasticized poly(vinyl chloride) (PVC-U) and chlorinated poly(vinyl chloride) (PVC-C)

ISO 12092:2000 Fittings, valves and other piping system components made of unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C), acrylonitrile-butadiene-styrene (ABS) and acrylonitrile-styrene-acrylester (ASA) for pipes underpressure – Resistance to internal pressure – Test method

ISO 15493:2003 Plastics piping systems for industrial applications – Acrylonitrile-butadiene-styrene (ABS), unplasticized poly(vinyl chloride) (PVC-U) and chlorinated poly(vinyl chloride) (PVC-C) – Specifications for components and the system – Metric series

ISO 15877-1:2003 Plastics piping systems for hot and cold water installations – Chlorinated poly(vinyl chloride) (PVC-C) – Part 1: General

ISO 15877-2:2003 Plastics piping systems for hot and cold water installations – Chlorinated poly(vinyl chloride) (PVC-C) – Part 2: Pipes

ISO 15877-3:2003 Plastics piping systems for hot and cold water installations – Chlorinated poly(vinyl chloride) (PVC-C) – Part 3: Fittings

ISO 15877-5:2003 Plastics piping systems for hot and cold water installations – Chlorinated poly(vinyl chloride) (PVC-C) – Part 5: Fitness for purpose of the system

ISO/TS 15877-7:2003 Plastics piping systems for hot and cold water installations – Chlorinated poly(vinyl chloride) (PVC-C) – Part 7: Guidance for the assessment of conformity

4.7.8 Trade name examples

Corzan, Lucalor, TempRite.

4.7.9 Property tables

Table 4.31 relates to examples only. Data cannot be generalized or used for design purposes.

Table 4.31 PVC-C: examples of properties

Miscellaneous properties	
Density (g/cm^3)	1.47–1.52
Shrinkage (%)	0.3–0.7
Absorption of water (%)	0.02–0.15
Mechanical properties	
Shore hardness, D	83–90
Rockwell hardness, M	40–70
Rockwell hardness, R	112–121
Stress at yield (MPa)	40–55
Strain at yield (%)	5
Tensile strength (MPa)	45–60
Elongation at break (%)	4–27
Tensile modulus (GPa)	2.3–3.2
Flexural strength (MPa)	82–105
Flexural modulus (GPa)	2.3–3.2
Compressive strength (MPa)	61
Compressive modulus (GPa)	1.5
Notched impact strength ASTM D256 (J/m)	50–290
Thermal properties	
HDT B (0.46 MPa) (°C)	100–120
HDT A (1.8 MPa) (°C)	85–106
Vicat softening point B (°C)	127
Continuous use temperature (°C)	80–105
Glass transition temperature (°C)	45
Minimum service temperature (°C)	~0
Thermal conductivity (W/m.K)	0.14–0.16
Specific heat (cal/g/°C)	0.35
Coefficient of thermal expansion (10^{-5}/°C)	6–8
Electrical properties	
Volume resistivity (ohm.cm)	10^{14}–10^{16}
Dielectric constant	3–6
Loss factor (10^{-4})	100–250
Dielectric strength (kV/mm)	20–60
Fire behaviour	
Oxygen index	50
UL94 fire rating	5VA to V0

Table 4.31 (Continued)

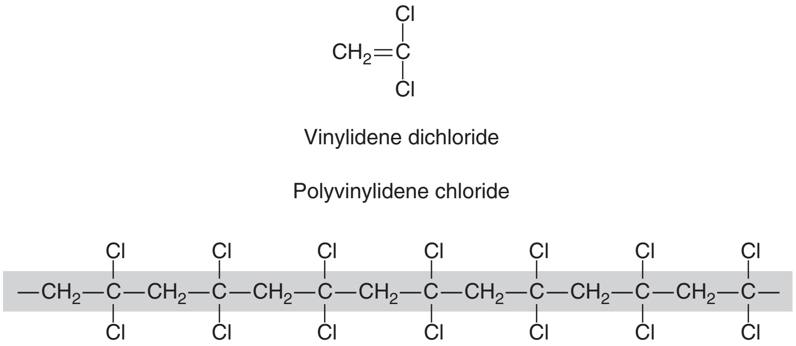
General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers are needed
Acids	Good behaviour
Bases	Good behaviour
Solvents	Good behaviour with aliphatic hydrocarbons. Attacked by aromatic hydrocarbons, chlorinated solvents, esters, ethers and ketones

4.8 Polyvinylidene chloride (PVDC)

Polyvinylidene chloride is produced by polymerization of vinylidene dichloride, as shown in Figure 4.38. The chlorine content can be as high as 73% versus 57% for PVCs.

In fact, only copolymers are industrialized, often with PVC in a minor percentage. The main interest is its excellent impermeability to water vapour and gases, suiting PVDC for the packaging industry.



$$CH_2{=}CCl_2$$

$$-[CH_2-CCl_2]_n-$$

Figure 4.38. Vinylidene dichloride, polyvinylidene chloride formulae

4.8.1 General properties

Advantages

PVDC is appreciated for its barrier effect to water vapour, gases and aromas as well as its chemical resistance (except to certain solvents), its relative flexibility, fireproofing, the possibility of food contact for special grades, transparency, gloss, sealability (including by high frequency and ultrasound), printability.

Drawbacks

PVDC is currently handicapped by the ecological problems associated with chlorine, the limited number of producers, its cost, limited resistance to light and some organic chemicals such as aromatic hydrocarbons, ketones etc., impact sensitivity the more so as the temperature decreases, high density, fume toxicity and corrosivity in the event of fire.

Special grades

PVDC is a speciality polymer produced in a limited range of grades with different copolymers and additives targeting barrier effects for packaging, coating and co-extrusion.

Latices are marketed for the coating of other polymers or papers.

Costs

The cost is higher than for PVC.

Applications

(See Chapter 2 for further information.)

Applications are far fewer than for PVC, mainly targeting:

- packaging
  ○ barrier films for food, pharmaceuticals, chemicals . . .
- barrier layer in multilayer films or sheets, and coatings with PVC, polyethylene and other polyolefins, BOPP (bi-axially oriented polypropylene), polyester, polyamide, polycarbonate.

4.8.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated between 70°C and 90°C and even 100°C.

Service temperatures are often lower under mechanical stress because of modulus decay, strain, creep, relaxation . . .

For example, for several grades, the HDTs A (1.8 MPa) are in the range from 54°C up to 65°C.

Minimum service temperatures are of the order of –15°C.

These results relate to some grades only and cannot be generalized.

4.8.3 Mechanical properties

PVDC is a flexible material with low modulus and tensile strength and rather high elongation at break, but impact strength can be weak.

The coefficient of friction of a given grade is, for example, 0.24.

Dimensional stability

Rigid PVDC is a crystalline polymer with average shrinkage and coefficient of thermal expansion but low water absorption by moisture exposure.

4.8.4 Ageing

Weathering

PVDC resists hydrolysis well but is naturally sensitive to light and UV. It must be protected.

Chemicals

PVDC shows good resistance to dilute acids, alkalis, greases, oils and alcohols.

Resistance is fair versus concentrated acids, aromatic hydrocarbons, ketones.

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide some idea and cannot be used for designing any parts or goods.

- Water vapour: PVDCs have permeabilities evaluated at 0.07 to 0.2 compared to a full range of 0.05 up to 400 for all tested plastics.
- Gases: PVDCs have permeabilities evaluated at:
  - air: 3 to 6 versus a full range of 3 up to 2750 for all tested plastics
  - carbon dioxide: 40 to 440 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 1 to 1.4 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 1.1 to 7 versus a full range of <1 up to 11 000 for all tested plastics
  - hydrogen: 400 to 900 versus a full range of 400 up to 20 000 for all tested plastics.

Fire resistance

Due to the high chlorine content, the fire resistance is inherently better than for hydrocarbon polymers and PVC but high amounts of chlorine are released during combustion. Oxygen indices are about 60 with a V0 UL94 rating.

4.8.5 Trade names

Diofan, Ixan, Saran, Saranex . . .

4.8.6 Property tables

Table 4.32 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.32 PVDC: examples of properties

Miscellaneous properties	
Density (g/cm³)	1.6–1.75
Shrinkage (%)	0.5–2.5
Absorption of water (%)	0.1
Mechanical properties	
Shore hardness, D	80–85
Rockwell hardness, M	30–50
Rockwell hardness, R	98–106
Stress at yield (MPa)	20–30
Tensile strength (MPa)	20–35
Elongation at break (%)	160–250
Tensile modulus (GPa)	0.35–0.5
Flexural strength (MPa)	41
Flexural modulus (GPa)	0.35–0.6
Compressive strength (MPa)	56
Notched impact strength ASTM D256 (J/m)	16–66
Thermal properties	
HDT B (0.46 MPa) (°C)	80–90
HDT A (1.8 MPa) (°C)	54–65
Continuous use temperature (°C)	70–100

Table 4.32 (Continued)

Glass transition temperature (°C)	−15
Minimum service temperature (°C)	~−15
Thermal conductivity (W/m.K)	0.13–0.2
Specific heat (cal/g/°C)	0.3
Coefficient of thermal expansion (10^{-5}/°C)	10–20
Electrical properties	
Volume resistivity (ohm.cm)	10^{12}–10^{16}
Dielectric constant	3–6
Loss factor (10^{-4})	500–800
Dielectric strength (kV/mm)	15–23
Fire behaviour	
Oxygen index	60
UL94 fire rating	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Protection needed
Dilute acids	Good behaviour
Concentrated acids	Fair behaviour
Bases	Good behaviour
Solvents	Good behaviour with greases, oils, alcohols Fair behaviour with aromatic hydrocarbons, ketones
Food contact	Possible for special grades

4.9 Other vinyl polymers

4.9.1 Polyvinyl alcohol (PVAL or PVOH)

See also preceding Section 4.4.2 relating to ethylene-vinyl alcohol copolymers.

These polymers are produced by a more or less complete hydrolysis of polyvinyl acetate.

The properties depend greatly on the degree of hydrolysis. The major interest of this family and, at the same time, the main disadvantage, is its solubility in water, which is:

- proportional to the degree of hydrolysis
- inversely proportional to the degree of polymerization.

In addition to their water solubility, PVALs are appreciated for their good mechanical properties in the dry state, resistance to common solvents, barrier effect in dry atmospheres, possibility of food contact for suitable grades, biodegradability.

On the other hand, the water solubility and high moisture absorption are an obstacle to their development in engineering applications. PVALs must often be protected with other polymers. The cost is in the range for engineering polymers.

Stresses at yield can be from 40 MPa up to 50 MPa with elongations at break varying from 100% to more than 200%. Density is about 1.23–1.30 g/cm^3 and coefficients of thermal expansion are roughly 7–8 × 10^{-5}/°C.

PVAL can be plasticized and processed by casting, dipping, injection, extrusion.

The main engineering applications, possibly in combination with other polymers, are, for example:

- films for packing chemicals, fertilizers, herbicides, disinfectants, dyes, colorants, scalers, cosmetics . . .
- release films for composite moulding

- solvent-resistant tubes and pipes
- membranes for pumps carrying petroleum or chemical products
- binders for ferrite cores

Trade names examples: Elvanol, Gohsenol, Mowiol, Polyviol, Rhodoviol . . .

4.9.2 Polyvinyl butyrate (PVB)

The only but important engineering application for PVB is as an interlayer film between two glass plies to manufacture safety glass for the automobile and building industries.

Visible light transmittance of safety glass with a 0.38 mm or 0.76 mm thick interlayer can be as high as 87% up to 89%.

PVBs are also used as binders for inks, and anticorrosion coatings.

Trade names examples: Butacite, Mowital . . .

4.9.3 Polyvinyl acetate (PVAC)

The homopolymer of vinyl acetate is not used as an engineering polymer but for adhesives and water-based emulsion paints (vinyl acetate is used as a minor comonomer for the copolymerization of PVC/VAC).

4.10 Polystyrene (PS, SB, SMA)

Standardized acronyms for polystyrenes and their derivatives are:

- PS for polystyrene
- SB for butadiene rubber-modified polystyrene or HIPS (high-impact polystyrene)
- SMA for styrene maleic anhydride.

From the simple chemical formulae of styrene and its polymer

$$\text{styrene: } CH_2=CH(C_6H_5)$$

$$\text{polystyrene: } -[CH_2-CH(C_6H_5)]_n-$$

are born several subfamilies according to the polymerization process, use of comonomers, blending with elastomers, and the use of reinforcements:

- **Homopolymers**, by polymerization of polystyrene alone. These homopolymers are rigid, brittle and transparent.
- **Copolymers**, by polymerization of polystyrene with:
  - ○ a rubber, the most commonly used being butadiene, to improve impact strength and behaviour at low temperature but altering rigidity
  - ○ maleic anhydride to improve thermal performances
  - ○ another comonomer such as acrylonitrile to improve mechanical or chemical performances.
- **Alloys**
  - ○ with elastomers such as polybutadiene, which confers very high impact strengths even at low temperature but alters transparency
  - ○ with other plastics to bridge the gap between the respective sets of properties for each of the used plastics.
- **Combination of copolymerization and blending** with rubbers, for example ABS . . .
- **Reinforcement**: glass fibres are used to increase rigidity at ambient and higher temperatures, as well as to decrease creep.

The main polymerization techniques are a bulk process, which is a continuous process, and a suspension method, which is discontinuous.

A metallocene-catalysed polymerization was used to produce syndiotactic polystyrene but its marketing was recently suspended.

This section deals with atactic polystyrene homopolymer, and high-impact polystyrene.

The properties of SMA are included in Table 4.36 and are not otherwise detailed.

For the homopolymer we can observe that the backbone is the same as for the previously examined polyolefins but the pendant groups are different. Properties vary with the degree of polymerization (generally 1500 up to 3000 units per chain), the structure and the possible addition of or copolymerization with a rubber.

ABS and other copolymers are examined in the following sections (4.11 and 4.12).

4.10.1 General properties

Advantages

Polystyrene is appreciated for its transparency, good mechanical properties and rigidity at room temperature, low price, attractive price/property ratios, fair dimensional stability, easy processing, inertness versus certain chemicals, weak absorption of water, fair density, good electrical insulation even in wet environments, feasibility of welding, versatility of processing methods, possibilities of food contact for specific grades, thermal insulation properties especially for foam, ease of joining. Polystyrene's capacity for foaming has allowed the development of mass-production foams for insulation and damping.

High-impact grades present better impact resistances even at low temperature, higher flexibility and environmental stress cracking resistance (ESCR). The butadiene-styrene block copolymers are transparent but the alloys made of polystyrene and polybutadiene are not.

Drawbacks

General drawbacks are the innate sensitivity to heat, low temperature, UV, light and weathering (but stabilized grades are marketed), weak impact resistance, poor scratch resistance, low flexibility, creep when the temperature rises, easy combustion with dripping and release of abundant black fumes, electrostatic build-up, some machining difficulties.

High-impact grades have lower rigidity, lower chemical resistance and are more difficult to join and weld. Alloys made of polystyrene and polybutadiene are opaque.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, compression, cast film, blown film, blow moulding, structural foam, light foam, co-extrusion, thermoforming, for thin or thick parts, easy flow, medium flow, fast set up . . .
- high molecular weight, excellent clarity; stabilized against heat, UV, light and/or weathering; antistatic, conductive, reinforced, food contact, clean, fireproofed, highly transparent, high fluidity, impact modified, high gloss, high ESCR . . .
- films and sheets, tubes, pipes, medical and laboratory parts; suitable for post galvanoplasty, electroplating or metallization; ignition-resistant for electronic components and fixtures . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide a rough idea. They are generally of the order of €1 per kilogram.

Processing

All the molten-state methods are usable: extrusion, injection, compression, blown film, blow moulding, thermoforming, foam, co-extrusion, machining, welding.

Applications

(See Chapter 2 for further information.)

The statistically identified consumptions of dense PS are roughly:

• packaging	43%
• appliances	14%
• housewares	9%
• refrigerators	6%
• furniture	5%
• toys	3%
• others	20%

Foam consumption is roughly 15–30% of the PS total, depending on the country.

Packaging

- Transparent packaging
- Containers, trays . . .
- Cups and dairy containers from thermoformed sheets
- Vacuum-formed packages
- Refrigeration and food packaging
- Dinnerware . . .

Appliances, house ware, furniture

- Air conditioners
- Video and audio tape cassettes
- TV components
- Microfloppy diskettes
- Refrigerator door linings
- Small appliances
- Service ware
- Cutlery, tumblers and thin-wall multicavity parts
- Toys
- Splash shields
- Toilet seats
- Knobs, buttons
- Components for furniture
- Lighting diffusers . . .

Industry

- Handles
- Tubing for corrosive liquids
- Tank covers
- Insulators . . .

Miscellaneous

- Enclosures
- Medical and laboratory parts
- Lenses
- Co-axial cable separators
- Studs, heels
- Sign panels . . .

4.10.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 50°C up to 80°C if softening temperatures are higher.

The UL temperature indices of specific grades can be 50–60°C for electrical and mechanical properties including impact.

Service temperatures can be lower under stress because of modulus decay, strain, creep, relaxation . . .

For example, for several grades of neat polystyrene, the HDTs A (1.8 MPa) are of the order of 70°C up to 90°C.

Figure 4.39 displays examples of modulus retention versus short-term temperature increase.

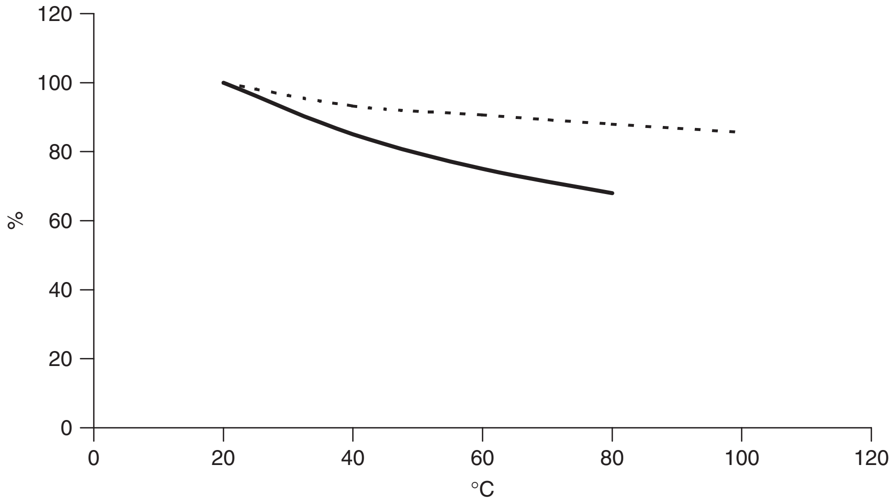


Figure 4.39. HIPS examples of modulus retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Characteristics such as elongation at break and impact strength are especially heat sensitive.

For example, for a given grade of polystyrene, after 1000 hr at 80°C:

- retention of tensile stress at yield is 83%
- retention of elongation at break is 70%.

SMA are specially designed for a slightly better heat resistance. The UL temperature indices of specific grades can be:

- 50–70°C for the electrical and mechanical properties including impact
- 50–75°C for the electrical properties alone.

At low temperatures, general-purpose grades are generally brittle at room temperature but special grades perform well down to –20°C or even –40°C according to the mechanical stresses undergone.

Figure 4.40 shows an example of impact strength versus low temperatures for a given impact-modified polystyrene.

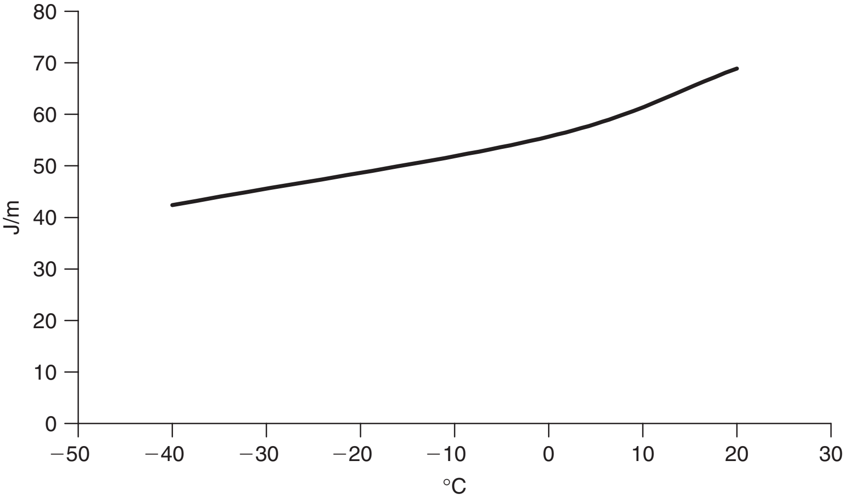


Figure 4.40. HIPS: examples of Notched Izod impact strengths versus sub-zero temperatures (°C)

The glass transition temperatures of polystyrene by DSC measurements are generally about 90°C.

These results relate to some grades only and cannot be generalized.

4.10.3 Optical properties

Non-alloyed polystyrenes are naturally highly transparent and certain grades are especially designed for optical applications.

Transmission of light can range from 80% up to 98% and haze can be as low as 0.65.

Refractive indices are about 1.57 to 1.6.

Alloys of polystyrene and polybutadiene or another rubber are not transparent but copolymers are.

These results relate to some grades only and cannot be generalized.

4.10.4 Mechanical properties

The mechanical properties are generally fair with low elongations at break and a brittle behaviour at room temperature. Moduli and hardnesses are higher than those of polyolefins.

The abrasion and scratch resistance of polystyrene depend on the roughness, type and morphology of the opposing surface but is limited and polystyrenes are not designed for antifriction applications.

Impact-modified grades are more impact resistant and less brittle but more flexible.

Friction

The coefficients of friction against steel are generally in an intermediate range, from 0.3 up to 0.35. For one polystyrene surface against another they are high, about 0.5.

These results relate to a few grades only and cannot be generalized.

Dimensional stability

Polystyrene is an amorphous polymer and shrinkage and coefficient of thermal expansion are rather low depending on the possible rubber content. The absorption and alteration by moisture exposure are low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For example, data are reported in the range from 0.33 to 0.35.

Creep

Amorphous non-alloyed polystyrenes have fair moduli slowly decreasing with a moderate increase in temperature involving fair creep moduli, for example:

- 2.3 to 3.3 GPa after 1 h at room temperature under 7 to 10 MPa
- 2.1 to 2.8 GPa after 1000 h at room temperature under 7 to 10 MPa.

In Figure 4.41(a) we can observe the rather moderate strains under moderate stresses.

In Figure 4.41(b) we can observe the rather moderate difference between engineering moduli, roughly 2 to 3 GPa, and creep modulus, roughly 1.5 to 1.8, after 1000 hr at ambient temperature.

These results relate to a few grades only and cannot be generalized.

Relaxation

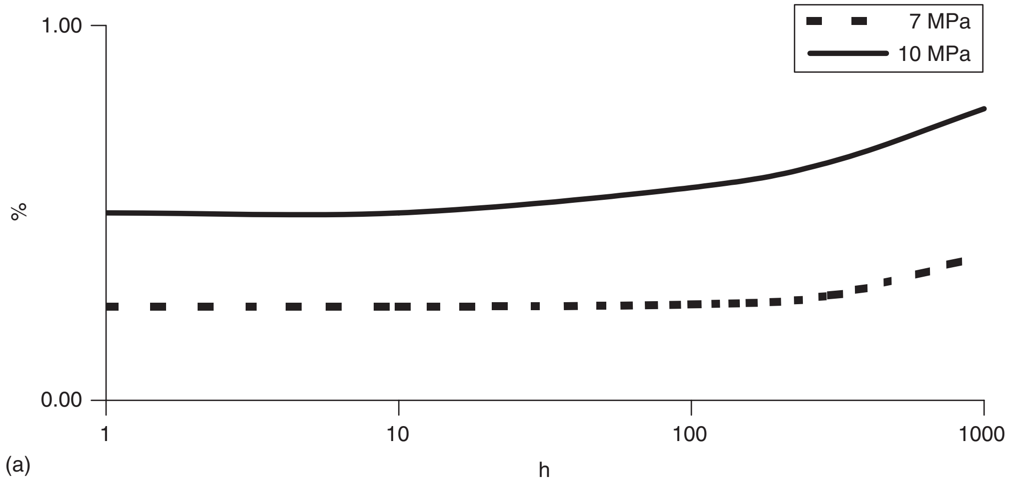
Figure 4.42 displays relaxation data plotted as the percentage of stress retention versus a logarithmic time scale in hours, showing a regular decrease of stress. These results confirm the creep data in the previous figure. This diagram is only given to illustrate the principle of relaxation; the data cannot be used for designing.

These results relate to a few grades only and cannot be generalized.

4.10.5 Ageing

Dynamic fatigue

The dynamic fatigue can be fair for well-adapted grades if care is taken to limit the strains by restricting the stresses to values in keeping with the low elongation at break.



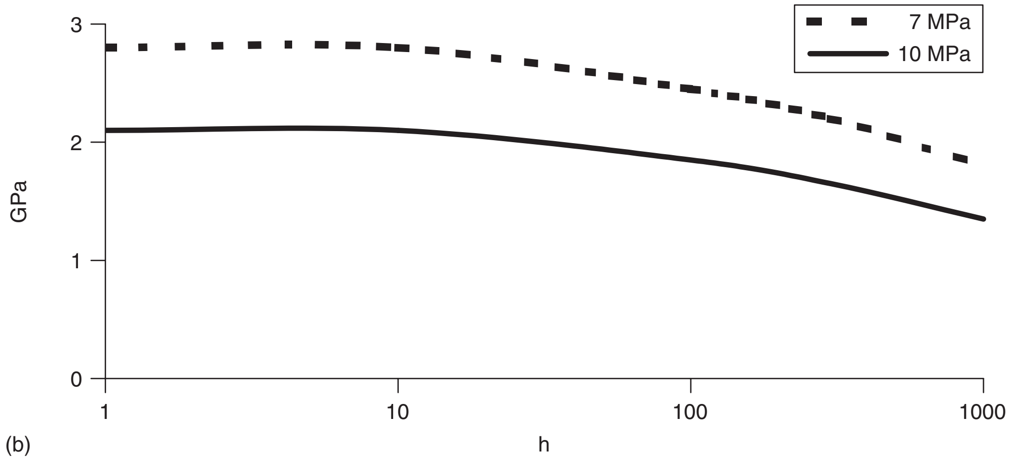


Figure 4.41. (a) Polystyrene creep: examples of strain (%) versus time (h) under various stresses; (b) Polystyrene creep: examples of creep modulus (GPa) versus time (h) under various stresses.

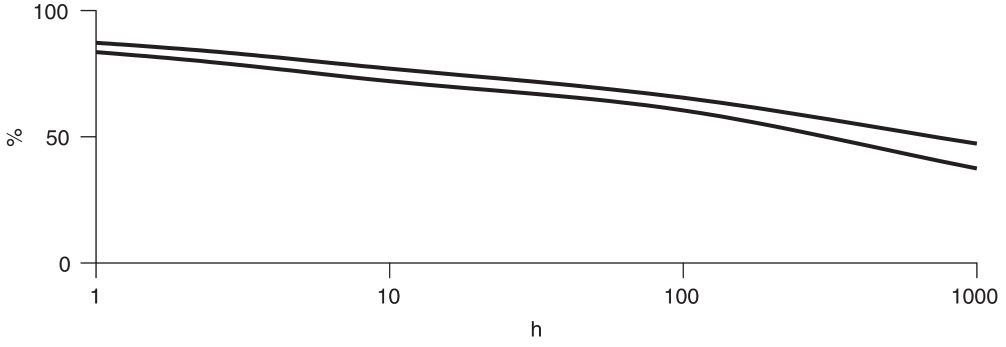


Figure 4.42. Stress relaxation of PS, examples of stress retention (%) versus time (h) under strains <1% at 20°C

For a given grade of HIPS, Figure 4.43 displays an example of an SN or Wöhler's curve for a notched sample.

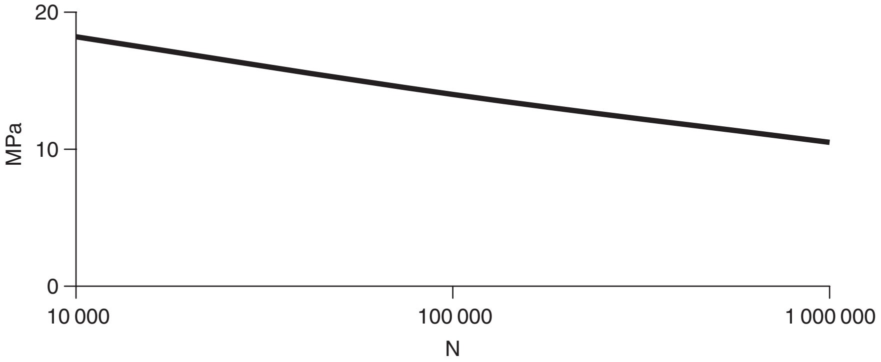


Figure 4.43. SN curve of polystyrene, examples of maximum stress S (MPa) versus number of cycles at rupture (N)

Weathering

Polystyrene resists hydrolysis well but is naturally sensitive to light and UV especially when alloyed with a UV-sensitive rubber such as polybutadiene. It must be protected by addition of anti-UV and other protective agents or by a suitable carbon black.

After weathering, the retention of properties for test bars (3 mm thick) is, for example:

- 85% for tensile strength after 6 months' outdoor exposure in Los Angeles for a protected glass fibre reinforced grade
- 89% for tensile strength after 12 months' outdoor exposure in Los Angeles for a protected glass fibre reinforced grade.

These results are examples only and cannot be generalized.

High-energy radiation

Polystyrenes show good behaviour and the most-resistant grades can resist doses of gamma rays of about 1000 Mrad, depending in a complex way on the power, dose and wall thickness of the part.

These results are examples only and cannot be generalized.

Behaviour at high frequencies

Polystyrenes have weak loss factors, about $1–30 \times 10^{-4}$, and do not heat up under high-frequency current. They cannot be welded by this technique.

Chemicals

Neat polystyrenes absorb little water and are not very sensitive to it but can have some propensity to stress cracking in the presence of certain chemicals.

Suitable grades are usable in contact with food and are used for food packaging.

Chemical resistance is generally:

- excellent to limited against inorganic and organic acids (except strong oxidizing acids), bases, vegetable oils, alcohols, aliphatic amines, beverages, condiments and numerous foodstuffs, polyglycols and numerous pharmaceuticals
- unsatisfactory against aldehydes, aromatic amines, esters, ethers, ketones, polyglycol ethers, aliphatic and aromatic hydrocarbons, chlorinated solvents, insecticides, essential oils.

Table 4.33 displays some general assessments of the behaviour of given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the polystyrenes. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.33 Polystyrene: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S
Acetic acid	>96	n
Acetic aldehyde	100	n
Acetic anhydride	100	n
Acetone	100	n
Acetonitrile	100	n
Acetophenone	100	n
Acetyl chloride	100	n
Aliphatic hydrocarbons	100	n
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonium hydroxide	30	S
Ammonium sulfate	50	S
Amyl acetate	100	n
Amyl chloride	100	n
Amyl alcohol	100	S
Aniline	100	n
Antimony chloride	10	S
Aqua regia	Unknown	n
Aromatic hydrocarbons	100	n
ASTM3 oil	100	l
Barium chloride	Saturated	S
Benzaldehyde	100	n
Benzene	100	n
Benzyl chloride	100	n
Benzyl alcohol	100	n
Boric acid	Unknown	S
Bromine (liquid)	100	n
Bromine water	Unknown	n
Butanol	100	l
Butanone	100	n
Butter	100	S
Butyl acetate	100	n
Butylamine	Unknown	n
Butylchloride	100	n
Butyric acid	Unknown	n
Calcium chloride	Unknown	S
Calcium hypochlorite	Solution	S
Carbon sulfide	100	n
Carbon tetrachloride	100	l to n
Castor oil	100	l
Cellosolve	100	n
Cellosolve acetate	100	n
Chlorinated hydrocarbons	100	n
Chlorinated solvents	100	n
Chlorine (dry gas)	100	n
Chlorine dioxide	Unknown	n
Chlorine water	Unknown	n
Chloroacetic acid	Unknown	S
Chlorobenzene	100	n
Chloroform	100	n
Chlorosulfonic acid	Unknown	n
Chromic acid	Unknown	l
Chromic acid	20	l
Citric acid	10	S
Copper sulfate	Unknown	l
Cresol	100	l
Cyclohexane	100	n
Cyclohexanol	100	l
Cyclohexanone	100	n
Decaline	100	n
Diacetone alcohol	100	l
Dichloroethane	100	n
Dichloroethylene	100	n
Dichloromethylene	100	n
Diethylamine	100	n
Diethyleneglycol	100	S
Diethylether	100	n
Diluted acids	Dilute	S
Diluted bases	Dilute	S
Dimethylformamide	100	n
Dioctylphthalate	100	n
Dioxan	100	n
Esters	100	n
Ethanol	40	S
Ethanol	Unknown	l
Ethanol	96	l
Ethylacetate	100	n
Ethylchloride	100	n
Ethylene glycol	100	S
Ethylhexanol	100	S
Fluorine	100	n
Formaldehyde	37	n
Formic acid	40	S
Formic acid	85	l
Freon 11	100	n
Freon 113	100	S
Freon 12	100	l

(*continued*)

Table 4.33 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Freon 21	100	n	Phosphoric acid	85	l
Freon 22	100	n	Potassium cyanide	Unknown	S
Freon 32	100	l	Potassium fluoride	Unknown	S
Furfural	100	n	Potassium hydroxide	45	l
Glycerol	100	S	Potassium permanganate	20	l
Heptane	100	n	Potassium permanganate	1	S
Hexane	100	n	Potassium sulfate	Unknown	S
Hydrobromic acid	48	l	Propanol	100	S
Hydrochloric acid	10	S	Propylene oxide	100	n
Hydrochloric acid	37	n	Pyridine	Unknown	n
Hydrofluoric acid	100	n	Sea water	100	S
Hydrofluoric acid	40–75	n	Silicone oil	100	S
Hydrogen peroxide	30	S	Silver nitrate	Unknown	S
Hydrogen peroxide	90	S	Sodium borate	Unknown	S
Hydrogen sulfide gas	Unknown	n	Sodium carbonate	10	S
Iron(III) chloride	Unknown	S	Sodium chloride	25	S
Isobutanol	100	S	Sodium cyanide	Unknown	S
Isooctane (Fuel A)	100	n	Sodium hydroxide	10	l
Isopropanol	100	S to l	Sodium hydroxide	55	S
Kerosene	100	n	Sodium hypochlorite	20	l
Lactic acid	90	n	Sodium nitrate	Solution	S
Lead acetate	10	S	Sodium oxalate	Unknown	S
Linseed oil	100	n	Strong acids	Concentrated	l to n
Liquid paraffin	100	n	Strong bases	Unknown	S
Magnesium chloride	Unknown	S	Styrene	100	n
Mercury chloride	Unknown	l	Sulfur dioxide (gas)	Unknown	S
Methane chloride	100	n	Sulfuric acid	10	l
Methanol	100	l	Sulfuric acid	85–98	n
Methylacetate	100	n	Sulfuric acid	Fuming	n
Methylbromide	100	n	Sulfurous anhydride (gas)	Unknown	S
Methylbutylketone	100	n	Tetrachloroethane	100	n
Methylchloride	100	n	Tetrachloroethylene	100	n
Methylene chloride	100	n	Tetrahydrofuran	100	n
Methylethylketone	100	n	Thionyl chloride	100	n
Mineral oil	100	l	Tin chloride	Unknown	S
Monochlorobenzene	100	n	Titanium tetrachloride	Unknown	n
Monoethyleneglycol	100	S	Toluene	100	n
Naphtha	Unknown	n	Transformer oil	100	S
Nickel chloride	Unknown	S	Trichloroacetic acid	Unknown	S
Nitric acid	10–65	l	Trichloroethane	100	n
Nitric acid	100	n	Trichloroethylene	100	n
Nitrobenzene	100	n	Tricresylphosphate	Unknown	n
Nonanol	100	S	Triethanolamine	Unknown	S
Oleic acid	Unknown	l	Turpentine oil	100	l
Olive oil	100	l	Urea	Solution	S
Oxalic acid	Unknown	S	Urine	Unknown	S
Ozone	Unknown	S	Vegetable oil	100	l
Pentylacetate	100	n	Water	100	S
Pentylchloride	100	n	Weak bases	Unknown	S
Perchloroethylene	100	n	White spirit	100	n
Petrol aliphatic	100	n	Wine	Unknown	S
Petroleum	100	l	Xylene	100	n
Phenol	Unknown	l	Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only provided to give an idea and cannot be used for designing any parts or goods.

- Water vapour: polystyrene has a permeability evaluated at about 30 to 35 compared to the full range of 0.05 up to 400 for all tested plastics.
- Gases: polystyrene has an intermediate permeability, evaluated at:
- ○ air: 160 versus a full range of 3 up to 2750 for all tested plastics
- ○ carbon dioxide: 1600 versus a full range of 30 up to 59 000 for all tested plastics
- ○ nitrogen: 54 versus a full range of 1 up to 3500 for all tested plastics
- ○ oxygen: 470 versus a full range of <1 up to 11 000 for all tested plastics
- ○ hydrogen: 2500 versus a full range of 400 up to 20 000 for all tested plastics.

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames, even after the ignition source is removed. Moreover, polystyrene drips while burning and releases abundant black fumes.

Oxygen indices are roughly 18–19 with a HB UL94 rating.

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties. UL94 V0 rating can be reached for some FR grades.

4.10.6 Electrical properties

Polystyrenes are good insulators even in a wet environment with high dielectric resistivities, fair rigidities and low loss factors. Special grades are marketed for electrical applications.

Antistatic and conductive grades are marketed.

4.10.7 Joining, decoration

Welding is easy by the thermal processes, possible with ultrasound but impossible by the high-frequency technique.

Gluing is easy. All precautions must be taken concerning health and safety according to local laws and regulations.

Polystyrene can generally be decorated by:

- painting: the applications are frequent and withstand severe uses: parts for automobiles, TV, radio, data-processing, toys, medical
- printing: flexography, offset, serigraphy, heliography
- metallization: vacuum deposition and galvanoplasty.

4.10.8 Crosslinked polystyrene (X-PS or PS-X)

Polystyrene can be exceptionally crosslinked, leading to a tough and transparent material with improved electrical and thermal properties used as a dielectric material. Table 4.34 displays examples of crosslinked polystyrene properties. The data cannot be used for designing.

Table 4.34 Crosslinked polystyrene: examples of properties

Miscellaneous properties	
Density (g/cm^3)	1.05
Absorption of water (%)	0.02–0.03
Mechanical properties	
Shore hardness, D	85–90
Rockwell hardness, R	110–120
Rockwell hardness, M	50–60
Tensile strength (MPa)	55–70
Tensile modulus (GPa)	1.65
Thermal properties	
Continuous use temperature (°C)	93
Thermal conductivity (W/m.K)	0.17
Coefficient of thermal expansion (10^{-5}/°C)	7–9
Electrical properties	
Volume resistivity (ohm.cm)	10^{15}
Dielectric constant	2.5
Loss factor (10^{-4})	2
Dielectric strength (kV/mm)	27–47
Fire behaviour	
Oxygen index (%)	18
UL94 fire rating	HB

4.10.9 Foams (EPS – expandable polystyrene)

Depending on the region, the consumption of expandable polystyrene is 15–30% of the polystyrene total.

Unlike industrial solid polymers, which are processed as carefully as possible to avoid the formation of bubbles, vacuoles etc., alveolar materials result from the desire to introduce, in a controlled way, a certain proportion of voids with the aim of:

- improving the thermal or phonic insulating character: foams for packaging, construction . . .
- making damping parts: foams for packaging . . .
- increasing flexibility.

The alveolar materials consist of a polymer skeleton surrounding the cells, which may be closed or partially or completely open to neighbouring cells or the outside.

The intrinsic properties come from those of the polystyrene with:

- a reduction in the mechanical properties due to the small quantity of material and the high proportion of gas
- a reduction in the chemical behaviour due to the highly divided nature of the material. The thin cell walls immediately absorb liquids and gases and are rapidly damaged.

Rigid polystyrene foams are produced by two processes:

- expansion of expandable polystyrene chips in a mould, the oldest process, leading to alveolar rigid AR/PS-M according to ISO standard 4898-1984. This technique allows the realization of blocks and the moulding of parts directly into their final shape
- extrusion with gas injection leading to alveolar rigid AR/PS-E according to ISO standard 4898-1984. This technique allows the realization of blocks and sheets, which can then be machined.

Generally, the properties of the polystyrene foams are:

- low densities, usually from 10 kg/m^3 up to 50 kg/m^3
- closed cells

- damping and insulating properties (thermal and acoustic), which makes it possible to use them in the building and packaging sectors
- a low absorption of water and a low permeability to water vapour; good hydrolysis resistance
- sometimes weak mechanical properties but suitable products withstand sufficient loads to be used for the insulation of terraces being used as car parks or for structural packaging of heavy parts such as car engines
- a limited or weak resistance to solvents and hydrocarbons
- a naturally low fire resistance that can be improved by a suitable formulation

Table 4.35 shows some examples of polystyrene foam properties. The data cannot be used for designing.

Table 4.35 Examples of polystyrene foam properties

Examples of moulded foam properties			
Density (kg/m^3)	15	20	30
Density (g/cm^3)	0.015	0.02	0.03
Thermal conductivity at 10°C (W/m.K)	0.036–0.038	0.033–0.036	0.031–0.035
Absorption of water after 7 days (%)	0.5–1.5	0.5–1.5	0.5–1.5
Absorption of water after 28 days (%)	1–3	1–3	1–3
Stress at 10% strain in compression (MPa)	0.060–0.110	0.110–0.160	0.200–0.250
Modulus of elasticity (GPa)	0.002–0.005	0.003–0.007	0.008–0.011
Service compression strength (MPa)	0.015–0.025	0.025–0.040	0.045–0.060
Tensile strength (MPa)	0.110–0.290	0.170–0.350	0.300–0.480
Flexural strength (MPa)	0.060–0.300	0.150–0.390	0.330–0.570
Coefficient of thermal expansion (10^{-5}/°C)	5–7	5–7	5–7
Examples of extruded foam properties			
Density (kg/m^3)	25	40	50
Density (g/cm^3)	0.025	0.04	0.05
Thermal conductivity at 10°C (W/m.K)	0.029	0.027	0.027
Absorption of water after 28 days (%)	0.3	0.1	0.1
Stress at 10% strain in compression (MPa)	0.220	0.500	0.700
Modulus of elasticity (GPa)	0.010	0.022	0.035
Service compression strength (MPa)	0.125	0.320	0.450
Compressive stress for deformation lower than 2% after 10 years (MPa)	0.060	0.170	0.200
Compressive stress for deformation lower than 2% after 20 years (MPa)	0.050	0.120	0.160
Coefficient of thermal expansion (10^{-5}/°C)	6–8	6–8	6–8
Service temperatures (°C)	−50 to +75	−50 to +75	−50 to +75

Figure 4.44 shows examples of specific modulus (modulus/density ratio) versus density of polystyrene foams.

Polystyrene foams have applications in the following areas.

Building and public works

- Heat insulation of buildings:
  - ○ roofs, walls (insulation from the interior or exterior), floors of buildings and hangars including heavy handling (aeronautical) and underfloor heating
  - ○ breeze blocks, prefabricated components, coatings, mortars and light concretes containing expanded beads . . .

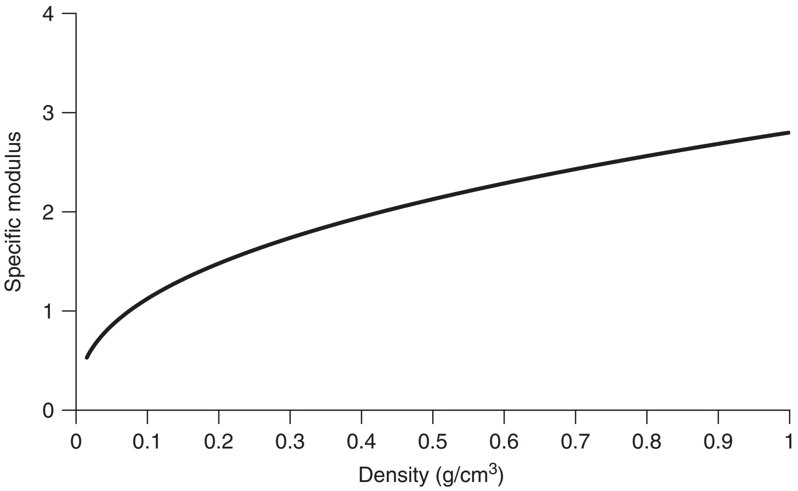


Figure 4.44. Modulus/density examples versus density of polystyrene foams

  - insulated panels for refrigerated warehouses and other cold storage facilities.
  - structural insulated panels
  - external panels of house or building with GFRP skins
  - disposable formworks
  - Conduits of cooling agents . . .
- Soundproofing of buildings:
  - floating floors reducing in particular the noise of impact.
- Public works: antifreeze bases of roads or railways . . .

Packaging: heat insulation, damping, structural functions

- Boxes, crates, cases for cooled foodstuffs: fish, ice creams . . .
- Packaging of electrical household appliances, TV, radio, office automation, electric tools . . .
- Structural industrial packaging: car engines . . .
- Packaging & display units.
- Flakes, chips, sheets . . .

Sports and leisure:

- Cores of sailboards, surfboards or beach boards with GFRP skins.
- Buoys and lifejackets . . .

Others

- Insulation of refrigerators, refrigerated coaches and boats.
- Artificial soil for horticulture.
- Models and mock-ups.
- Advertising elements.
- Puzzles.
- Hives.
- Raising of ships by filling with pre-expanded beads.
- Decorative beams for house interiors with laminate UP/FV skins.

Trade name examples: Bexfoam, Combat EPS, Resogaz, Styrodur, Styrofoam, Styropor, WeatherEX . . .

4.10.10 Specific ISO standards concerning polystyrene

ISO 1622-1:1994 Plastics – Polystyrene (PS) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 1622-2:1995 Plastics – Polystyrene (PS) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 2561:1974 Plastics – Determination of residual styrene monomer in polystyrene by gas chromatography

ISO 2897-1:1997 Plastics – Impact-resistant polystyrene (PS-I) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 2897-2:2003 Plastics – Impact-resistant polystyrene (PS-I) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 14631:1999 Extruded sheets of impact-modified polystyrene (PS-I) – Requirements and test methods

4.10.11 Trade name examples

Amphenol, Ancorene, Andrez, Avance, Bapolan, Bendalite, Bexfoam, Bextrene, BP Polystyrene, Carex, Carines, Celluliner, Cellulite, Climaflex, Combat EPS, Cyrene, Distrene, Dylene, Frimp, Hanarene, Intelin, Loalin, Loavar, Lustrex, Piccolastic, Plax Polystyrene, Plexine, Polyfibre, Polyflex, Polyweld, Portex, Resogaz, Rexol, Rexolite XPS, Ronilla, Roofmate, Styraloy, Styramic, Styrex, Styrite, Styrodur, Styrofoam, Styron, Styroplas, Styropor, Transpex, Trolitul, Waterlite, WeatherEX.

4.10.12 Property tables

Table 4.36 relates to examples only and cannot be generalized. The data cannot be used for designing. See also Table 4.34 for crosslinked polystyrene properties and Table 4.35 for foam properties.

Table 4.36 Polystyrenes: examples of properties

	Homopolymer		Heat resistant		Impact modified	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.04	1.05	1.04	1.05	1.03	1.06
Shrinkage (%)	0.1	0.7	0.2	0.7	0.2	0.7
Absorption of water (%)	0.01	0.04	0.01	0.04	0.05	0.30
Mechanical properties						
Shore hardness, D	85	90	90	95	60	75
Rockwell hardness, M	60	75	75	85	<10	<10
Stress at yield (MPa)	35	60	40	60	20	40
Strain at yield (%)	1	4	1	4		
Tensile strength (MPa)	35	60	40	60	20	45
Elongation at break (%)	1	4	1	4	20	65
Tensile modulus (GPa)	2.5	3.5	3.0	3.5	1.5	3.0
Flexural modulus (GPa)	2.5	3.5	3.0	3.5	1.5	3.0
Notched impact strength ASTM D256 (J/m)	20	25	20	25	100	350

(*continued*)

Table 4.36 (Continued)

	Homopolymer		Heat resistant		Impact modified	
	Min.	Max.	Min.	Max.	Min.	Max.
Thermal properties						
HDT B (0.46 MPa) (°C)	75	100	90	110	75	100
HDT A (1.8 MPa) (°C)	70	90	85	95	70	80
Vicat softening point A (°C)	84	106	99	103	82	101
Vicat softening point B (°C)	78	89	95	101	78	97
Continuous use temperature (°C)	65	80	75	90	60	80
Glass transition temperature (°C)	90	90	90	90	90	90
Brittle point (°C)	20	20	20	20	−40	−20
Thermal conductivity (W/m.K)	0.16	0.16	0.16	0.16	0.12	0.12
Specific heat (cal/g/°C)	0.32	0.32	0.32	0.32	0.35	0.35
Coefficient of thermal expansion (10^{-5}/°C)	5	8	6	8	5	20
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{17}	10^{16}	10^{16}	10^{16}	10^{16}
Dielectric constant	2.4	2.7	2.4	2.7	2.4	4.8
Loss factor (10^{-4})	1	28	1	28	4	20
Dielectric strength (kV/mm)	16	28			12	24
Arc resistance (s)	60	80			20	100
Fire behaviour						
Oxygen index (%)	18	19	18	19	18	19
UL94 fire rating	HB	HB	HB	HB	HB	HB
Special grades	FR V0		30% GF reinforced		Conductive	
Miscellaneous properties						
Density (g/cm³)	1.13	1.17	1.3			1.1
Shrinkage (%)	0.3	0.6	0.1			
Absorption of water (%)	0.05	0.30	0.07	0.1		
Mechanical properties						
Shore hardness, D	60	80	90	95		
Rockwell hardness, M	<10	<10	75	85		
Stress at yield (MPa)	20	30				
Strain at yield (%)	0.9	1				
Tensile strength (MPa)	15	30	85			27
Elongation at break (%)	2	50	1			36
Tensile modulus (GPa)	2	2.5				1.6
Flexural modulus (GPa)	2	2.5	6			
Notched impact strength ASTM D256 (J/m)	60	150	50		NB	
Thermal properties						
HDT B (0.46 MPa) (°C)	85	100	105			
HDT A (1.8 MPa) (°C)	80	85	100			
Continuous use temperature (°C)	50	80	50	70		
Glass transition temperature (°C)	90	90	90	90		
Brittle point (°C)	−40	−20				
Thermal conductivity (W/m.K)	0.12	0.12				
Specific heat (cal/g/°C)	0.35	0.35				
Coefficient of thermal expansion (10^{-5}/°C)	5	15	2.5			
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{15}	10^{16}	10^{2}	10^{7}
Dielectric constant	2.8	3	3.2			
Loss factor (10^{-4})	6	10	50			
Dielectric strength (kV/mm)	15	18	15			
Fire behaviour						
Oxygen index (%)	28	28	18	19		
UL94 fire rating	V0	V0	HB			

Table 4.36 (Continued)

	SMA		SMA 20% GF		SMA FR	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.05	1.08	1.2	1.2	1.2	1.2
Shrinkage (%)	0.4	0.8	0.2	0.3	0.5	0.5
Absorption of water (%)	0.1	0.3	0.1	0.3	0.1	0.3
Mechanical properties						
Shore hardness, D	83	85	83	85	83	85
Rockwell hardness, M	40	50	40	50	40	50
Stress at yield (MPa)	35	50	56	75	20	25
Strain at yield (%)			2	3	2	2
Tensile strength (MPa)	35	55	56	75	20	25
Elongation at break (%)	2	30	2	3	2	2
Tensile modulus (GPa)	2.4	3	5	6	1.8	2
Flexural modulus (GPa)	2.3	3.3	5	6	1.9	2
Notched impact strength ASTM D256 (J/m)	20	100	100	140	40	70
Thermal properties						
HDT A (1.8 MPa) (°C)	100	110	105	120	110	110
Continuous use temperature (°C)	80	100	85	100	85	100
Glass transition temperature (°C)	110	115	110	115	110	115
Coefficient of thermal expansion (10^{-5}/°C)	7	8	2	4	2	6
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}				
Dielectric constant	2.8	2.8				
Loss factor (10^{-4})	40	40				
Dielectric strength (kV/mm)	16	16				
Fire behaviour						
Oxygen index (%)	18	19	18	19		
UL94 fire rating	HB	HB	HB	HB	V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat unmodified polystyrenes.

Light	Risks of yellowing and embrittlement
Weak acids	Good behaviour
Strong acids	Good to limited behaviour except oxidizing acids
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Good to limited resistance against vegetable oils, alcohols, aliphatic amines, beverages, condiments and numerous foodstuffs, polyglycols and numerous pharmaceuticals Unsatisfactory against aldehydes, aromatic amines, esters, ethers, ketones, polyglycol ethers, aliphatic and aromatic hydrocarbons, chlorinated solvents, insecticides, essential oils
Food contact	Possible for special grades

4.11 Acrylonitrile-butadiene-styrene (ABS), methylmethacrylate-acrylonitrile-butadiene-styrene (MABS)

- ABS is often an alloy of styrene acrylonitrile (SAN) and polybutadiene rubber but sometimes it is a copolymer.

Acrylonitrile improves the gloss, mechanical and chemical performances of polystyrene. Butadiene improves impact strength but alters weathering and optical properties for the alloys.

- MABS is a copolymer of methylmethacrylate, acrylonitrile and butadiene. MABS combines the properties of ABS with transparency.

The properties of ABS vary broadly with the respective levels of each monomer, which can be:

- between 40% and 60% for styrene
- between 15% and 35% for acrylonitrile
- between 5% and 30% for butadiene.

4.11.1 General properties

Advantages

ABS is appreciated for its good mechanical properties including impact strength, attractive price/property ratios, fair dimensional stability, gloss, good low-temperature properties, easy processing, inertia and ESCR versus certain chemicals, weak absorption of water, fair density, good electrical insulation even in wet environments, feasibility of welding, versatility of processing methods, possibilities of food contact for specific grades, ease of joining.

The MABS and ABS copolymers are transparent.

Drawbacks

General drawbacks are the natural sensitivity to heat, UV, light and weathering (but stabilized grades are marketed), cost, poor scratch resistance, creep when the temperature rises, easy combustion with dripping, electrostatic build-up, opacity of alloys made of styrene-acrylonitrile and polybutadiene.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, compression, blow moulding, co-extrusion, thermoforming, structural foam, easy flow, medium flow . . .
- high heat grade, stabilized against UV, light and/or weathering; high transparency, antistatic, conductive, reinforced, food contact, fireproofed, high fluidity, impact modified, high gloss . . .
- films and sheets, tubes, pipes; suitable for post galvanoplasty, electroplating or metallization; ignition-resistant for electronic components and fixtures . . .

Costs

The costs as for all plastics fluctuate greatly with the crude oil price, and are only given to provide a general idea. They are generally of the order of some Euros per kilogram.

Processing

All the molten-state methods are usable: extrusion, injection, compression, blow moulding, thermoforming, co-extrusion, machining, welding.

Applications

(See Chapter 2 for further information.)

The statistically identified consumptions vary broadly according to the source but three sectors are predominant with market shares of about 20%:

• automotive & transportation	21–28%
• appliances	20–23%
• EE	11–21%
• recreational vehicles, boats and others	9%
• pipe, conduits, fittings	4–13%
• furniture	4%
• medical	4%

Some examples are quoted below without claiming to be exhaustive:

Automotive

- interior and exterior trims . . .
- Radiator grilles
- Instrument panels
- Glove box doors
- Consoles
- Housing of heating systems.
- Steering column trim . . .

Appliances, house wares, furniture

- Refrigerator door linings, refrigerator inner liners, trays . . .
- Domestic appliance housings, vacuum cleaners, small appliances, food mixers, electric shavers, electric toothbrushes . . .
- Electroplated parts, handles . . .
- Air conditioners . . .
- TV components and housings, video and audio tape cassettes . . .
- Telephone handsets . . .
- Lighting diffusers . . .
- Sanitary ware, paper towel and soap dispensers, bathroom cabinets, shelves . . .
- Toys . . .
- Components for furniture . . .
- Rigid luggage, vanity cases . . .

EE

- Telecommunication equipment . . .
- Consumer electronic equipment . . .
- Power tool housings . . .
- Computer housings, transparent and translucent covers for PCs and copiers, keyboards, business machine equipment . . .

Industry

- Tubing, pipes and fittings for aggressive environments and corrosive liquids
- Insulators . . .
- Housings . . .
- Handles . . .

Miscellaneous

- Enclosures
- Food packaging
- Cosmetics packaging . . .
- Fuselage of recreational plane
- Recreational vehicles, boats . . .

4.11.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 60°C up to 100°C or even 110°C for heat-resistant grades if softening temperatures are higher.

The UL temperature indices of specific grades can be:

- 50–80°C for the electrical and mechanical properties, including impact
- 50–95°C for the electrical properties alone.

Service temperatures can be lower under stress because of modulus decay, strain, creep, relaxation . . .

For example, for several grades of neat ABS, the HDTs A (1.8 MPa) are of the order of 80°C up to 120°C.

Figure 4.45 displays examples of modulus retention versus short-term temperature increase.

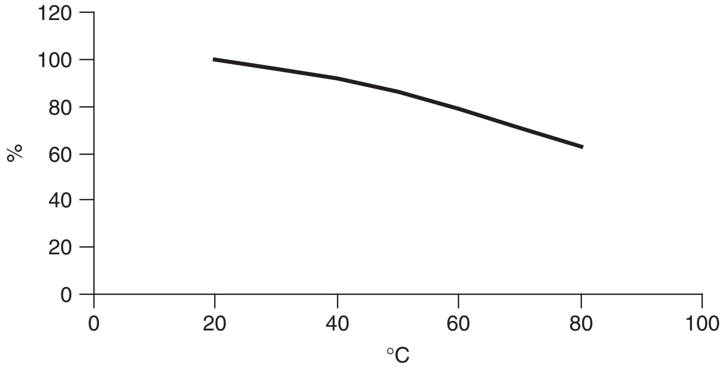


Figure 4.45. ABS examples of modulus retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Characteristics such as elongation at break and impact strength are especially heat sensitive.

At low temperatures, ABS is much less brittle than polystyrene and performs well down to –20°C or –40°C, according to the grade.

Figure 4.46 shows an example of impact strength versus low temperatures for a given ABS.

The glass transition temperatures of ABS by DSC measurements are generally about 95°C up to 115°C.

These results relate to some grades only and cannot be generalized.

4.11.3 Optical properties

Alloyed ABS is naturally opaque but comonomers are transparent.

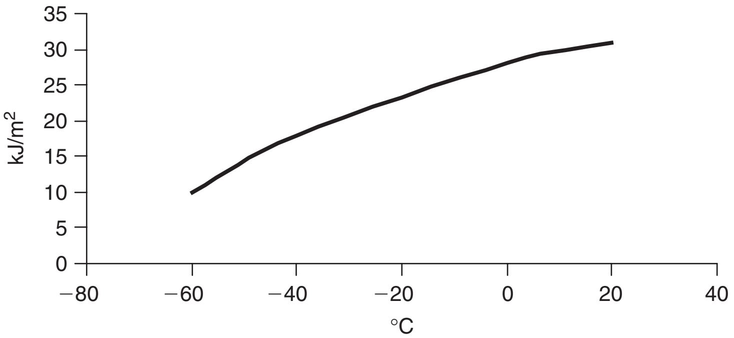


Figure 4.46. ABS: examples of notched impact strengths versus low temperatures (°C)

Transmission of light can vary from 60% up to 92% with haze of 3–4% and refractive index of about 1.52–1.53.

These results relate to some grades only and cannot be generalized.

4.11.4 Mechanical properties

The mechanical properties are generally fair with a much better impact strength than polystyrene. Moduli and hardnesses are higher than those of polyolefins. The abrasion and scratch resistance of ABS depend on the roughness, type and morphology of the opposing sliding surface but is limited and ABS is not designed for antifriction applications.

Dimensional stability

Shrinkage and coefficient of thermal expansion are in a rather low or average range for a polymer, depending on the rubber content. The absorption and alteration by moisture exposure are low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For example, data are reported in the range from 0.35 to 0.39.

Creep

Neat ABS grades have fair moduli at room temperature involving fair creep moduli, for example:

- 2.0–2.5 GPa after 1 h at room temperature under 7–14 MPa
- 1.4–2.1 GPa after 1000 h at room temperature under 7–14 MPa

From Figure 4.47(a) we can see:

- the big difference in creep modulus between two neat grades and a glass fibre (GF) reinforced ABS at room temperature
- the higher propensity to creep of the neat high-impact (HI) grade after 10 h, the more so as the time rises.

From Figure 4.47(b) we can observe the difference in creep moduli at room temperature (uppermost curve) and at moderate temperatures of 38°C and above.

These results relate to a few grades only and cannot be generalized.

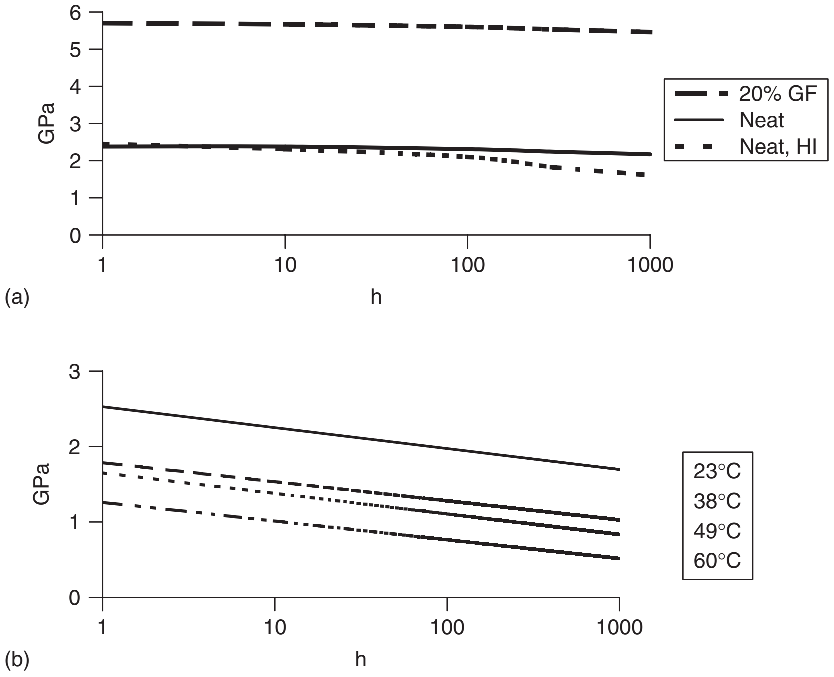


Figure 4.47 (a) Neat & 20% GF ABS creep: examples of creep modulus (GPa) at room temperature versus time (h) under 14 MPa loading; (b) Neat ABS creep: examples of creep modulus (GPa) at various temperatures versus time (h) under 7 MPa loading

4.11.5 Ageing

Dynamic fatigue

The dynamic fatigue can be fair for well-adapted grades if care is taken to limit the strains by restricting the stresses to values in keeping with the elongation at break.

For a given grade of ABS, Figure 4.48 displays an example of an SN or Wöhler's curve.

Weathering

ABS resists hydrolysis well but is naturally sensitive to light and UV the more so as the amount of polybutadiene increases. It must be protected by addition of anti-UV and other protective agents or by a film of UV-resistant polymer such as PVDF.

High-energy radiation

After gamma or electron beam sterilization, the impact strength of a given grade decreases by 25% after 25 kGy or 30% after 100 kGy, and the ABS yellows more or less permanently.

These results are examples only and cannot be generalized.

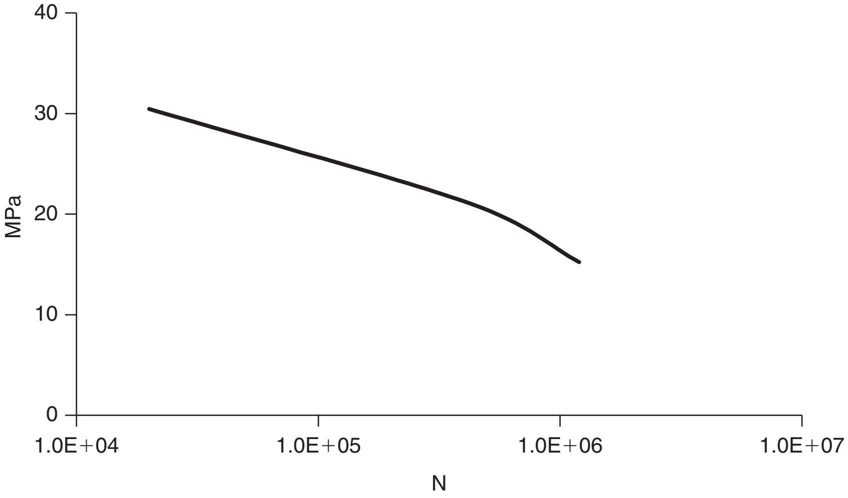


Figure 4.48. SN curve of ABS, examples of maximum stress S (MPa) versus number of cycles at failure (N)

Behaviour at high frequencies

ABS grades have loss factors in the range of 20–160 × 10^{-4} and are not generally welded under high-frequency current.

Chemicals

Neat ABS absorbs little water and is not very sensitive to it. Resistance to stress cracking is better than that of polystyrene.

Suitable grades are usable in contact with food and are used for food packaging.

Chemical resistance, which varies with the amounts of acrylonitrile and butadiene, is generally:

- excellent to limited against dilute inorganic and organic acids except strongly oxidizing acids; bases, saturated aliphatic hydrocarbons, vegetable oils, polyglycols and numerous foodstuffs
- unsatisfactory against concentrated strong acids, oxidizing agents, aldehydes, aromatic amines, esters, ethers, ketones, polyglycol ethers, aromatic hydrocarbons, chlorinated solvents . . .

Table 4.37 displays general assessments of behaviour in the presence of a range of chemicals after prolonged immersion at room temperature for given grades, which are not necessarily representative of all the ABS grades. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.37 ABS: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S	Acetonitrile	100	n
Acetic acid	25	l	Acetophenone	100	n
Acetic acid	⩾50	n	Acetyl chloride	100	n
Acetic aldehyde	100	n	Aliphatic hydrocarbons	100	S to l
Acetic anhydride	100	n	Allylic alcohol	96	n
Acetone	100	n	Aluminium chloride	Solution	S

(*continued*)

Table 4.37 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Aluminium sulfate	Unknown	S	Cyclohexane	100	l
Ammonium chloride	Solution	S	Cyclohexanol	100	l
Ammonium hydroxide	Dilute	S	Cyclohexanone	100	n
Ammonium hydroxide	30	l	Cyclohexylamine	Unknown	n
Ammonium nitrate	Unknown	S	Decaline	100	S
Ammonium sulfate	50	S	Diacetone alcohol	100	n
Amyl acetate	100	n	Dichloroethane	100	n
Amyl alcohol	100	n	Dichloroethylene	100	n
Aniline	100	n	Diethylamine	100	n
Antimony chloride	10	S	Diethyleneglycol	100	S
Aqua regia	Unknown	n	Diethylether	100	n
Arsenic acid	Unknown	S	Dimethylamine	100	n
ASTM1 oil	100	S	Dimethylformamide	100	n
ASTM2 oil	100	S	Dioctylphthalate	100	n
ASTM3 oil	100	l	Dioxan	100	n
Barium carbonate	Saturated	S	Ethanol	40–96	l
Barium chloride	Saturated	S	Ethanoldiamine	100	S
Beer	Unknown	S	Ethylacetate	100	n
Benzaldehyde	100	n	Ethylchloride	100	n
Benzene	100	n	Ethylene glycol	Unknown	S
Benzoic acid	Saturated	S	Ethylene glycol	100	S
Benzyl chloride	100	n	Ethylenebromide	100	n
Benzyl alcohol	100	n	Ethylhexanol	100	S
Boric acid	Unknown	S	Fluorine	100	S
Bromine (liquid)	100	n	Fluosilicic acid	Unknown	S
Butanol	100	n	Formaldehyde	35	S
Butanone	100	n	Formic acid	85–100	n
Butyl acetate	100	n	Formic acid	40	l
Butylamine	Unknown	n	Freon 11	100	n
Butylchloride	100	n	Freon 113	100	l
Butyric acid	Unknown	n	Freon 115	100	l
Butyric acid	100	n	Freon 12	100	S
Butyrylchloride	100	n	Freon 13b1	100	l
Calcium chloride	Unknown	S	Freon 21	100	l
Calcium hypochlorite	Solution	S	Freon 22	100	n
Carbon sulfide	100	n	Freon 32	100	l
Carbon tetrachloride	100	n	Furfural	100	n
Castor oil	100	S	Furfuryl alcohol	100	n
Cellosolve	100	n	Glucose	Dilute	S
Cellosolve acetate	100	n	Glycerol	100	S
Cetyl alcohol	Unknown	S	Heptane	100	S
Chlorine (dry gas)	100	n	Hexane	100	l
Chlorine (wet)	Unknown	n	Household bleach	Unknown	S
Chlorine dioxide	Unknown	n	Hydrochloric acid	10	S
Chloroacetic acid	Unknown	n	Hydrochloric acid	20–36	l
Chlorobenzene	100	n	Hydrochloric acid	Concentrated	n
Chloroform	100	n	Hydrofluoric acid	4	S
Chlorosulfonic acid	100	n	Hydrofluoric acid	40–100	n
Chromic acid	10	l	Hydrogen peroxide	3	S
Chromic acid	50	n	Hydrogen peroxide	10 V	l
Citric acid	10 to saturated	S	Hydrogen peroxide	30	l to n
Colza oil	100	S	Hydrogen peroxide	90	n
Copper sulfate	Unknown	S	Hydrogen sulfide gas	Unknown	S
Cresol	100	n	Iron(III) chloride	Unknown	S

Table 4.37 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Isobutanol	100	l
Isooctane (Fuel A)	100	l
Isopropanol	100	S
Isopropylacetate	100	n
Kerosene	100	S
Lactic acid	10	S
Lead acetate	10	S
Linseed oil	100	S
Liquid paraffin	100	S
Magnesium carbonate	Saturated	S
Magnesium chloride	Unknown	S
Magnesium sulfate	Unknown	S
Margarine	100	S
Mercury	100	S
Mercury chloride	Unknown	S
Methanol	100	l
Methylacetate	100	n
Methylbromide	100	n
Methylbutylketone	100	l
Methylene chloride	100	n
Methylethylketone	100	n
Milk	100	S
Mineral oil	100	S
Molasses	Unknown	S
Monochlorobenzene	100	n
Monoethyleneglycol	100	S
Mustard	Unknown	S
Naphtha	Unknown	S
Nickel chloride	Unknown	S
Nitric acid	5–10	S
Nitric acid	25	l
Nitric acid	65–100	n
Nitrobenzene	100	n
Nitromethane	100	n
Nitropropane	100	S
Nonanol	100	S
Oleic acid	Unknown	S
Olive oil	100	S
Oxalic acid	Unknown	S
Ozone	Unknown	n
Pentane	100	n
Pentanol	100	n
Pentylacetate	100	n
Perchloroethylene	100	n
Petrol aliphatic	100	n
Petroleum	100	l
Petroleum ether (ligroin)	Unknown	S
Phenol	5–90	n
Phosphoric acid	85	S
Phthalic acid	Saturated	S
Picric acid	Solution	n
Potassium cyanide	Unknown	S
Potassium fluoride	Unknown	S
Potassium hydroxide	45	S
Potassium permanganate	20	l
Potassium permanganate	Solution	S
Potassium sulfate	Unknown	S
Propanol	100	S
Propionic acid	100	n
Propylene oxide	100	n
Pyridine	100	n
Sea water	100	S
Silicone oil	100	S
Silver nitrate	Unknown	S
Sodium borate	Unknown	S
Sodium carbonate	10	S
Sodium chloride	25	S
Sodium cyanide	Unknown	S
Sodium fluoride	Saturated	S
Sodium hydroxide	10–55	S
Sodium hypochlorite	2–20	S
Sodium nitrate	Solution	S
Sodium perborate	Unknown	S
Styrene	100	n
Sulfur dioxide (gas)	Unknown	n
Sulfuric acid	2–70	S
Sulfuric acid	85 to fuming	n
Sulfurous acid	Solution	n
Sulfurous anhydride (gas)	Unknown	n
Tetrachloroethane	100	n
Tetrachloroethylene	100	n
Tetrahydrofuran	100	n
Thionyl chloride	100	n
Tin chloride	Unknown	S
Titanium tetrachloride	Unknown	l
Toluene	100	n
Transformer oil	100	S
Trichloroacetic acid	Unknown	l
Trichlorobenzene	Unknown	n
Trichloroethane	100	n
Trichloroethylene	100	n
Tricresylphosphate	Unknown	n
Triethanolamine	Unknown	S
Triethylamine	Unknown	l
Triethylene glycol	Unknown	S
Turpentine oil	100	n
Urea	Solution	S
Uric acid	Unknown	S
Vegetable oil	100	S
Vinyl acetate	100	n
Water	100	S
White spirit	100	S
Wine	Unknown	S
Xylene	100	n
Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory; V: by volume

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames, even after the ignition source is removed.

Oxygen indices are roughly 18–19 with a HB UL94 rating.

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties. UL94 V0 rating can be reached for some FR grades.

4.11.6 Electrical properties

ABS are good insulators even in a wet environment and are used for insulating housings of electric appliances, power tools. Special grades are marketed for electrical applications.

Antistatic grades are marketed.

4.11.7 Joining, decoration

Welding is easy by the thermal processes and possible with ultrasound but the high-frequency technique is unsuitable.

Gluing is easy. All precautions must be taken concerning health and safety according to local laws and regulations.

ABS can generally be decorated by:

- painting: the applications are frequent and withstand severe uses: parts for automobiles, TV, radio, data processing, toys, medical uses
- printing: flexography, offset, serigraphy, heliography
- metallization: vacuum deposition and galvanoplasty.

4.11.8 Specific ISO standards concerning ABS and MABS

ISO 727-1:2002 Fittings made from unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C) or acrylonitrile/butadiene/styrene (ABS) with plain sockets for pipes under pressure – Part 1: Metric series

ISO 727-2:2002 Fittings made from unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C) or acrylonitrile/butadiene/styrene (ABS) with plain sockets for pipes under pressure – Part 2: Inch-based series

ISO 2507-3:1995 Thermoplastics pipes and fittings – Vicat softening temperature – Part 3: Test conditions for acrylonitrile/butadiene/styrene (ABS) and acrylonitrile/styrene/acrylic ester (ASA) pipes and fittings

ISO 2580-1:2002 Plastics – Acrylonitrile-butadiene-styrene (ABS) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 2580-2:2003 Plastics – Acrylonitrile-butadiene-styrene (ABS) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 7245:1984 Pipes and fittings of acrylonitrile/butadiene/styrene (ABS) – General specification for moulding and extrusion materials

ISO 7682:2003 Plastics piping systems for soil and waste discharge (low and high temperature) inside buildings – Acrylonitrile-butadiene-styrene (ABS)

ISO 8283-4:1992 Plastics pipes and fittings – Dimensions of sockets and spigots for discharge systems inside buildings – Part 4: Acrylonitrile/butadiene/styrene (ABS)

ISO 8361-3:1991 Thermoplastics pipes and fittings – Water absorption – Part 3: Test conditions for acrylonitrile/butadiene/styrene (ABS) pipes and fittings

ISO 10366-1:2002 Plastics – Methyl methacrylate-acrylonitrile-butadiene-styrene (MABS) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 10366-2:2003 Plastics – Methyl methacrylate-acrylonitrile-butadiene-styrene (MABS) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 12092:2000 Fittings, valves and other piping system components made of unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C), acrylonitrile-butadiene-styrene (ABS) and acrylonitrile-styrene-acrylester (ASA) for pipes under pressure – Resistance to internal pressure – Test method

ISO 15493:2003 Plastics piping systems for industrial applications – Acrylonitrile-butadiene-styrene (ABS), unplasticized poly(vinyl chloride) (PVC-U) and chlorinated poly(vinyl chloride) (PVC-C) – Specifications for components and the system – Metric series

4.11.9 Trade name examples

Cycolac, Lustran ABS, Magnum, Novodur, Polylac, Terluran, Terlux . . .

4.11.10 Property tables

Table 4.38 relates to examples only and cannot be generalized. Data cannot be used for design purposes.

Table 4.38 ABS: examples of properties

	Heat resistant		High impact		MABS	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.00	1.15	1.00	1.10	1.08	1.08
Shrinkage (%)	0.4	0.9	0.4	0.9	0.5	0.6
Absorption of water (%)	0.10	0.80	0.10	0.80	0.35	0.7
Mechanical properties						
Shore hardness, D	80	85	75	85		
Rockwell hardness, M	30	50	<10	50		
Stress at yield (MPa)	30	64	20	57	42	48
Strain at yield (%)					4	4
Tensile strength (MPa)	30	60	30	45		
Elongation at break (%)	2	100	2	100	12	20
Tensile modulus (GPa)	1.5	3	1	2.5	1.9	2
Flexural modulus (GPa)	2	3	1	2.5		
Creep modulus 1000 h (GPa)					1.25	1.25
Notched impact strength ASTM D256 (J/m)	100	350	300	500	60	100
Thermal properties						
HDT B (0.46 MPa) (°C)	100	125	90	110	93	94
HDT A (1.8 MPa) (°C)	85	120	80	100	87	90
Vicat softening point A (°C)	114	125	98	114		
Vicat softening point B (°C)	103	115	83	103		
Continuous use temperature (°C)	75	110	65	100		
Glass transition temperature (°C)	105	115	95	110	107	107
Brittle point (°C)	−40	−20	−40	−20		
Thermal conductivity (W/m.K)	0.20	0.40	0.20	0.40		
Specific heat (cal/g/°C)	0.30	0.40	0.30	0.40		
Coefficient of thermal expansion (10^{-5}/°C)	6	10	6	13	9.5	9.5

(*continued*)

Table 4.38 (Continued)

	Heat resistant		High impact		MABS	
	Min.	Max.	Min.	Max.	Min.	Max.
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{16}	10^{16}	10^{13}	10^{15}
Dielectric constant	2.4	5	2.4	5	2.8	3
Loss factor (10^{-4})	20	350	20	350	130	160
Dielectric strength (kV/mm)	12	20	12	20	34	37
Arc resistance (s)	45	85	45	85		
Fire behaviour						
Oxygen index (%)	18	19	18	19	18	19
UL94 fire rating	HB	HB	HB	HB	HB	HB
Special grades	UL94 V0		Antistatic		15% GF	
Miscellaneous properties						
Density (g/cm^3)	1.15	1.24	1.05		1.17	1.19
Shrinkage (%)	0.3	0.8			<0.4	<0.4
Absorption of water (%)	0.10	0.80			0.3	0.3
Mechanical properties						
Shore hardness, D	80	90	75	80	75	80
Rockwell hardness, R	75	100	90	91	83	85
Rockwell hardness, M	30	70	<10	70	<10	40
Stress at yield (MPa)	25	60	48	50	60	65
Tensile strength (MPa)	30	50			80	86
Elongation at break (%)	2	80	30	40	3	3.5
Tensile modulus (GPa)	2	3	2.6		4.5	6.1
Flexural modulus (GPa)	2	4	2.3		3.9	4.1
Creep modulus 1000 h (GPa)			2.2			
Notched impact strength ASTM D256 (J/m)	70	350			60	70
Thermal properties						
HDT B (0.46 MPa) (°C)	90	120	99		105	117
HDT A (1.8 MPa) (°C)	80	110			102	111
Vicat softening point A (°C)	98	105	106	106	109	113
Vicat softening point B (°C)	83	97	96	97	102	116
Continuous use temperature (°C)	65	95			85	100
Glass transition temperature (°C)	105	115				
Brittle point (°C)	–40	–20				
Thermal conductivity (W/m.K)	0.17	0.17			0.19	0.19
Coefficient of thermal expansion (10^{-5}/°C)	6	11			3	3.5
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{15}			10^{14}	10^{14}
Dielectric constant	3	3			3.4	3.4
Loss factor (10^{-4})	120	120			170	170
Fire behaviour						
Oxygen index (%)			18	19	18	19
UL94 fire rating	V0	V0	HB	HB	HB	HB

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Risks of yellowing and embrittlement
Weak acids	Good behaviour
Strong acids	Limited to unsatisfactory behaviour
Bases	Good to limited behaviour
Solvents	Good to limited resistance against vegetable oils, saturated aliphatic hydrocarbons, polyglycols and numerous foodstuffs Unsatisfactory against aldehydes, aromatic amines, esters, ethers, ketones, polyglycol ethers, aromatic and certain aliphatic hydrocarbons, chlorinated solvents . . .
Food contact	Possible for special grades

4.12 Styrene acrylonitrile (SAN), acrylate rubber modified styrene acrylonitrile (ASA), acrylonitrile EPDM styrene (AES or AEPDS), acrylonitrile chlorinated polyethylene styrene (ACS)

- Styrene acrylonitrile (SAN) is copolymerized from styrene and acrylonitrile:

$$\text{styrene: } CH_2{=}CH(C_6H_5)$$

$$\text{acrylonitrile: } CH_2{=}CH(CN)$$

The backbone is identical to that of polystyrene but some pendant groups are different.

- ASA is an acrylate rubber-modified styrene acrylonitrile copolymer
- AES (or AEPDS) is an acrylonitrile-(ethylene-propylene-diene)-styrene
- ACS is an acrylonitrile-(chlorinated polyethylene)-styrene.

Acrylonitrile improves the gloss, mechanical and chemical performances of polystyrene.

Acrylate rubber, EPDM and chlorinated polyethylene improve impact strength, replacing the polybutadiene of ABS:

- acrylate rubber leads to better chemical resistance
- EPDM leads to better weathering resistance
- CPE offers a good balance of chemical and weathering resistance.

Properties vary broadly with the respective levels of each monomer.

Where no other information is given, the following properties relate to SAN.

4.12.1 General properties

Advantages

SAN is appreciated for its gloss; resistance to oils, fats, greases, stress cracking, food staining, cleaning agents and crazing; pleasing appearance especially when coloured; stiffness, attractive price/property ratios, fair dimensional stability, fair absorption of water, good electrical insulation even in wet environments, feasibility of welding, possibilities of food contact for specific grades, ease of joining and printing.

Rubber-modified SAN are appreciated for their better impact strength and low-temperature behaviour.

Drawbacks

General drawbacks are the natural sensitivity to heat, UV, light and weathering (but stabilized grades are marketed), cost, creep when the temperature rises, easy combustion with dripping, electrostatic build-up, limited number of producers.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, easy flow . . .
- high heat grade, stabilized against UV, light and/or weathering; high transparency, antistatic, high hardness, reinforced, food contact, fireproofed, high toughness, high impact, high or low gloss, improved chemical resistance . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, but are generally slightly higher than those of ABS.

Processing

All the molten-state methods are usable: extrusion, injection, thermoforming, co-extrusion, machining, welding.

Applications

(See Chapter 2 for further information.)

Some examples are quoted below without claiming to be exhaustive:

Automotive

- Tail lights
- Reflectors . . .

Appliances, house wares, furniture

- Kitchenware such as mixing bowls and basins; small appliances, food mixers, coffee filters, outer casings of thermally insulated jugs . . .
- Tableware, drinking tumblers, cutlery, jars and beakers, storage containers for foods . . .
- Bathroom fittings, toothbrushes, toothbrush handles, sanitary ware, soap dispensers, shower cubicle, shelves . . .
- Dishwasher parts, washing machine trims . . .
- Radio dials, TV set screens, hi-fi covers . . .
- Refrigerator parts: trays, fittings, shelves . . .
- Cylindrical impellers for air-conditioners . . .
- Picnic ware . . .
- Toys . . .
- Components for furniture . . .

EE

- Outer covers of printers, calculators, instruments, transparent covers for PCs and copiers, business machine equipment . . .
- Telecommunications equipment . . .
- Consumer electronic equipment . . .

Industry

- Outer covers for instruments, machines and lamps . . .
- Lenses . . .
- Handles . . .

Miscellaneous

- Cosmetics packaging . . .
- Writing and drawing equipment . . .

4.12.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 70°C up to 90°C if softening temperatures are higher.

The UL temperature indices of specific grades can be lower, down to 50°C for the electrical and mechanical properties including impact.

Service temperatures can be lower under stress because of modulus decay, strain, creep, relaxation . . .

For example, for several grades of neat SAN and ASA, the HDTs A (1.8 MPa) are of the order of 75°C up to 100°C.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Characteristics such as elongation at break and impact strength are especially heat sensitive.

The glass transition temperatures of SAN by DSC measurements are generally about 115°C. SAN is brittle at room temperature but ASA has higher impact strength at low temperatures.

These results relate to some grades only and cannot be generalized.

4.12.3 Optical properties

SAN and ASA are naturally transparent with high light transmission, possibly superior to 90%, and a refractive index of about 1.56–1.57 for a SAN grade. Haze is low, about 0.4–0.8%.

These results relate to some grades only and cannot be generalized.

4.12.4 Mechanical properties

The mechanical properties are generally fair with a much better impact strength for ASA than for SAN. Moduli of SAN are higher than those of polyolefins and decrease more slowly as temperature rises, as we can see from Figure 4.49.

The abrasion and scratch resistances of SAN are fair but depend on the roughness, type and morphology of the opposing sliding surface.

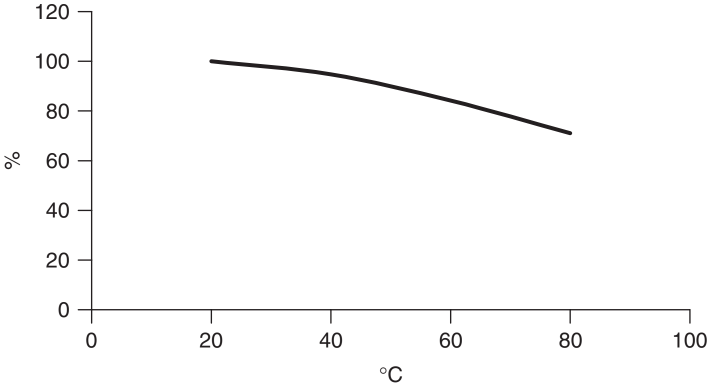


Figure 4.49. SAN examples of modulus retention (%) versus temperature (°C)

Dimensional stability

Shrinkage and coefficient of thermal expansion are in a rather low or average range for a polymer, depending on the ratio of comonomers. The absorption and alteration by moisture exposure are low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation.

Creep

Neat SAN grades have fair moduli at room temperature involving fair creep moduli, for example:

- 3.5 GPa after 1 h
- 2.8 GPa after 1000 h.

Neat ASA grades have lower moduli at room temperature involving lower creep moduli, for example:

- 1.8 GPa after 1 h
- 1.4 GPa after 1000 h.

From Figure 4.50(a) we can see, for grades different to those above, the difference in creep moduli between SAN and ASA under the same loading at room temperature.

Figure 4.50(b) shows the large difference in creep moduli at room temperature (upper curve) and 60°C for an ASA grade different from the previous one.

These results relate to a few grades only and cannot be generalized.

4.12.5 Ageing

Dynamic fatigue

The dynamic fatigue can be fair for well-adapted grades if care is taken to limit the strains by restricting the stresses to values in keeping with the elongation at break.

For a given grade of SAN, stress amplitude measured in accordance with DIN 53 442 is about 25 MPa for a failure at 10^7 cycles.

Weathering

ASA resists hydrolysis well and is naturally much less sensitive to light and UV than ABS. Retention of mechanical performances is far better and yellowing is far lower.

Chemicals

SAN and ASA absorb little water and are not very sensitive to it. Resistance to stress cracking is better than that of polystyrene.

Suitable grades are usable in contact with food.

Chemical behaviour depends on the styrene/acrylonitrile ratio and the amount of other monomers, if present.

Chemical resistance is generally:

- excellent to limited against dilute inorganic and organic acids except strongly oxidizing acids; bases, oils and greases, saturated aliphatic hydrocarbons, vegetable oils, polyglycols and numerous foodstuffs, alcohols (variable with the nature of the alcohol)
- unsatisfactory against concentrated strong acids, oxidizing agents, aldehydes, aromatic amines, esters, ethers, ketones, polyglycol ethers, aromatic hydrocarbons, chlorinated solvents . . .

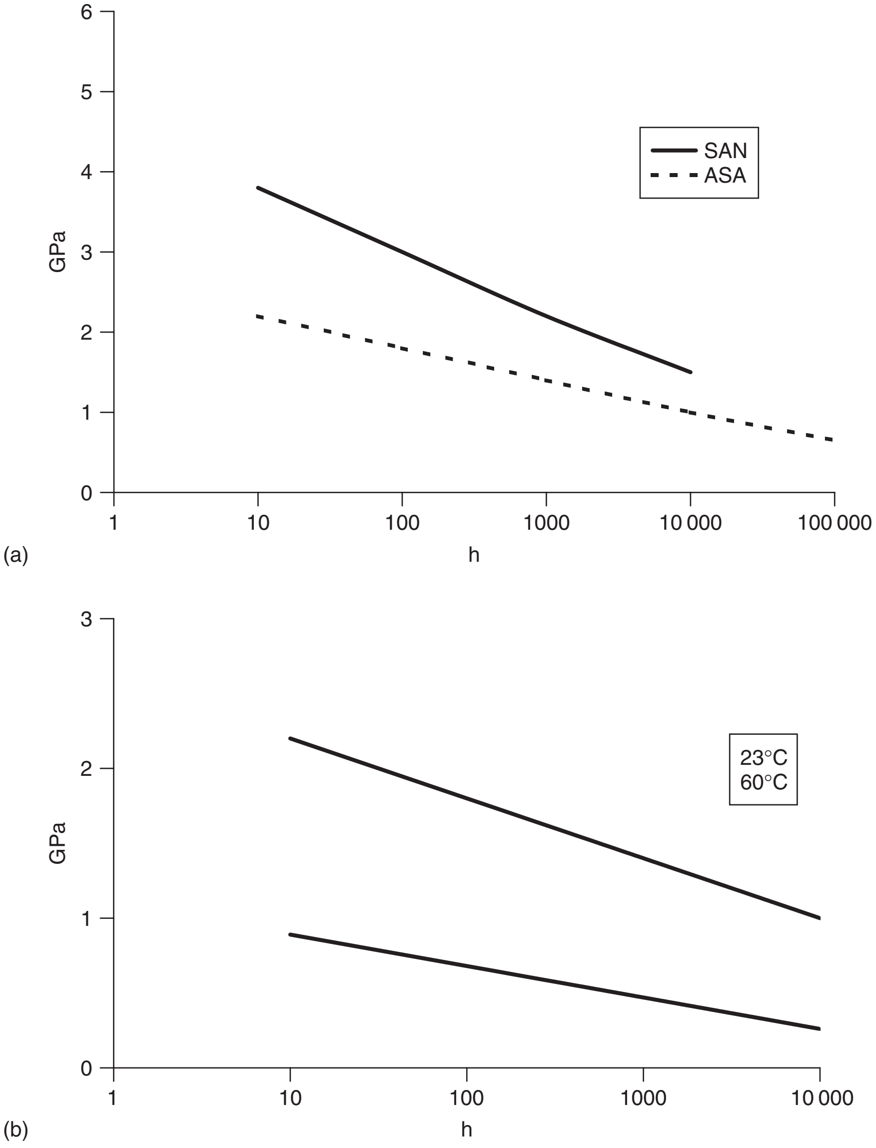


Figure 4.50. (a) SAN & ASA creep: examples of creep modulus (GPa) at room temperature versus time (h) under 20 MPa loading; (b) ASA creep: examples of creep modulus (GPa) at various temperature versus time (h) under 15 MPa loading

Table 4.39 displays general assessments of behaviour in the presence of a range of chemicals after prolonged immersion at room temperature for given grades, which are not necessarily representative of all the SAN grades. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames, even after the ignition source is removed.

Oxygen indices are roughly 18–19 with a HB UL94 rating.

Table 4.39 SAN: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10–40	S	Dichloroethane	100	n
Acetic acid	>96	n	Dichloroethylene	100	n
Acetic aldehyde	100	n	Diethyleneglycol	100	S
Acetic anhydride	100	n	Diethylether	100	n
Acetone	100	n	Dimethylamine	100	S
Acetonitrile	100	n	Dimethylformamide	100	n
Acetophenone	100	n	Dioctylphthalate	100	n
Aliphatic hydrocarbons	100	l	Dioxan	100	n
Aluminium chloride	Solution	S	Ethanol	40–96	S
Aluminium sulfate	Unknown	S	Ethanol	Unknown	l
Ammonium hydroxide	30	S	Ethylacetate	100	n
Ammonium sulfate	50	S	Ethylene glycol	100	S
Amyl acetate	100	n	Ethylhexanol	100	S
Amyl alcohol	100	S	Fluorine	100	n
Aniline	100	n	Formaldehyde	37	S
Aqua regia	Unknown	n	Freon 11	100	l
ASTM1 oil	100	S	Freon 113	100	n
ASTM2 oil	100	S	Freon 12	100	l
ASTM3 oil	100	l	Freon 32	100	l
Barium chloride	Saturated	S	Furfural	100	n
Benzaldehyde	100	n	Glycerol	100	S
Benzene	100	n	Hexane	100	S
Benzoic acid	Saturated	S	Household bleach	Unknown	S
Benzyl alcohol	100	n	Hydrochloric acid	10–36	S
Boric acid	Unknown	S	Hydrofluoric acid	40	l
Bromine (liquid)	100	n	Hydrogen peroxide	3	S
Butanol	100	S	Hydrogen sulfide gas	Unknown	S
Butanone	100	n	Iron(III) chloride	Unknown	S
Butyl acetate	100	n	Isobutanol	100	l
Butyric acid	Unknown	n	Isooctane (Fuel A)	100	S
Calcium chloride	Unknown	S	Isopropanol	100	S
Calcium hypochlorite	Solution	S	Kerosene	100	S
Carbon sulfide	100	n	Lactic acid	10–90	S
Carbon tetrachloride	100	l	Linseed oil	100	S
Castor oil	100	S	Liquid paraffin	100	S
Cellosolve	100	n	Magnesium chloride	Unknown	S
Cellosolve acetate	100	n	Mercury chloride	Unknown	S
Chlorine (dry gas)	100	n	Methanol	100	n
Chlorine dioxide	Unknown	n	Methylbromide	100	n
Chloroacetic acid	Unknown	l	Methylbutylketone	100	n
Chlorobenzene	100	n	Methylene chloride	100	n
Chloroform	100	n	Methylethylketone	100	n
Chlorosulfonic acid	Unknown	n	Mineral oil	100	S
Chromic acid	20	S	Monochlorobenzene	100	n
Citric acid	10	S	Monoethyleneglycol	100	S
Colza oil	100	S	Naphtha	Unknown	S
Copper sulfate	Unknown	S	Nickel chloride	Unknown	S
Cresol	100	l	Nitric acid	5–25	S
Cyclohexane	100	S	Nitric acid	65	l
Cyclohexanol	100	S	Nitric acid	100	n
Cyclohexanone	100	n	Nitrobenzene	100	n
Decaline	100	S	Nonanol	100	S
Diacetone alcohol	100	n	Oleic acid	Unknown	S
Dibutylphthalate	100	n	Olive oil	100	S

Table 4.39 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Oxalic acid	Dilute	S	Sodium hypochlorite	13–20	S
Ozone	Unknown	S	Sodium nitrate	Solution	S
Pentylacetate	100	n	Sulfuric acid	2–25	S
Perchloroethylene	100	l	Sulfuric acid	70 to fuming	n
Petroleum	100	S	Tetrachloroethane	100	n
Phenol	Unknown	n	Tetrachloroethylene	100	l
Phosphoric acid	85	l	Tetrahydrofuran	100	n
Potassium fluoride	Unknown	S	Thionyl chloride	100	n
Potassium hydroxide	10–45	S	Titanium tetrachloride	Unknown	n
Potassium permanganate	20	S	Toluene	100	n
Potassium sulfate	Unknown	S	Trichloroethane	100	n
Propanol	100	S	Trichloroethylene	100	n
Propylene oxide	100	n	Tricresylphosphate	Unknown	n
Pyridine	Unknown	n	Triethanolamine	Unknown	S
Silver nitrate	Unknown	S	Turpentine oil	100	l
Sodium borate	Unknown	S	Water	100	S
Sodium carbonate	10	S	White spirit	100	S
Sodium chloride	25	S	Wine	Unknown	S
Sodium cyanide	Unknown	S	Xylene	100	n
Sodium hydroxide	10–55	S	Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties.

4.12.6 Electrical properties

SAN and ASA are good insulators even in wet environments and are used for insulating housings of electric appliances, power tools. Special grades are marketed for electrical applications and others for antistatic parts.

4.12.7 Joining, decoration

Welding is easy by the thermal processes and possible with ultrasound.

Gluing is easy. All precautions must be taken concerning health and safety according to local laws and regulations.

SAN and ASA can generally be decorated by:

- painting: the applications are frequent and withstand severe uses: parts for automobiles, TV, radio, data processing, toys, medical uses
- printing: flexography, offset, serigraphy, heliography
- metallization: vacuum deposition and galvanoplasty.

4.12.8 Specific ISO standards concerning SAN, ASA, AEPDS and ACS

ISO 12092:2000 Fittings, valves and other piping system components made of unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C), acrylonitrile-butadiene-styrene (ABS) and acrylonitrile-styrene-acrylester (ASA) for pipes under pressure – Resistance to internal pressure – Test method

ISO 4894-1:1997 Plastics – Styrene/acrylonitrile (SAN) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 4894-2:1995 Plastics – Styrene/acrylonitrile (SAN) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 19220:2004 Plastics piping systems for soil and waste discharge (low and high temperature) inside buildings – Styrene copolymer blends (SAN + PVC)

ISO 2507-3:1995 Thermoplastics pipes and fittings – Vicat softening temperature – Part 3: Test conditions for acrylonitrile/butadiene/styrene (ABS) and acrylonitrile/styrene/acrylic ester (ASA) pipes and fittings

ISO 6402-1:2002 Plastics – Acrylonitrile-styrene-acrylate (ASA), acrylonitrile-(ethylene-propylene-diene)-styrene (AEPDS) and acrylonitrile-(chlorinated polyethylene)-styrene (ACS) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 6402-2:2003 Plastics – Acrylonitrile-styrene-acrylate (ASA), acrylonitrile-(ethylene-propylene-diene)-styrene (AEPDS) and acrylonitrile-(chlorinated polyethylene)-styrene (ACS) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 7246:1984 Pipes and fittings of acrylonitrile/styrene/acrylester (ASA) – General specification for moulding and extrusion materials

ISO 12092:2000 Fittings, valves and other piping system components made of unplasticized poly(vinyl chloride) (PVC-U), chlorinated poly(vinyl chloride) (PVC-C), acrylonitrile-butadiene-styrene (ABS) and acrylonitrile-styrene-acrylester (ASA) for pipes under pressure – Resistance to internal pressure – Test method

4.12.9 Trade name examples

Luran, Luran S, Lustran SAN, Starex SAN, Tyril

4.12.10 Property tables

Table 4.40 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.40 SAN and ASA: examples of properties

	SAN		SAN antistatic		ASA	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.06	1.10	1.07	1.09	1.05	1.07
Shrinkage (%)	0.2	0.7	0.2	0.4	0.4	0.7
Absorption of water (%)	0.15	0.30	0.2	0.3	0.20	0.30
Mechanical properties						
Shore hardness, D	80	95	91	92	75	80
Rockwell hardness, R	100	>120	>120	>120	83	100
Rockwell hardness, M	30	80	75	76	<10	30
Stress at yield (MPa)	60	85	65	75	35	40
Strain at yield (%)	2	5				
Tensile strength (MPa)	65	85			47	56
Elongation at break (%)	2	6.5			15	40

Table 4.40 (Continued)

	SAN		SAN antistatic		ASA	
	Min.	Max.	Min.	Max.	Min.	Max.
Tensile modulus (GPa)	2.8	4	2.8	3.5	2	2.6
Flexural modulus (GPa)	3.5	4.2	3.5	3.7	1.5	2.4
Notched impact strength ASTM D256 (J/m)	10	30			100	600
Thermal properties						
HDT B (0.46 MPa) (°C)	95	105			80	101
HDT A (1.8 MPa) (°C)	90	100	90	92	75	96
Vicat softening point A (°C)	104	111				
Vicat softening point B (°C)	97	102			102	103
Continuous use temperature (°C)	85	95	80	85	80	90
Glass transition temperature (°C)	115	115				
Brittle point (°C)	20	20				
Thermal conductivity (W/m.K)	0.15	0.15			0.17	0.17
Specific heat (cal/g/°C)	0.33	0.33			0.33	0.33
Coefficient of thermal expansion (10^{-5}/°C)	6	8			5	11
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{13}	10^{14}	10^{14}	10^{15}
Dielectric constant	2.5	3.4			3.3	3.8
Loss factor (10^{-4})	70	100			90	340
Dielectric strength (kV/mm)	12	24				
Arc resistance (s)	100	150				
Fire behaviour						
Oxygen index (%)	18	19	18	19	18	19
UL94 fire rating	HB	HB	HB	HB	HB	HB

Glass fibre reinforced	SAN 10% GF		SAN 20% GF		SAN 30% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.15	1.16	1.20	1.25	1.30	1.31
Shrinkage (%)	0.2	0.4	0.1	0.3	0.1	0.3
Absorption of water (%)	0.10	0.30	0.10	0.30	0.10	0.30
Mechanical properties						
Shore hardness, D	90	95	90	95	95	95
Rockwell hardness, M	89	91	89	91	90	92
Stress at yield (MPa)	90	100	110	120	125	130
Strain at yield (%)			1	2		
Tensile strength (MPa)			100	120		
Elongation at break (%)	1	3	1	3	1	3
Tensile modulus (GPa)			8	11		
Flexural modulus (GPa)	5	6	7	8	9	9.5
Notched impact strength ASTM D256 (J/m)	40	50	50	60	55	65
Thermal properties						
HDT B (0.46 MPa) (°C)			105	110		
HDT A (1.8 MPa) (°C)	100	105	95	106	106	109
Continuous use temperature (°C)	85	95	85	95	85	95
Glass transition temperature (°C)	115	115	115	115	115	115
Brittle point (°C)	20	20	20	20	20	20
Coefficient of thermal expansion (10^{-5}/°C)			2	4		
Fire behaviour						
Oxygen index (%)	18	19	18	19	18	19
UL94 fire rating	HB	HB	HB	HB	HB	HB

4.13 Polyamides or nylons (PA)

Polyamides or nylons are:

- homopolymers of an amino acid
- copolymers of a diamine and a diacid.

$$H_2N{-}R{-}COOH \text{ leads to: } H_2N{-}R{-}CO{-}(NH{-}R{-}CO{-})_n{-}NH{-}R{-}COOH$$

$$H_2N{-}Ra{-}NH_2 + HOOC{-}Rb{-}COOH \text{ lead to: } {-}(HN{-}Ra{-}NH{-}CO{-}Rb{-}CO)_n{-}$$

The polyamides differ by the nature and lengths of the units between amide groups and by the arrangement of these amide groups. Certain properties are clearly affected by the length of the chains.

The most commonly used polyamides are linear but special ones are semi-aromatic with an aromatic diacid and a linear diamine or a linear diacid and an aromatic diamine.

- **PA 66** is a copolymer of hexamethylenediamine (C_6 diamine) and adipic acid (C_6 diacid).
- **PA 6** is the homopolymer of a C_6 amino acid.
- **PA 11** and **PA 12** are the homopolymers of C_{11} and C_{12} amino acids, respectively.
- **PA 610** is a copolymer of C_6 diamine and C_{10} diacid.
- **PA 612** is a copolymer of C_6 diamine and C_{12} diacid.
- **PA 46** is a copolymer of C_4 diamine and C_6 diacid.
- **Semi-aromatic PAs** are copolymers of an aromatic diacid and a linear diamine or a linear diacid and an aromatic diamine. Polyphthalamide (PPA) and polyarylamide (PAA) are semi-aromatic, semi-crystalline PAs. Some amorphous semi-aromatic PAs are transparent.
- **Liquid PA** is a block copolymer of caprolactam and a prepolymer.

All the PAs are engineering polymers with good mechanical performances, fair heat and fatigue resistances, interesting low-temperature behaviour, and resistance to oils, greases, hydrocarbons and numerous common solvents, but each subfamily has its features:

- PA 66 is the oldest, the best known, with the predominant share of the consumption of all polyamides – and is among the cheapest.
- PA 6 is the cheapest and technically very close to PA 66, but is far less used.
- PA 11 and PA 12 are more flexible, have a better behaviour at low temperature and are less sensitive to water and moisture but are more expensive. Their market share is only a few percent of the total polyamide consumption.
- PA 610 and PA 612 have intermediate properties between PA 66 and PA 11. Concerning sensitivity to water and moisture they are nearer to PA 11, and nearer to PA 66 for rigidity.
- PA 46 has better property retention when the temperature rises: higher HDT and higher modulus at high temperature.
- Semi-aromatic PAs generally have a weak and slow absorption of water, a high rigidity, and are claimed to be more resistant to weathering and oils. For example, properties of polyphthalamides are intermediate between those of PA 66 and polyphenylene sulfide (PPS).
- Some amorphous semi-aromatic PAs are transparent.
- Liquid PAs can be processed in the liquid state, which simplifies tools and processing machines.

Polyamides are often:

- reinforced with mineral fillers, glass or carbon fibres.
- modified with specific additives to improve impact behaviour, tribological properties, etc.

The amide groups of the backbone are hydrophilic and, consequently, polyamides are also hydrophilic, the more so the higher the amide ratio. The absorbed water plasticizes the polyamides leading to higher impact resistances and lower strengths and moduli. When comparing properties of various polyamides careful attention must be paid to the moisture content of the considered materials. Tests can be made on samples:

- dry as moulded
- wet after:
  - ○ storage at 50% RH for 24 h or more
  - ○ immersion in water for 24 h or more.

For example:

- a given grade of PA 66 has a yield stress of 90 MPa in the dry state versus 50 MPa at equilibrium with a 50% RH environment
- another grade of PA 66 has an impact strength of 12 kJ/m^2 in the dry state versus 24 kJ/m^2 at equilibrium with a 50% RH environment.

Figure 4.51(a) compares the water absorption of several subfamilies of polyamides under the same conditions (low moisture).

Figure 4.51(b)–(d) display in a simplified manner the evolution of basic polyamide properties for various neat grades.

Figure 4.51(e) Displays the combined influences of polyamide structure and additives:

- mineral fillers
- glass fibres
- impact modifier and glass fibres.

Note that the modulus scale is four times that of Figure 4.51(c).

4.13.1 Polyamides 66 and 6 (PA 66 and PA 6)

4.13.1.1 General properties

Advantages

PA 66 and PA 6 are engineering polymers with good mechanical performances; fair heat and fatigue resistances; rather interesting low-temperature behaviour, resistance to oils,

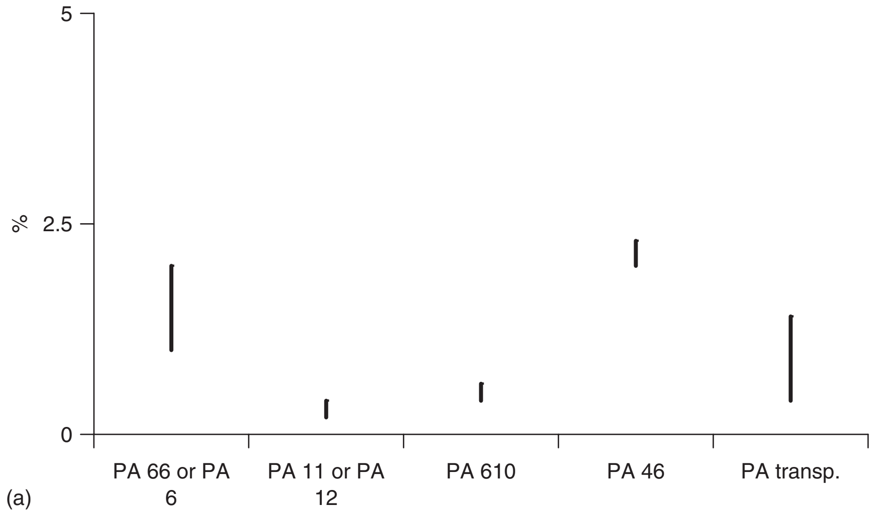


Figure 4.51. (a) Neat PA: water absorption (%)

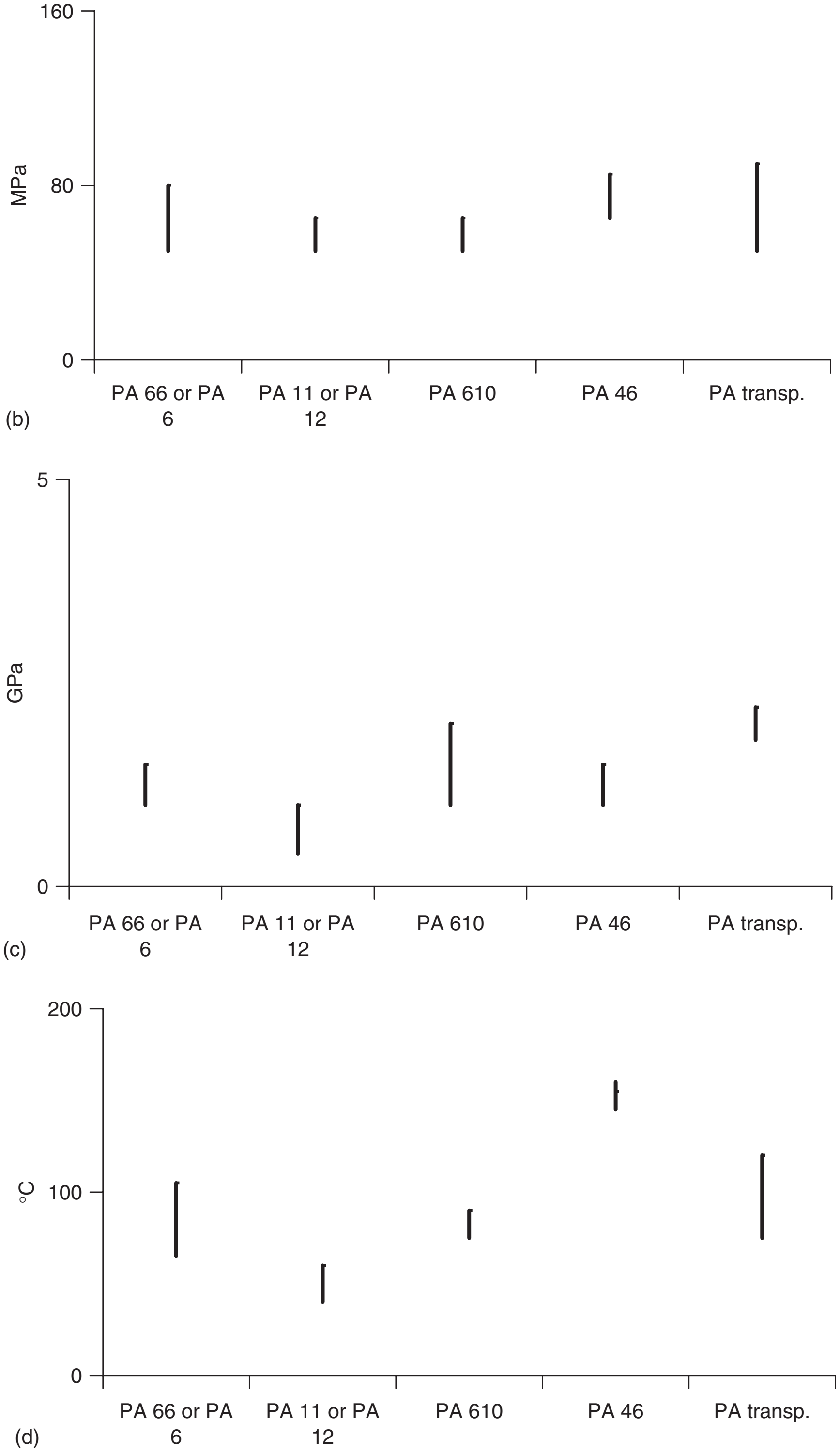


Figure 4.51. (continued) *(b) Neat PA: stress at yield examples (MPa); (c) Neat PA: modulus examples (GPa); (d) Neat PA: HDT A (°C)*

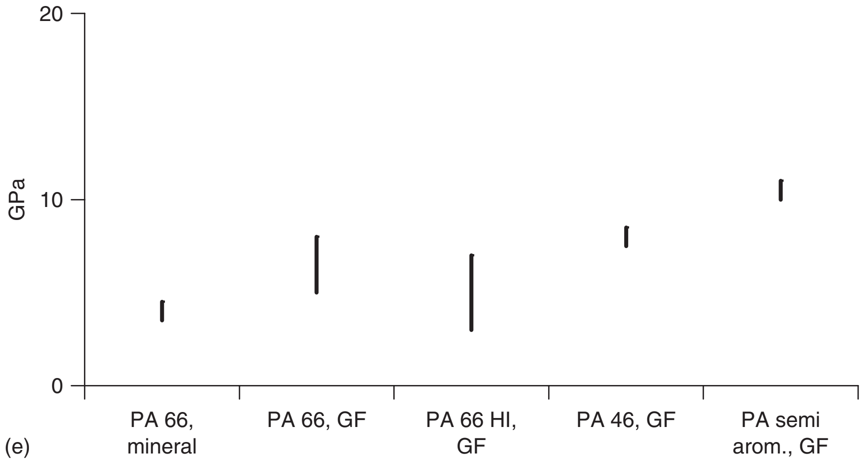


Figure 4.51. (continued) (e) Reinforced PA: tensile modulus (GPa)

greases, hydrocarbons and numerous current solvents; fair antifriction properties enhanced by formulation; super-tough qualities with high impact resistance.

PA 66 is the oldest, the best known, the most used, with probably more than 70% of the total polyamide consumption, and is among the cheapest.

PA 6 is technically very close to PA 66 but is far less used, perhaps about 20%.

Drawbacks

More expensive than commodities such as polyolefins, PVC and polystyrene; brittle when dry, sensitive to water (swelling up to 10%, decrease in mechanical and electrical properties); opaque or translucent; require UV and weathering protection; significant shrinkage after moulding; inherent flammability (but FR grades are marketed).

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, compression, cast film, blown film, blow moulding, co-extrusion, for thin or thick parts . . .
- stabilized against heat, hydrolysis, UV, light and/or weathering; antistatic, conductive, reinforced, food contact, fireproofed, low warpage, impact modified, resistant to hot oils and greases, plasticized . . .
- for films, sheets, large parts, slow or fast crystallization rate . . .

Costs

The costs, as for all plastics, fluctuate with the crude oil price, and are only given to provide an idea. They are generally of the order of a few Euros per kilogram.

Processing

All the molten-state methods are usable: extrusion, injection, compression, blown film, blow moulding, thermoforming, structural foam, co-extrusion, machining for high hardness grades, welding.

Applications

(See Chapter 2 for further information.)

The annual consumption for Europe, the USA and Japan slightly exceeds 2 million tonnes.

More than 60% of polyamides are reinforced with glass fibres (in more than 80% of reinforced grades) or mineral fillers (more than 10%).

The transportation sector is the main outlet, followed by EE, films, appliances and numerous other sectors:

• transportation	32%
• electricity, electronics	19%
• film	14%
• appliances, power tools, consumer products	11%
• industry	6%
• sheet, rods, tubes	4%
• filaments	4%
• others	10%

Polyamides as a family of thermoplastics have a fair growth rate and the following examples of applications are quoted without claiming to be exhaustive:

- automobile: wheel trims, grilles, wings, trap doors for gasoline, engine covers, clutch pedals, intake manifolds, headlight parabolas, spoilers, radiator tank fittings, door handles, window winders, interconnection boxes, decorative parts, air and water filter elements, airbag canisters . . .
- electricity, electrical household appliances: cases and fuse holders, junction boxes, miniature junction boxes, inlet and outlet cable channels, housings of power tools, casings of projectors, switches, contactors, socket outlets, connectors, air resonators, washing machine pulleys . . .
- self-lubricating parts: bearings, rods . . .
- technical parts: gears, screws and bolts, pulleys, collars, valve casings, rings, clips, ventilators, cooling fans, tanks and containers . . .
- Sports and leisure: wheels, saddle stems, crank gear for bicycles; ski boots, roller skates, toys, building sets, snowmobile bumpers, grass and leaf blower parts and housings . . .
- Films, sheets and plates for packaging and thermoforming, barrier layers of multilayer films . . .
- Filaments, fibres . . .

4.13.1.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 80°C up to 150°C if softening temperatures are higher.

The UL temperature indices of specific grades can be:

- 65–140°C for the electrical properties alone
- 65–115°C for the electrical and mechanical properties including impact.

Service temperatures are distinctly lower under loading because of modulus decay, strain, creep, relaxation . . .

For example:

- for a given grade of neat PA 6, the short-term modulus retention at 150°C is 25% of the value at 20°C
- for a given grade of 30% glass fibre reinforced PA 6, the short-term modulus retention at 150°C is 65% of the value at 20°C

- for a given grade of 50% glass fibre reinforced PA 6, the short-term modulus retention at 150°C is 55% of the value at 20°C
- HDTs under 1.8 MPa are of the order of:
  - ○ impact grade 60–100°C
  - ○ general purpose 60–105°C
  - ○ mineral filled 160–180°C
  - ○ low SGF level 230–250°C

Figure 4.52 displays examples of modulus retention versus short-term temperature increase for a neat and two glass fibre reinforced PA 6 grades.

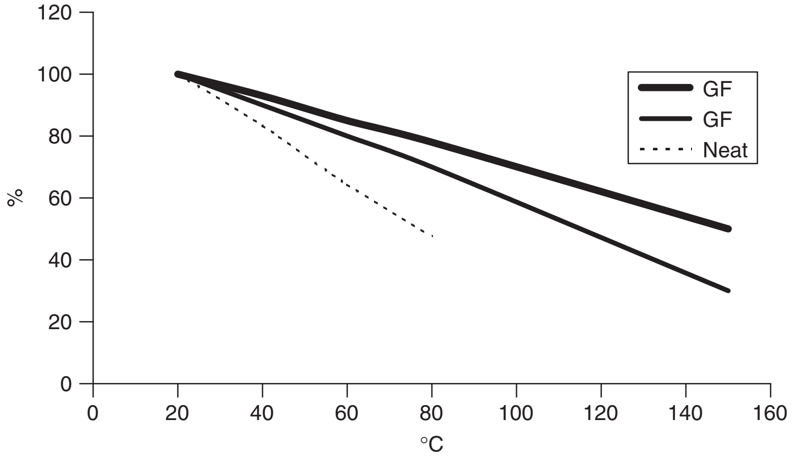


Figure 4.52. Neat & GF PA: examples of modulus retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Characteristics such as elongation at break and impact strength are especially heat sensitive.

- After 5000 h in air at 150°C, neat PA 6 and 66 have a modulus of 0.4 GPa measured at 150°C.
- After 5000 h in air at 150°C, glass fibre reinforced PA 6 and 66 have a tensile strength of 70–80 MPa and a modulus of 4 GPa measured at 150°C.
- After 5000 h in air at 170°C, glass fibre reinforced PA 6 and 66 have a tensile strength of 50–70 MPa and a modulus of 3.5 GPa measured at 170°C.

At low temperatures, general-purpose grades generally have a brittle point of −65°C down to −80°C.

Figure 4.53 shows, for two very different neat PA examples, the impact strength variations versus low temperatures.

These results relate to some grades only and cannot be generalized.

4.13.1.3 Optical properties

Polyamides 6 and 66 are translucent to opaque according to the thickness and the grade.

The refractive index can be, for example, in the range of 1.53 up to 1.565.

These results relate to some grades only and cannot be generalized.

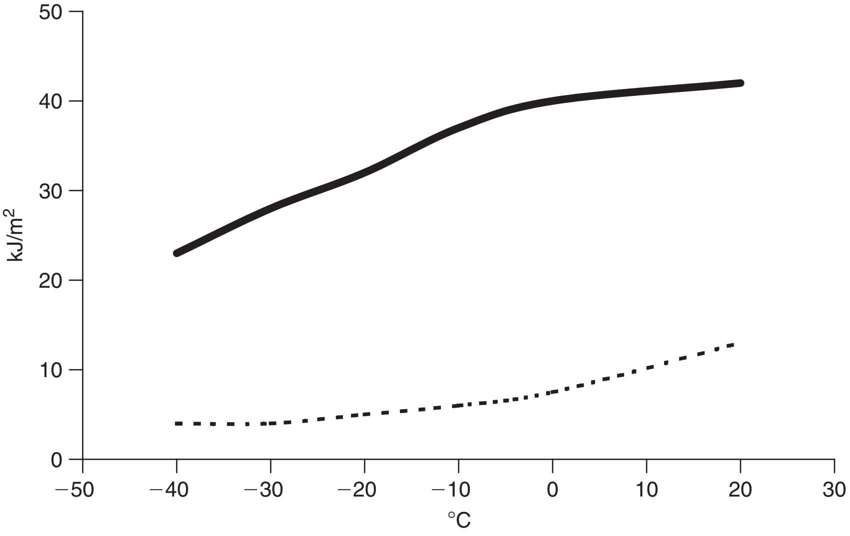


Figure 4.53. Neat PA: examples of Notched Charpy impact (kJ/m^2) versus low temperatures (°C)

4.13.1.4 Mechanical properties

The mechanical properties are generally good with high elongations at break but much more limited strains at yield. Moduli and hardnesses are fair to high according to the moisture content. The abrasion resistance is generally fair to good, depending on the roughness, type and morphology of the opposing sliding surface. Polyamide grades are especially designed for antifriction applications.

Crystallinity and molecular orientation improve the mechanical properties but are harmful to notched impact resistance.

Friction

Table 4.41 displays some examples of tribological properties of neat and reinforced polyamides (the figure preceding the reinforcement or additive indicates its % loading). The coefficients of friction are in a good range, from 0.1 up to 0.3 for the static coefficients, and wear varies from near 1 (excellent) up to more than 100 (fair).

These results relate to a few grades only and cannot be generalized.

Dimensional stability

Shrinkage and coefficient of thermal expansion are those of semi-crystalline polymers, that is to say, rather high. The absorption and swelling by moisture exposure are high (see Figure 4.54).

Creep depends on reinforcement, moisture content and temperature.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For example, the following data are reported:

- 0.39 for a 33% glass fibre reinforced PA 6.
- 0.40 for an extruded PA 66.
- 0.32–0.34 for a mineral-filled PA 66.

These results relate to a few grades only and cannot be generalized.

Table 4.41 Property examples of several self-lubricating polyamide grades

Polymer & filler	Tribological additives (%)	Coefficient of friction		Wear (arbitrary unit)
		Static	Dynamic	
		Unreinforced polyamides		
PA6	15 PTFE	0.18	0.11	120
PA66	15 PTFE	0.17	0.11	100
PA66	13 PTFE/2 silicone	0.1	0.11	120
		Glass fibre reinforced polyamides		
PA6 30 GF	5 MoS_2	0.3	0.3	2.2
PA66 30 GF	5 MoS_2	0.3	0.3	2.8
PA6 30 GF	15 PTFE	0.26	0.1	2
PA66 30 GF	15 PTFE	0.22	0.08	1.9
PA6 30 GF	13 PTFE/2 silicone	0.19	0.13	2
PA66 30 GF	13 PTFE/2 silicone	0.17	0.1	2.3
		Carbon fibre reinforced polyamides		
PA66 10 CF		0.22		
PA6 20 CF		0.22		
PA66 20 CF		0.2		
PA6 30 CF		0.2		
PA66 30 CF		0.19		
PA66 15 CF	20 PTFE	0.11	0.08	1.5
PA66 15 CF	13 PTFE/2 silicone	0.12	0.08	0.8
PA66 30 CF	15 PTFE	0.16	0.1	1
PA66 30 CF	13 PTFE/2 silicone	0.13	0.09	2

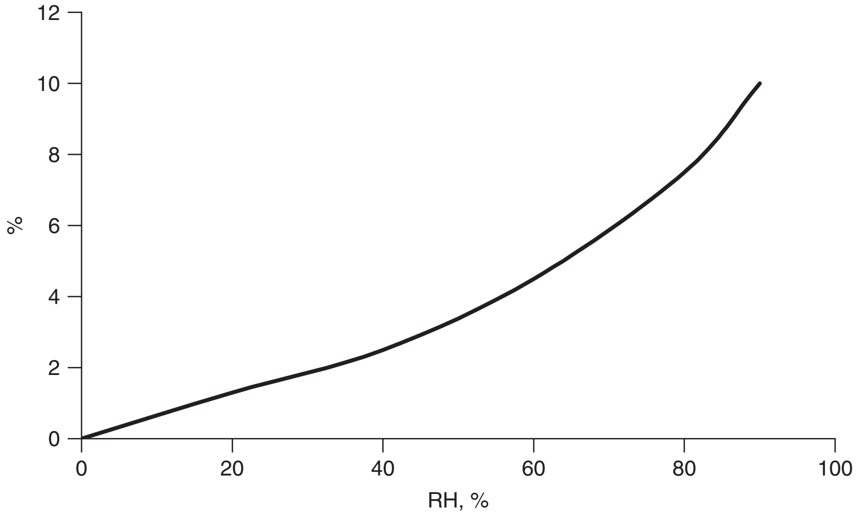


Figure 4.54. Neat PA: moisture absorption (%) versus RH (%)

Creep

Thermoplastic neat polyamides 6 and 66 at equilibrium with a 50% RH environment have rather low moduli involving high strains for moderate loading. Consequently creep moduli are also low (see Figure 4.55(a)), the more so as the temperature rises. Reinforcement with glass fibres completely changes the creep behaviour leading to fair and rather high creep moduli for moderate temperatures (see Figure 4.55(b)).

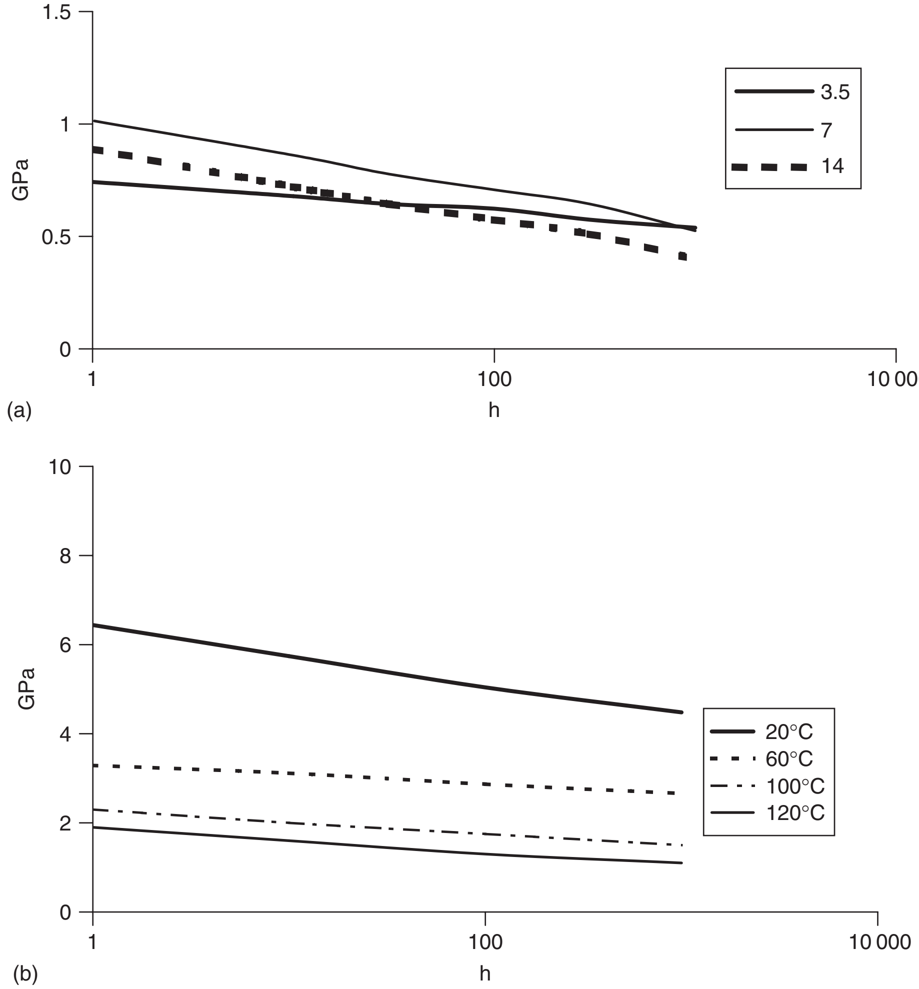


Figure 4.55 (a) Neat PA creep: examples of creep modulus (GPa) versus time (h) for various loadings (3.5 to 14 MPa); (b) Glass fibre reinforced PA creep: examples of creep modulus (GPa) versus time (h) at various temperatures under 14 MPa

From Figure 4.55(a) we can observe the different behaviours of three neat polyamides 6 or 66 and the modest creep moduli for limited loadings.

Figure 4.55(b) displays:

- the high creep moduli of glass fibre reinforced PA by comparison with neat polyamides (Figure 4.55(a)); the modulus scale is nearly seven times that of Figure 4.55(a)
- the fast decrease of creep modulus when the temperature rises moderately from ambient to 60°C. Designers must be vigilant when computing the wall thickness of a part to be used at ambient temperatures but exposed to sunlight (60°C) during warm weather.

These results relate to a few grades only and cannot be generalized.

Relaxation

Figure 4.56 displays relaxation data as percentage of stress retention plotted versus logarithmic time (h) showing a regular decrease of stress. This diagram is only given to illustrate the principle of relaxation; the data cannot be used for designing.

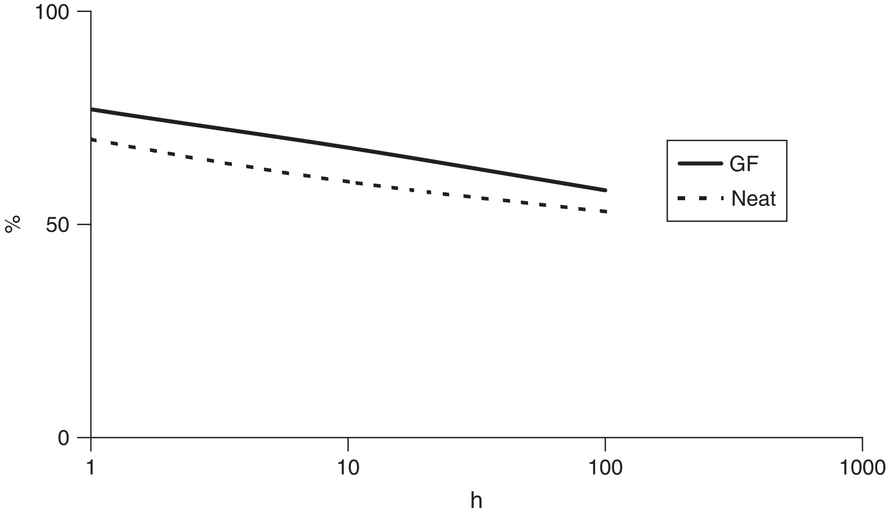


Figure 4.56. Stress relaxation of PA: examples of stress retention (%) versus time (h) under 0.4% strain at 20°C

4.13.1.5 Ageing

Dynamic fatigue

The dynamic fatigue can be fair or good for well-adapted grades if care is taken to limit the strains by restricting the stresses to values in keeping with the low modulus.

For a given grade of neat impact-modified PA 6, failure occurs after 2 million cycles under 14 MPa.

Figure 4.57 displays an example of an SN or Wöhler's curve, concerning flexural tests with maximum stress of ±S and average stress of 0, for a given grade of glass fibre reinforced PA 66 (upper curve).

Weathering

Polyamide is naturally sensitive to light and UV. It must be protected by addition of anti-UV and other protective agents.

After weathering of test bars (3 mm thick) in a sunny climate, the property retentions are, for example:

- 50% for tensile strength, 3% for elongation at break after 6 months for a natural non-protected grade
- 32% for tensile strength, 2% for elongation at break after 5 years for a natural non-protected grade
- 99% for tensile strength, 38% for elongation at break after 6 months for a UV-protected grade.
- 89% for tensile strength, 22% for elongation at break after 5 years for a UV-protected grade.

These results are examples only and cannot be generalized.

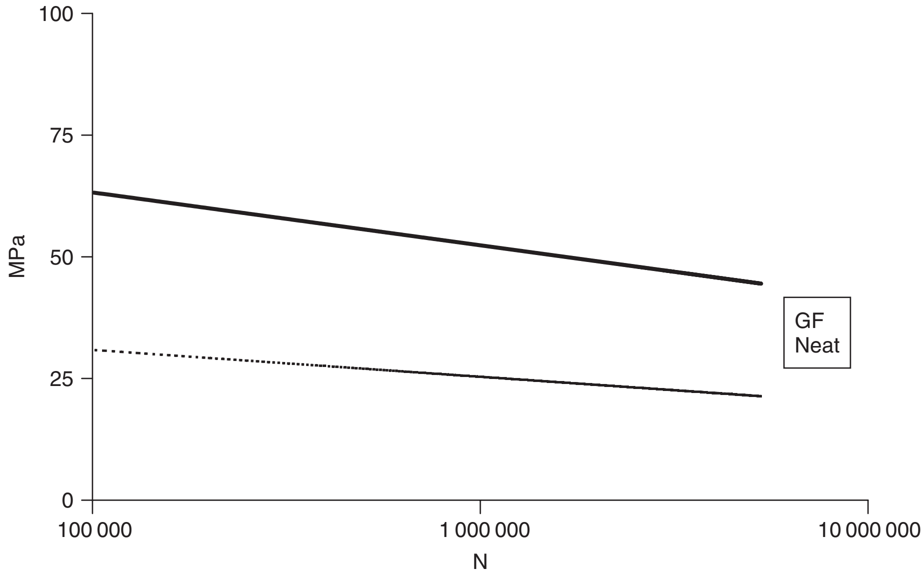


Figure 4.57. SN curve of 30% GF PA: examples of maximum stress S (MPa) versus number of cycles at rupture (N)

Behaviour at high frequencies

Polyamides have high loss factors, about 100–600 × 10^{-4}, and heat up under high-frequency current. They can be welded by this technique.

Chemicals

Polyamides absorb water and are sensitive to it. Special grades are marketed for their hydrolysis resistance.

Suitable grades are usable in contact with food.

Chemical resistance is generally good to limited at room temperature versus dilute bases and weak acids, oils, greases, hydrocarbons, certain chlorinated solvents, cosmetics, aldehydes, some alcohols, ketones, esters, glycols. Polyamides are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols.

Crystallinity increases impermeability and, consequently, chemical resistance.

Table 4.42 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all polyamides 6 and 66. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide an idea and cannot be used for designing any parts or goods.

- Water vapour: polyamides 6 and 66 have a permeability evaluated at 9 up to 70 for a full range of 0.05 up to 400 for all tested plastics.

Table 4.42 PA 66: examples of chemical behaviour

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	l
Acetic acid	25 to >96	n
Acetic aldehyde	100	l
Acetic anhydride	100	l
Acetone	100	S
Acetonitrile	100	S
Acetophenone	100	S
Acrylic acid	100	l
Aldehydes	Unknown	S
Aliphatic hydrocarbons	100	S
Alum	Solution	S
Aluminium chloride	Solution	l
Aluminium sulfate	Unknown	S
Ammonia gas	100	l
Ammonium chloride	Solution	S
Ammonium hydroxide	30	S
Ammonium sulfate	50	S
Amyl acetate	100	S
Amyl alcohol	100	S
Aniline	100	n
Antimony chloride	10	l
Aqua regia	Unknown	n
Aromatic hydrocarbons	100	S
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Beer	Unknown	S
Benzaldehyde	100	l
Benzene	100	S
Benzoic acid	Saturated	n
Benzylchloride	100	S
Benzyl alcohol	100	l
Boric acid	Unknown	S
Bromine (liquid)	100	n
Bromine water	Solution	n
Butane gas	100	S
Butanol	100	S
Butanone	100	l
Butyl acetate	100	S
Butylamine	Unknown	S
Butylchloride	100	l
Calcium chloride	Unknown	l
Calcium hypochlorite	Solution	n
Carbon sulfide	100	l to S
Carbon tetrachloride	100	l to S
Castor oil	100	S
Cellosolve	100	S
Cellosolve acetate	100	S
Chlorine (dry gas)	100	n
Chlorine water	Unknown	n
Chloroacetic acid	Unknown	n
Chlorobenzene	100	l
Chloroform	100	n
Chlorosulfonic acid	100	n
Chromic acid	10–50	n
Citric acid	10	S
Citric acid	Saturated	l
Colza oil	100	S
Copper sulfate	Unknown	l
Cresol	100	n
Cyclohexane	100	S
Cyclohexanol	100	l
Cyclohexanone	100	S
Decaline	100	S
Diacetone alcohol	100	S
Dibutylphthalate	100	S
Dichloroethane	100	l
Dichloroethylene	100	S
Diethylamine	100	S
Diethyleneglycol	100	S
Diethylether	100	S
Diisopropylbenzene	100	S
Dimethylamine	100	S
Dimethylformamide	100	l
Dioctylphthalate	100	S
Dioxan	100	S
Esters	100	S
Ethanol	Unknown	S
Ethanol	96	l
Ethylacetate	100	l
Ethylchloride	100	S
Ethylene glycol	100	S
Ethylhexanol	100	l
Fluorine	100	n
Fluosilicic acid	Unknown	l
Formaldehyde	35	S
Formaldehyde	37	l
Formic acid	10–100	n
Freon 11	100	S
Freon 113	100	S
Freon 12	100	S
Freon 21	100	S
Freon 22	100	S
Freon 32	100	S
Fruit juice	Unknown	S
Furfural	100	S
Glycerol	100	S
Grease	100	S
Hexane	100	S
Household bleach	Unknown	n
Hydrobromic acid	48	n
Hydrochloric acid	10–36	n
Hydrofluoric acid	40–100	n
Hydrogen peroxide	3–90	n
Hydrogen sulfide gas	Unknown	S
Iron(III) chloride	Unknown	l
Isobutanol	100	l

(*Continued*)

Table 4.42 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Isooctane (Fuel A)	100	S
Isopropanol	100	l to S
Kerosene	100	S
Lactic acid	10–90	l
Lead acetate	10	S
Linseed oil	100	S
Liquid paraffin	100	S
Magnesium chloride	Unknown	S
Magnesium hydroxide	Unknown	S
Mercury	100	S
Mercury chloride	Unknown	l
Methane chloride	100	S
Methanol	100	l
Methylbromide	100	S
Methylbutylketone	100	S
Methylchloride	100	S
Methylene chloride	100	n
Methylethylketone	100	l
Methylglycol	Unknown	S
Milk	100	S
Mineral oil	100	S
Molasses	Unknown	S
Monochlorobenzene	100	l
Monoethanolamine	Unknown	S
Monoethyleneglycol	100	l
Mustard	Unknown	S
Naphtha	Unknown	S
Naphthalene	100	S
Nickel chloride	Unknown	S
Nitric acid	10–100	n
Nitrobenzene	100	l
Nitromethane	100	S
Nitropropane	100	S
Nonanol	100	l
Oleic acid	100	S
Oleum @ 10%	Pure	n
Olive oil	100	S
Oxalic acid	Dilute	l
Ozone	100	n
Pentylacetate	100	S
Perchloric acid	10–70	n
Perchloroethylene	100	l
Petrol aliphatic	100	S
Petrol high-octane	100	S
Petroleum	100	S
Petroleum ether (ligroin)	Unknown	S
Phenol	Solution	n
Phosphoric acid	50–95	n
Potassium cyanide	Unknown	S
Potassium dichromate	5	l
Potassium hydroxide	Solution	l
Potassium hydroxide	10	S
Potassium hydroxide	45	l
Potassium permanganate	1–20	n
Potassium sulfate	Unknown	S
Propanol	100	S
Propionic acid	100	l
Propylene oxide	100	S
Pyridine	100	S
Sea water	100	l
Silicone oil	100	S
Silver nitrate	Unknown	S
Soap	Unknown	S
Sodium acetate	Saturated	S
Sodium bisulfite	Solution	S
Sodium borate	Unknown	S
Sodium carbonate	10–50	S
Sodium chloride	25	S
Sodium cyanide	Unknown	S
Sodium hydroxide	10–40	l
Sodium hydroxide	55	n
Sodium hypochlorite	13–20	n
Sodium nitrate	Solution	S
Stearic acid	Unknown	S
Strong acids	Concentrated	n
Styrene	100	S
Sulfur dioxide (gas)	Unknown	n
Sulfuric acid	2 to fuming	n
Sulfurous anhydride (gas)	Unknown	n
Tartaric acid	Solution	S
Tetrachloroethylene	100	l
Tetrahydrofuran	100	S
Thionyl chloride	100	n
Tin chloride	Unknown	n
Toluene	100	S
Town gas (benzene-free)	100	S
Transformer oil	100	S
Trichloroacetic acid	Unknown	n
Trichloroethane	100	l
Trichloroethylene	100	l
Tricresylphosphate	Unknown	S
Triethanolamine	Unknown	S
Trimethylbenzene	100	S
Turpentine oil	100	S
Urea	Solution	S
Uric acid	Unknown	S
Vegetable oil	100	S
Vinegar	Unknown	S
Vinyl chloride	Unknown	l
Water	100	l
Weak acids	Unknown	l
White spirit	100	S
Wine	Unknown	S
Xylene	100	S
Zinc chloride	Unknown	n

S: satisfactory; l: limited; n: not satisfactory

- Gases: polyamides 6 and 66 have a rather low permeability, evaluated at:
  - ○ carbon dioxide: 90 up to 125 versus a full range of 30 up to 59 000 for all tested plastics
  - ○ nitrogen: 7 up to 9 versus a full range of 1 up to 3500 for all tested plastics
  - ○ oxygen: 25 up to 50 versus a full range of <1 up to 11 000 for all tested plastics
  - ○ hydrogen: 950 versus a full range of 400 up to 20 000 for all tested plastics.

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames. Moreover, polyamides drip while burning.

Oxygen indices are roughly 21 to 27 with a V2 or HB UL94 rating.

Special formulations, possibly halogen-free, make it possible to improve this behaviour, sometimes to the detriment of other properties. UL94 V0 rating can be reached for some FR grades with oxygen indices of the order of 31–40.

4.13.1.6 Electrical properties

Polyamides are fair insulators in a dry environment and at ambient temperature, with fair dielectric resistivities and rigidities, and high loss factors. Special grades are marketed for electrical applications.

In wet environments and/or when the temperature rises, the resistivities decrease, as we can see from Figure 4.58(a) and (b).

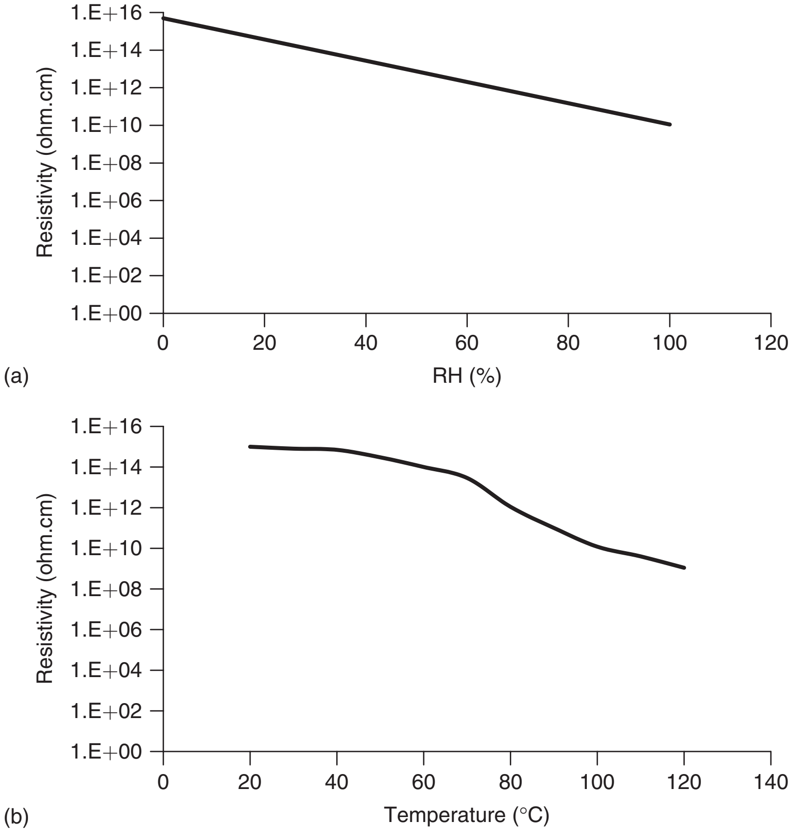


Figure 4.58. (a) Neat PA: examples of resistivity (ohm.cm) versus relative hygrometry (%); (b) Neat PA: examples of resistivity (ohm.cm) versus temperature (°C)

4.13.1.7 Joining, decoration

Welding is feasible by all processes.

Gluing is easy. All precautions must be taken concerning health and safety according to local laws and regulations.

Polyamides can generally be decorated by painting, metallization, printing, flexography, offset, serigraphy, heliography.

4.13.1.8 Specific ISO standards concerning polyamides

ISO 1140:2004 Fibre ropes – Polyamide – 3-, 4- and 8-strand ropes

ISO 1874-1:1992 Plastics – Polyamide (PA) moulding and extrusion materials – Part 1: Designation

ISO 1874-2:1995 Plastics – Polyamide (PA) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 15987:2003 Plastics – Film and sheeting – Biaxially oriented polyamide (nylon) films.

4.13.1.9 Trade name examples

Akulon, Durethan, Fabelnyl, Grilon, Maranyl, Nylatron, Nylon, Orgamide, Technyl, Sniamid, Ultramid, Zytel . . .

4.13.1.10 Property tables

Table 4.43 relates to examples only and cannot be generalized. Data indiscriminately relate to dry or wet samples and cannot be used for designing.

Table 4.43 Neat, reinforced and modified polyamides 6 and 66: examples of properties

	PA 66		Impact PA 66		PA 6	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.13	1.15	1.05	1.10	1.12	1.14
Shrinkage (%)	0.7	3.0	1.2	3.0	0.5	1.5
Absorption of water (%)	1.0	3.0	1.0	3.0	1.6	1.9
Mechanical properties						
Shore hardness, D	80	95	70	85	80	95
Rockwell hardness, M	30	85	<10	50	30	85
Stress at yield (MPa)	45	85	35	50	50	90
Tensile strength (MPa)	50	95	40	50	50	95
Elongation at break (%)	150	300	150	300	200	300
Tensile modulus (GPa)	1.0	3.5	0.8	1.2	0.8	2.0
Flexural modulus (GPa)	0.8	3.0	0.8	1.2	0.8	2.0
Notched impact strength ASTM D256 (J/m)	50	150	70	NB	50	160
Thermal properties						
HDT B (0.46 MPa) (°C)	180	240	160	210	150	190
HDT A (1.8 MPa) (°C)	65	105	60	100	60	80
Continuous use temperature (°C)	80	150	80	130	80	150
Melting temperature (°C)	250	265	240	265	215	220
Brittle point (°C)	−80	−65	−80	−65		
Thermal conductivity (W/m.K)	0.25	0.25	0.24	0.25	0.24	0.24
Specific heat (cal/g/°C)	0.55	0.55	0.55	0.58	0.58	0.58
Coefficient of thermal expansion (10^{-5}/°C)	5	14	5	14	5	12

Table 4.43 (Continued)

	PA 66		Impact PA 66		PA 6	
	Min.	Max.	Min.	Max.	Min.	Max.
Electrical properties						
Volume resistivity (ohm.cm)	10^{12}	10^{14}	10^{13}	10^{14}	10^{12}	10^{14}
Dielectric constant	4	5	3	4	4	5
Loss factor (10^{-4})	100	400	200	1200	100	600
Dielectric strength (kV/mm)	20	30	30	35	10	20
Arc resistance (s)	130	140				
Fire behaviour						
Oxygen index (%)	21	23	21	23	21	23
UL94 fire rating	HB	V2	HB	V2	HB	V2
Reinforced PA 66	30% GF		PA 66 Impact 15–30% GF		30% Mineral	
Miscellaneous properties						
Density (g/cm^3)	1.37	1.37	1.25	1.35	1.35	1.38
Shrinkage (%)	0.5	0.5	0.2	0.6	0.6	1.0
Absorption of water (%)	0.8	1.1	0.6	1	0.8	1.2
Mechanical properties						
Shore hardness, D	80	95	70	90	80	95
Rockwell hardness, M	30	85	<10	70	30	85
Stress at yield (MPa)	100	125	90	120	55	55
Strain at yield (%)	5	8				
Tensile strength (MPa)	100	125	90	120	55	55
Elongation at break (%)	5	8	3	10	70	70
Tensile modulus (GPa)	5	8	3	7	4	4
Flexural modulus (GPa)	5	8	3	7	4	4
Notched impact strength ASTM D256 (J/m)	130	160	150	270	100	200
Thermal properties						
HDT B (0.46 MPa) (°C)	235	255	220	250	230	230
HDT A (1.8 MPa) (°C)	230	255	200	240	180	180
Continuous use temperature (°C)	100	150	100	140	100	150
Glass transition temperature (°C)	50	60	50	60	50	60
Melting temperature (°C)	235	255	235	255	235	255
Thermal conductivity (W/m.K)	0.28	0.28	0.3	0.3	0.38	0.38
Coefficient of thermal expansion (10^{-5}/°C)	2	3	2	3	4	5
Electrical properties						
Volume resistivity (ohm.cm)	10^{12}	10^{13}	10^{12}	10^{13}	10^{11}	10^{12}
Dielectric constant	3.9	4.4	3.9	4.4	3.4	4
Loss factor (10^{-4})	100	1500	200	1000	200	1500
Dielectric strength (kV/mm)	25	25	21	23	25	30
Fire behaviour						
Oxygen index (%)	21	23	23	23	26	27
UL94 fire rating	HB	HB	HB	HB	HB	HB
Reinforced and FR PA 6 or 66	50% GF		FR unreinforced		FR GF	
Miscellaneous properties						
Density (g/cm^3)	1.56	1.57	1.15	1.16	1.55	1.55
Shrinkage (%)	0.1	0.5	0.8	1.3	0.2	0.7
Absorption of water (%)	0.6	1	0.8	1.1	1.8	1.8
Mechanical properties						
Shore hardness, D	85	90	85	90	85	90
Rockwell hardness, R	115	124	108	122	113	123
Stress at yield (MPa)	150	240	50	80	75	105

(*Continued*)

Table 4.43 (Continued)

Reinforced and FR PA 6 or 66	50% GF		FR unreinforced		FR GF	
Elongation at break (%)	2	3	16	20	2.4	3
Tensile modulus (GPa)	9	16	2	3.7	5	9
Flexural modulus (GPa)	8	14	2	3.5	4	9
Thermal properties						
HDT B (0.46 MPa) (°C)	220	255	200	200	215	215
HDT A (1.8 MPa) (°C)	215	230	75	75	200	200
Continuous use temperature (°C)	100	150				
Melting temperature (°C)	220	250	220	250	220	250
Thermal conductivity (W/m.K)						
Coefficient of thermal expansion (10^{-5}/°C)	1.5	2	6	7	5	5
Electrical properties						
Volume resistivity (ohm.cm)	10^{11}	10^{15}	10^{12}	10^{15}	10^{12}	10^{15}
Dielectric constant	3.8	9	3.6	4	3.8	4.5
Loss factor (10^{-4})	100	1500			210	900
Dielectric strength (kV/mm)	22	35	28	37	20	21
Fire behaviour						
Oxygen index (%)	23	23	36	36	30	30
UL94 fire rating	HB	HB	V0	V0	V0	V0

Reinforced and modified PA 6 or 66	30% CF		Self-lubricating GF		Conductive for electro-painting	
Miscellaneous properties						
Density (g/cm^3)	1.26	1.26	1.4	1.5	2	2.03
Shrinkage (%)			0.2	0.3	0.3	1
Absorption of water (%)			0.8	1.2	0.5	1
Mechanical properties						
Tensile strength (MPa)	230	230	120	140	110	115
Elongation at break (%)			3	3	3	3
Tensile modulus (GPa)	19	19			6.8	6.8
Flexural modulus (GPa)			6.9	7.1	7	7.1
Notched impact strength ASTM D256 (J/m)	80	100	100	130		
Thermal properties						
HDT A (1.8 MPa) (°C)	215	255	210	210		
Continuous use temperature (°C)					<160	<160
Electrical properties						
Volume resistivity (ohm.cm)	10^2	10^2			10^4	10^4
Fire behaviour						
UL94 fire rating	HB	HB	HB	HB	HB	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers are needed
Weak acids	Good to limited behaviour
Strong acids	Unsatisfactory
Weak bases	Good behaviour
Strong bases	Limited behaviour
Solvents	Chemical resistance is generally good to limited at room temperature versus dilute bases and weak acids, oils, greases, hydrocarbons, certain chlorinated solvents, cosmetics, aldehydes, some alcohols, ketones, esters, glycols. Polyamides are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols
Food contact	Possible for special grades

4.13.2 Polyamides 11 and 12 (PA 11 and PA 12)

4.13.2.1 General properties

Compared to PA 6 and PA 66, PA 11 and PA 12 are more flexible, have better behaviour at low temperature and are adapted to extreme climates, are less sensitive to water and moisture, but are more expensive. Their market share is only a few percent of the total polyamide consumption.

PA 11 and 12 have good stress cracking resistance, a low density and a high abrasion resistance.

The heat behaviour can be increased through radiation crosslinking.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, powdering . . .
- stabilized against heat, hydrolysis, UV, light and/or weathering; antistatic, conductive, reinforced, food contact, fireproofed, plasticized, impact modified, resistant to hot oils and greases . . .
- For powdering, wire coating, antifriction parts . . .

Costs

The costs, as for all plastics, fluctuate with the crude oil price; however, PA 11 and PA 12 are more expensive than PA 6 and PA 66.

Processing

All the molten-state methods are usable: extrusion, injection, compression, blown film, blow moulding, thermoforming, co-extrusion, machining for high hardness grades, welding. Powdering is used to make coatings.

Applications

(See Chapter 2 for further information.)

Examples of applications are, without claiming to be exhaustive:

- automobile: hydraulic, fuel and water hoses; truck air brake hoses; monolayer and multilayer plastic fuel lines . . .
- electricity, electrical household appliances: electrical cables, optical fibres, flexible telephone cables, inlet and outlet cable channels, housings of microscopes, connectors . . .
- anticorrosion, protection: offshore drilling, offshore oil & gas production and test lines, gas & water injection lines, gas lift lines, pipes, fittings, valves, lined pipes; powdering within the healthcare equipment & oil industries; internal coating in new and refurbished injection tubing, production tubing and flow lines; production risers, choke & kill lines, nitrogen lines, hydraulic lines; buried gas pipelines; co-extruded pipes with MDPE and HDPE to increase their performances; dirty water and effluent pipes used in aggressive environments . . .
- drinkable water transportation equipment and water treatment plants: powder-coated metal parts . . .
- self-lubricating parts: bearings, rods . . .
- technical parts: pneumatic and hydraulic hoses; petrochemical, fuel handling and hydraulic applications; gears, collars, valve casings, rings, clips . . .

- sports and leisure: ski boots, toys, snowmobile parts . . .
- films, sheets and plates for packaging . . .
- powdering . . .

4.13.2.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 80°C up to 150°C if softening temperatures are higher.

The UL temperature indices of specific grades can be 65°C for electrical and mechanical properties including impact.

Service temperatures can be lower under loading because of modulus decay, strain, creep, relaxation . . .

For example, HDTs under 1.8 MPa for neat PA 11 or 12 are of the order of 40°C up to 60°C.

Figure 4.59 displays examples of tensile strength retention versus short-term temperature increase for neat, glass fibre (GF) and glass bead (GB) PA 12 grades.

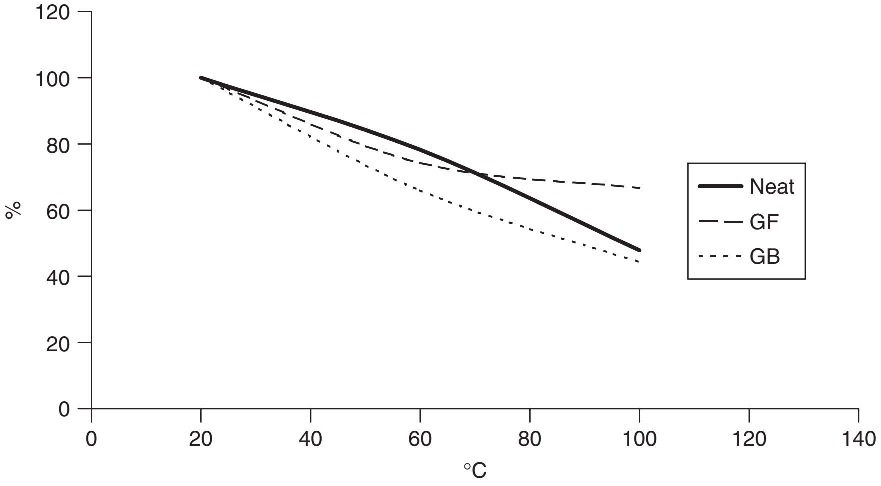


Figure 4.59. PA 12: examples of tensile strength retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Characteristics such as elongation at break and impact strength are especially heat sensitive.

Figure 4.60 shows examples of the half-lives (50% mechanical performance retention) based on tensile strength versus the temperature of ageing in air. For ten years of continuous use in an unstressed state, the acceptable temperatures are about 85–105°C.

At low temperatures, general-purpose grades generally have a brittle point of −70°C down to −120°C.

These results relate to some grades only and cannot be generalized.

4.13.2.3 Optical properties

Polyamides 11 and 12 are translucent to opaque according to the thickness and the grade.

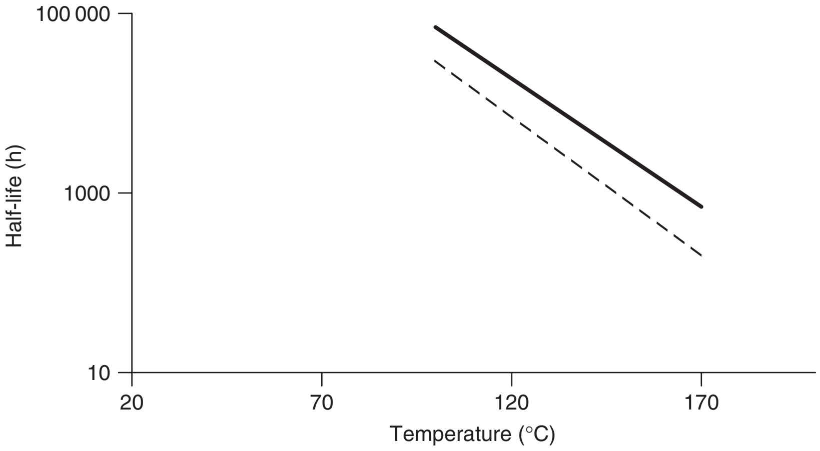


Figure 4.60. PA 12: examples of half life (h) versus temperature (°C)

4.13.2.4 Mechanical properties

The mechanical properties are generally good, with high elongations at break but much more limited strains at yield. Moduli and hardnesses are lower than those of PA 6 and PA 66 and some grades are plasticized to improve flexibility. PA 11 and PA 12 are less sensitive to the moisture content. The abrasion resistance is generally good, depending on the roughness, type and morphology of the opposing sliding surface. Polyamide 11 and 12 grades are suitable for antifriction applications.

Dimensional stability

Shrinkage and coefficient of thermal expansion are rather high. The absorption and swelling by moisture exposure is lower than for PA 6 and 66. Creep depends on reinforcement, moisture content and temperature.

Creep

Thermoplastic neat polyamides 11 and 12 at equilibrium with a 50% RH environment have low moduli involving high strains for moderate loading. Consequently, creep moduli are also low (see Figure 4.61(a)). Reinforcement with glass fibres completely changes the creep behaviour leading to fair creep moduli at room temperature (Figure 4.61(b)).

In Figure 4.61(a) we can see the different behaviours of two neat polyamide 12 grades and the modest creep moduli for limited loadings.

Figure 4.61(b) displays the high creep moduli of glass fibre reinforced PA 12 for comparison with the neat PA 12 in Figure 4.61(a). It should be noted that the modulus scale is ten times that of Figure 4.61(a) and, moreover, with five to seven times heavier loads.

These results relate to a few grades only and cannot be generalized.

4.13.2.5 Ageing

Dynamic fatigue

The dynamic fatigue can be fair or good for well-adapted grades if care is taken to limit the strains by restricting the stresses to values in keeping with the low modulus.

Weathering

Polyamide 11 and 12 must be protected by addition of anti-UV and other protective agents.

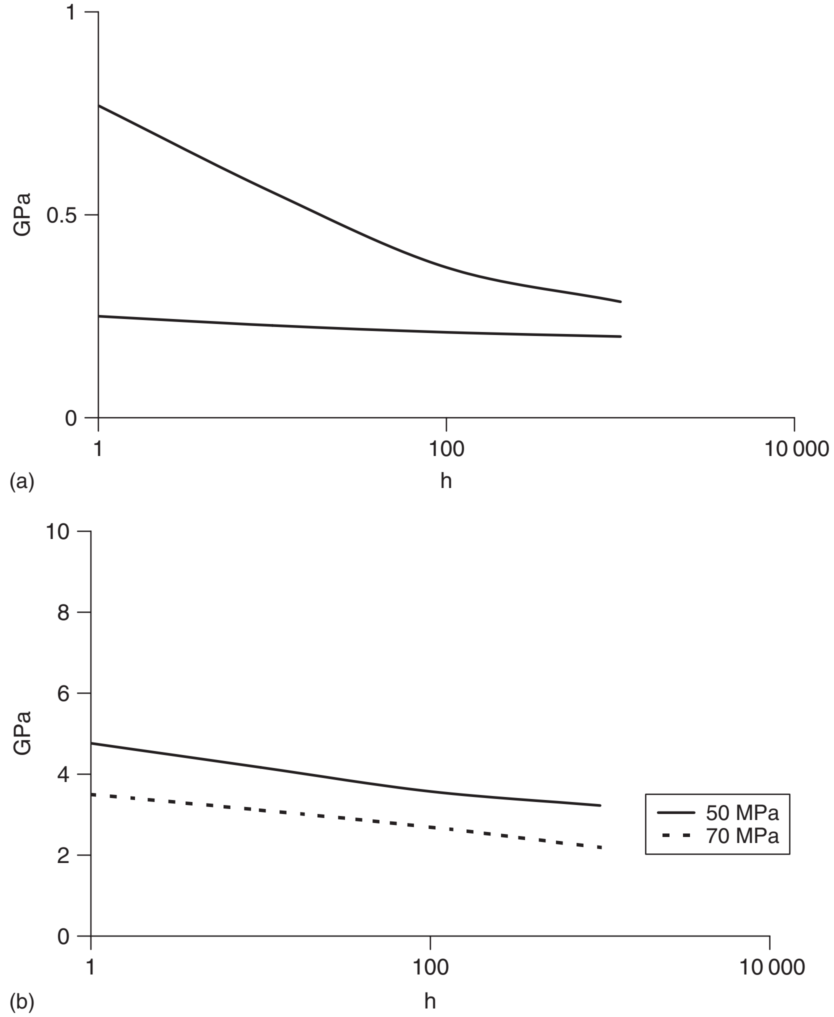


Figure 4.61. (a) Neat PA 12 creep: examples of creep modulus (GPa) versus time (h) under 10 MPa; (b) Glass fibre reinforced PA 12 creep: examples of creep modulus (GPa) versus time (h) under 50 and 70 MPa

Behaviour at high frequencies

Polyamides have high loss factors, about 100–2000 × 10^{-4}, and heat up under high-frequency current. They can be welded by this technique.

Chemicals

Compared with PA 6 or 66, polyamides 11 and 12 absorb less water and are less sensitive to it. Special grades are marketed for their hydrolysis resistance.

Suitable grades are usable in contact with food.

Chemical resistance is generally good to limited at room temperature versus dilute bases and weak acids, oils, greases, hydrocarbons, certain chlorinated solvents, cosmetics, aldehydes, some alcohols, ketones, esters, glycols. Polyamides are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols.

Table 4.44 displays general assessments of behaviour in the presence of a range of chemicals after prolonged immersion at room temperature for given grades, which are not necessarily representative of all polyamides 11 and 12. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.44 PA 11 or 12: examples of chemical behaviour

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	l
Acetic acid	>50	n
Acetic aldehyde	100	S
Acetic anhydride	100	l
Acetone	100	S
Acetonitrile	100	S
Acetophenone	100	S
Acetyl chloride	100	l
Acetylene	100	S
Alum	Solution	S
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonia	30	S
Ammonia gas	100	S
Ammonia liquid	100	S
Ammonium hydroxide	30	S
Ammonium sulfate	50	S
Amyl acetate	100	S
Amyl alcohol	100	S
Aniline	100	n
Aqua regia	Unknown	n
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Beer	Unknown	S
Benzaldehyde	100	l
Benzene	100	l
Benzylchloride	100	l
Benzyl alcohol	100	l
Boric acid	Unknown	S
Bromine	Unknown	n
Bromine (dry gas)	100	n
Bromine (liquid)	100	n
Butane	100	S
Butane gas	100	S
Butanol	100	l
Butyl acetate	100	S
Butylamine	Unknown	l
Butylchloride	100	l
Calcium chloride	Unknown	S
Calcium hydroxide	Unknown	S
Carbon sulfide	100	l
Carbon tetrachloride	100	l to n
Castor oil	100	S
Cellosolve	100	S
Chlorine (dry gas)	100	n
Chlorine (wet)	Unknown	n
Chlorine water	Unknown	l
Chloroacetic acid	Unknown	n
Chloroform	100	n
Chlorosulfonic acid	Unknown	n
Chromic acid	Unknown	n
Chromic acid	>10	n
Citric acid	10	S
Colza oil	100	S
Copper sulfate	Unknown	S
Cresol	100	n
Cyclohexane	100	S
Cyclohexanol	100	l
Cyclohexanone	100	l
Decaline	100	S
Diacetone alcohol	100	S
Diethylamine	100	l
Diethyleneglycol	100	S
Diethylether	100	S
Dimethylformamide	100	l
Dioctylphthalate	100	S
Dioxan	100	S
Ethanol	Unknown	l
Ethanol	96	S
Ethylacetate	100	S
Ethylchloride	100	S
Ethylene glycol	100	S
Ethylene oxide	100	S
Fluorine	100	n
Formaldehyde	Unknown	S
Formaldehyde	37	l
Formic acid	⩾10	n
Freon 12	100	S
Freon 22	100	S
Freon 32	100	S
Furfural	100	S
Furfuryl alcohol	100	S
Glucose	Unknown	S
Glycerol	100	S
Glycol	Unknown	S
Grease	100	S
Groundnut oil	100	S
Hexane	100	S
Household bleach	Unknown	l
Hydrobromic acid	48	n

(*Continued*)

Table 4.44 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Hydrochloric acid	$\geqslant 10$	n
Hydrofluoric acid	40	n
Hydrogen	100	S
Hydrogen peroxide	Unknown	S
Hydrogen peroxide	30–90	n
Hydrogen sulfide gas	Unknown	l
Iron(III) chloride	Unknown	n
Isooctane (Fuel A)	100	S
Isopropanol	100	l
Kerosene	100	S
Lactic acid	90	l
Lactic acid	Unknown	S
Lead acetate	10	l
Lead tetraethyl	Unknown	S
Linseed oil	100	S
Liquid paraffin	100	S
Magnesium chloride	Unknown	S
Mercury chloride	Unknown	n
Methane	100	S
Methanol	100	S
Methylacetate	100	S
Methylbromide	100	l
Methylchloride	100	S
Methylene chloride	100	n
Methylethylketone	100	S
Methylisobutylketone	Unknown	S
Milk	100	S
Mineral oil	100	S
Molasses	Unknown	S
Monoethanolamine	Unknown	S
Mustard	Unknown	S
Naphtha	Unknown	S
Naphthalene	100	S
Nitric acid	$\geqslant 5$	n
Oleic acid	Unknown	S
Olive oil	100	S
Oxalic acid	Unknown	l
Oxygen	Unknown	S
Ozone	Unknown	l
Perchloroethylene	100	l
Petrol	100	S
Petrol high-octane	100	S
Petroleum	100	S
Phenol	Unknown	n
Phosphoric acid	50	l
Phosphoric acid	$\geqslant 85$	n
Picric acid	Solution	l
Potassium cyanide	Unknown	S
Potassium ferrocyanide	Saturated	S
Potassium hydroxide	45	l
Potassium nitrate	Saturated	S
Potassium permanganate	$\geqslant 10$	n
Potassium sulfate	Unknown	S
Propane	100	S
Propanol	100	l
Propionic acid	100	n
Propylene oxide	100	S
Pyridine	Unknown	l
Sea water	100	S
Silicone oil	100	S
Silver nitrate	Unknown	S
Soap	Unknown	S
Sodium borate	Unknown	S
Sodium carbonate	10–50	S
Sodium chloride	25	S
Sodium cyanide	Unknown	S
Sodium hydroxide	10–40	S
Sodium hydroxide	<40	S
Sodium hydroxide	Solution	l
Sodium hydroxide	55	l
Sodium hypochlorite	20	l
Sodium nitrate	Solution	S
Stearic acid	Unknown	S
Stearic acid	Saturated	S
Styrene	100	S
Sulfur	Unknown	S
Sulfur dioxide (gas)	Unknown	n
Sulfuric acid	2	S
Sulfuric acid	10	l
Sulfuric acid	20–25	S
Sulfuric acid	50	l
Sulfuric acid	70 to fuming	n
Sulfurous anhydride (gas)	Unknown	n
Tartaric acid	Solution	S
Tetrahydrofuran	100	S
Thionyl chloride	100	n
Toluene	100	S
Town gas (benzene-free)	100	S
Transformer oil	100	S
Trichloroacetic acid	Unknown	n
Trichloroethane	100	l
Trichloroethylene	100	l
Tricresylphosphate	Unknown	S
Triethanolamine	Unknown	S
Turpentine oil	100	S
Uric acid	Unknown	S
Vegetable oil	100	S
Vinegar	Unknown	S
Vinyl chloride	Unknown	n
Vinyl acetate	100	l
Water	100	S
Wine	Unknown	S
Xylene	100	S
Zinc chloride	Unknown	l

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide some idea and cannot be used for designing any parts or goods.

- Water vapour: polyamides 11 and 12 have a low permeability, evaluated as of the order of 0.2 up to 3 for a full range of 0.05 up to 400 for all tested plastics.
- Gases: the permeabilities of polyamides 11 and 12 are evaluated at:
- ○ carbon dioxide: 1500 up to 3400 versus a full range of 30 up to 59 000 for all tested plastics
- ○ nitrogen: 31 up to 175 versus a full range of 1 up to 3500 for all tested plastics
- ○ oxygen: 350 up to 900 versus a full range of <1 up to 11 000 for all tested plastics
- ○ hydrogen: 3200 versus a full range of 400 up to 20 000 for all tested plastics.

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames. Moreover, polyamide drips while burning.

Special formulations, which may be halogen-free, make it possible to improve this behaviour, sometimes to the detriment of other properties. UL94 V0 rating can be reached for some FR grades.

4.13.2.6 Electrical properties

Polyamides are fair insulators in a dry environment and at ambient temperature, with fair dielectric resistivities and rigidities, and high loss factors. Special grades are marketed for electrical applications. Resistivities are less sensitive to moisture than PA 6 or 66.

Figure 4.62(a) displays examples of resistivity versus hygrometry for two grades of PA 12.

Figure 4.62(b) displays examples of resistivity versus temperature for one grade of PA 12.

4.13.2.7 Joining, decoration

Welding is feasible by all processes.

Gluing is easy. All precautions must be taken concerning health and safety according to local laws and regulations.

Polyamides can generally be decorated by painting, metallization, printing, flexography, offset, serigraphy, heliography.

4.13.2.8 Specific ISO standards concerning polyamides

ISO 1140:2004 Fibre ropes – Polyamide – 3-, 4- and 8-strand ropes

ISO 1874-1:1992 Plastics – Polyamide (PA) moulding and extrusion materials – Part 1: Designation

ISO 1874-2:1995 Plastics – Polyamide (PA) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 15987:2003 Plastics – Film and sheeting – Biaxially oriented polyamide (nylon) films

4.13.2.9 Trade name examples

Grilamid, Rilsan, Vestamid . . .

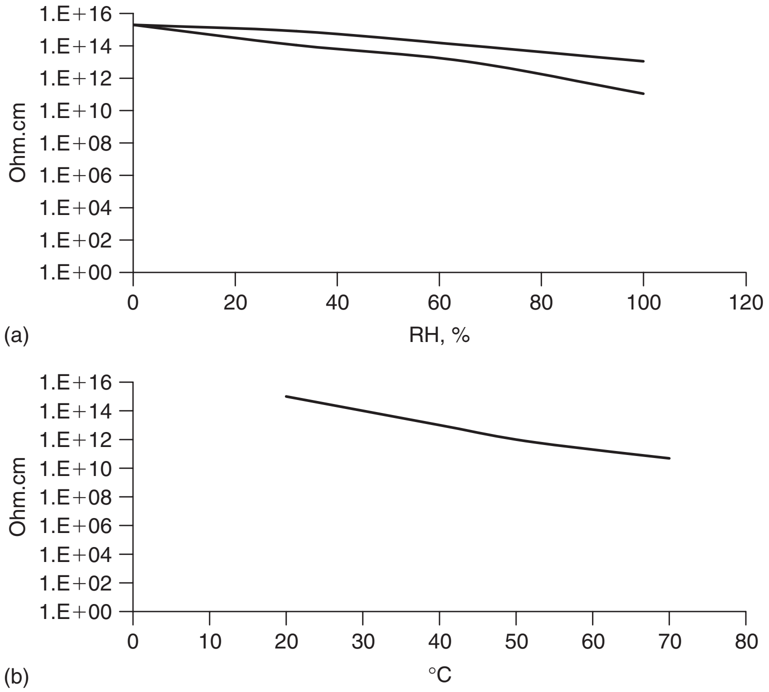


Figure 4.62. (a) Neat PA 12: examples of resistivity (ohm.cm) versus relative hygrometry (%); (b) Neat PA 12: examples of resistivity (ohm.cm) versus temperature (°C)

4.13.2.10 Property tables

Table 4.45 relates to examples only and cannot be generalized. Data indiscriminately relate to dry or wet samples and cannot be used for design purposes.

4.13.3 Linear polyamides intermediate between PA 6 or 66 and PA 11 or PA 12: PA 610 and PA 612

PA 610 and PA 612 have intermediate properties between PA 66 and PA 11.

Concerning sensitivity to water and moisture they are nearer to PA 11, and for rigidity and mechanical performances they are nearer to PA 66.

The number of producers and grades are limited.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 80°C up to 150°C if softening temperatures are higher.

The UL temperature indices of specific grades can be 65–120°C for electrical and mechanical properties including impact.

Service temperatures can be lower under loading because of modulus decay, strain, creep, relaxation . . .

For example, HDTs under 1.8 MPa for neat PA 610 or 612 are in a range from about 66°C up to 90°C.

Chemicals

Compared to PA 6 or 66, polyamides 610 and 612 absorb less water and are less sensitive to it. Special grades are marketed for their hydrolysis resistance.

Table 4.45 Neat, reinforced and modified polyamides 11 and 12: examples of properties

	PA 11 or 12		Plasticized PA 11 or 12		30% GF PA 12	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.01	1.06	1.03	1.03	1.22	1.22
Shrinkage (%)	0.7	1.5				
Absorption of water (%)	0.2	0.4				
Mechanical properties						
Shore hardness, D	58	80				
Rockwell hardness, M	<10	30				
Stress at yield (MPa)	50	65	25	25	115	115
Strain at yield (%)			30	30	5	5
Tensile strength (MPa)	50	65	40	40	115	115
Elongation at break (%)	250	400	>50	>50	6	6
Tensile modulus (GPa)	0.9	1.2	0.4	0.4	6	6
Flexural modulus (GPa)	0.9	1.2				
Notched impact strength ASTM D256 (J/m)	70	NB				
Thermal properties						
HDT B (0.46 MPa) (°C)	130	155	95	100		
HDT A (1.8 MPa) (°C)	50	60	45	45	165	165
Continuous use temperature (°C)	80	150	80	90	90	120
Melting temperature (°C)	175	190	173	173	178	178
Brittle point (°C)	−120	−70				
Thermal conductivity (W/m.K)	0.33	0.33				
Specific heat (cal/g/°C)	0.50	0.60				
Coefficient of thermal expansion (10^{-5}/°C)	9	15	14	16	2	15
Electrical properties						
Volume resistivity (ohm.cm)	10^{14}	10^{14}	10^{11}	10^{12}	10^{12}	10^{13}
Dielectric constant	3	9	4	4	4	4
Loss factor (10^{-4})	200	2000	1300	1300	450	450
Dielectric strength (kV/mm)	25	30	32	32	35	35
Fire behaviour						
UL94 fire rating	HB	HB	HB	HB	HB	HB

	50% Glass beads		Self-lubricating graphite		Conductive	
Miscellaneous properties						
Density (g/cm^3)	1.44	1.44	1.08	1.08	1.16	1.16
Mechanical properties						
Stress at yield (MPa)	45	45	45	45	50	50
Strain at yield (%)	7	7	12	12	10	10
Tensile strength (MPa)	40	40	40	40	40	40
Elongation at break (%)	25	25	40	40	30	30
Tensile modulus (GPa)	2.3	2.3			1.9	1.9
Thermal properties						
HDT B (0.46 MPa) (°C)			140	140	135	135
HDT A (1.8 MPa) (°C)	65	65	65	65	65	65
Continuous use temperature (°C)	80	120	80	110	80	110
Melting temperature (°C)	178	178	178	178	178	178
Coefficient of thermal expansion (10^{-5}/°C)	12	12	8	13	12	13
Electrical properties						
Volume resistivity (ohm.cm)	10^{12}	10^{13}	10^{12}	10^{13}	10^{2}	10^{2}
Dielectric constant	4	4				
Loss factor (10^{-4})	300	>300				
Dielectric strength (kV/mm)	34	34	21	21		
Fire behaviour						
UL94 fire rating	HB	HB	HB	HB	HB	HB

(*Continued*)

Table 4.45 (Continued)

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.	
Light	UV stabilizers are needed
Weak acids	Good to limited behaviour
Strong acids	Unsatisfactory
Weak bases	Good behaviour
Strong bases	Limited behaviour
Solvents	Chemical resistance is generally good to limited at room temperature versus dilute bases and weak acids, oils, greases, hydrocarbons, certain chlorinated solvents, cosmetics, aldehydes, some alcohols, ketones, esters, glycols. Polyamides are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols
Food contact	Possible for special grades

Chemical resistance is generally good to limited at room temperature versus dilute bases and weak acids, oils, greases, hydrocarbons, certain chlorinated solvents, cosmetics, aldehydes, some alcohols, ketones, esters, glycols. Polyamides are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols.

Table 4.46 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all polyamides 610 and 612. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.46 PA 610: examples of chemical behaviour

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	l	Butanol	100	l
Acetic acid	100	n	Butyl acetate	100	S
Acetic aldehyde	100	l	Butylamine	Unknown	l
Acetic anhydride	100	l	Butylchloride	100	l
Acetone	100	S	Butyric acid	Unknown	S
Acetonitrile	100	S	Calcium chloride	Unknown	l
Acetophenone	100	S	Carbon sulfide	100	l
Acrylic acid	100	n	Carbon tetrachloride	100	S
Aluminium chloride	10	S	Castor oil	100	S
Aluminium sulfate	Unknown	S	Cellosolve	100	S
Ammonium hydroxide	35	l	Cellosolve acetate	100	S
Ammonium sulfate	50	S	Chlorine (dry gas)	100	n
Amyl acetate	100	S	Chlorine water	Unknown	n
Amyl alcohol	100	S	Chloroacetic acid	Unknown	n
Aniline	100	l	Chlorobenzene	100	l
Antimony chloride	10	n	Chloroform	Unknown	n
Aqua regia	Unknown	n	Chlorosulfonic acid	100	n
Arsenic acid	Unknown	S	Chromic acid	Unknown	n
ASTM1 oil	100	S	Citric acid	10	S
ASTM2 oil	100	S	Cod-liver oil	Unknown	S
ASTM3 oil	100	S	Colza oil	100	S
Barium chloride	Unknown	S	Copper sulfate	Unknown	l
Benzaldehyde	100	n	Cotton oil	100	S
Benzene	100	S	Cresol	100	n
Benzylchloride	100	l	Cyclohexane	100	S
Benzyl alcohol	100	n	Cyclohexanol	100	S
Boric acid	Unknown	S	Cyclohexanone	100	S
Bromine (liquid)	100	n	Decaline	100	S

Table 4.46 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Diethylamine	100	l	Nitrobenzene	100	l
Diethyleneglycol	100	S	Nitromethane	100	l
Diethylether	100	S	Nitropropane	100	S
Dimethylamine	100	l	Oleic acid	Unknown	S
Dimethylformamide	100	S	Olive oil	100	S
Dimethylhydrazine	100	S	Oxalic acid	Solution	l
Dioctylphthalate	100	S	Perchloroethylene	100	S
Dioxan	100	S	Petroleum	100	S
Ethanol	100	l	Phenol	Unknown	n
Ethylacetate	100	l	Phosphoric acid	85	n
Ethylamine	100	S	Potassium cyanide	Unknown	S
Ethylchloride	100	S	Potassium fluoride	Unknown	S
Ethylene dichloride	100	l	Potassium hydroxide	50	l
Ethylene glycol	100	S	Potassium permanganate	25	n
Ethylenebromide	100	S	Potassium sulfate	Unknown	S
Formaldehyde	40	l	Propanol	100	l
Formic acid	90	n	Propionic acid	Unknown	n
Freon 11	100	S	Propylene oxide	Unknown	S
Freon 113	100	S	Pyridine	Unknown	S
Freon 115	100	S	Sea water	Unknown	S
Freon 12	100	S	Silicone oil	100	S
Freon 13b1	100	S	Silver nitrate	Unknown	S
Freon 21	100	S	Sodium borate	Unknown	S
Freon 22	100	S	Sodium carbonate	10	S
Freon 32	100	S	Sodium chloride	25	S
Furfural	100	n	Sodium cyanide	Unknown	S
Glycerol	100	S	Sodium hydroxide	10–60	S
Hexane	100	S	Sodium hypochlorite	20	n
Hydrazine	100	S	Sodium nitrate	Unknown	S
Hydrobromic acid	48	n	Styrene	100	S
Hydrochloric acid	⩾10	n	Sulfur dioxide (dry)	Unknown	S
Hydrofluoric acid	40	n	Sulfuric acid	⩾10	n
Hydrogen peroxide	35	n	Tetrahydrofuran	100	S
Hydrogen sulfide gas	Unknown	S	Thionyl chloride	100	n
Iron(III) chloride	Unknown	n	Toluene	100	S
Isooctane (Fuel A)	100	S	Transformer oil	100	S
Isopropanol	100	l	Trichloroacetic acid	Unknown	n
Lactic acid	90	n	Trichloroethane	100	S
Lead acetate	10	n	Trichloroethylene	100	l
Linseed oil	100	S	Tricresylphosphate	Unknown	S
Liquid paraffin	100	S	Triethanolamine	Unknown	S
Lubricating oils	100	S	Triethylamine	Unknown	S
Magnesium chloride	Unknown	S	Turpentine oil	100	S
Manganese sulfate	Unknown	S	Vegetable oil	100	S
Mercury chloride	Unknown	n	Vinyl chloride	Unknown	S
Methanol	100	l	Vinyl acetate	100	S
Methylethylketone	100	S	Water	100	S
Molasses	Unknown	S	White spirit	100	S
Monoethanolamine	Unknown	S	Wine	Unknown	S
Motor oil	100	S	Xylene	100	S
Nitric acid	>10	n	Zinc chloride	Unknown	n

S: satisfactory; l: limited; n: not satisfactory

Specific ISO standards concerning polyamides

ISO 1140:2004 Fibre ropes – Polyamide – 3-, 4- and 8-strand ropes

ISO 1874-1:1992 Plastics – Polyamide (PA) moulding and extrusion materials – Part 1: Designation

ISO 1874-2:1995 Plastics – Polyamide (PA) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 15987:2003 Plastics – Film and sheeting – Biaxially oriented polyamide (nylon) films

Trade name examples

Grilamid, Zytel . . .

Property tables

Table 4.47 relates to examples only and cannot be generalized. Data indiscriminately relate to dry or wet samples and cannot be used for design purposes.

Table 4.47 Neat and reinforced polyamides 610 and 612: examples of properties

	PA 610		PA 612		33% GF PA 612	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.07	1.10	1.06	1.06	1.32	1.32
Shrinkage (%)	0.6	1.3	1.1	1.3		
Absorption of water (%)	0.4	0.6	0.2	0.4	0.2	0.2
Mechanical properties						
Shore hardness, D	70	85	82	85		
Rockwell hardness, R	70	116	103	114		
Rockwell hardness, M	<10	50	40	50		
Stress at yield (MPa)	50	70				
Tensile strength (MPa)	45	90	52	61	138	165
Elongation at break (%)	150	300	100	340	5	5
Tensile modulus (GPa)	1	2.1	1.2	2		
Flexural modulus (GPa)	1	2.3			6	8
Notched impact strength ASTM D256 (J/m)	30	80	43	75	128	128
Thermal properties						
HDT B (0.46 MPa) (°C)	160	175	160	180		
HDT A (1.8 MPa) (°C)	75	85	66	90	210	210
Continuous use temperature (°C)	80	150				
Melting temperature (°C)	210	220	212	212	212	212
Brittle point (°C)			−126	−107		
Thermal conductivity (W/m.K)	0.21	0.23				
Specific heat (cal/g/°C)	0.4	0.4				
Coefficient of thermal expansion (10^{-5}/°C)	6	14	9	9	2.3	2.3
Electrical properties						
Volume resistivity (ohm.cm)	10^{12}	10^{15}	10^{11}	10^{13}		
Dielectric constant	3	6	3	6		
Loss factor (10^{-4})	70	900	200	1500		
Dielectric strength (kV/mm)	16	26				
Fire behaviour						
Oxygen index (%)	23	27				
UL94 fire rating	HB	V2	HB	V2		

4.13.4 Polyamide 46 (PA 46)

PA 46 has better retention of properties when the temperature rises than PA 6 and 66: higher HDT, and higher modulus at high temperature.

On the other hand, the high level of amide groups leads to high moisture sensitivity.

There is only one producer and the number of grades is limited:

- injection: low, medium or high viscosity
- heat and/or oil stabilized; glass fibre and/or mineral reinforced, fireproofed, low warpage . . .
- for electrical applications . . .

Costs

The costs are higher than those of PA 6 and 66 and, as for all plastics, fluctuate greatly with the crude oil price.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at:

- 125–165°C for a service life of 5000 h
- 115–150°C for a service life of 10 000 h
- 110–140°C for a service life of 20 000 h.

Service temperatures are noticeably lower under loading because of modulus decay, strain, creep, relaxation . . .

For example:

- the short-term modulus retention at 120°C as a percentage of the value at 20°C is roughly:
  - ○ 24% for a neat grade
  - ○ 31% for a mineral-filled grade
  - ○ 49% for a glass fibre reinforced grade
- HDTs under 1.8 MPa are of the order of:
  - ○ General purpose 160°C
  - ○ 40% mineral-filled 245°C
  - ○ 30% short glass fibres 285°C.

Mechanical properties

The mechanical properties are generally good with high elongations at break but much more limited strains at yield. Moduli and hardnesses are fair to high according to the moisture content.

Creep

Thermoplastic neat polyamide 46 at equilibrium with a 50% RH environment has a rather low modulus involving high strains for moderate loading. Consequently, creep moduli are also rather low at 23°C but change moderately when the temperature rises. Reinforcement with glass fibres completely changes the creep behaviour, leading to fair and rather high creep moduli for moderate temperatures.

Figure 4.63 highlights the different behaviours of neat and glass fibre or mineral-filled polyamides 46.

These results relate to some grades only and cannot be generalized.

Dynamic fatigue

The dynamic fatigue can be fair or good for well-adapted grades if care is taken to limit the strains by restricting the stresses to values in keeping with the low modulus.

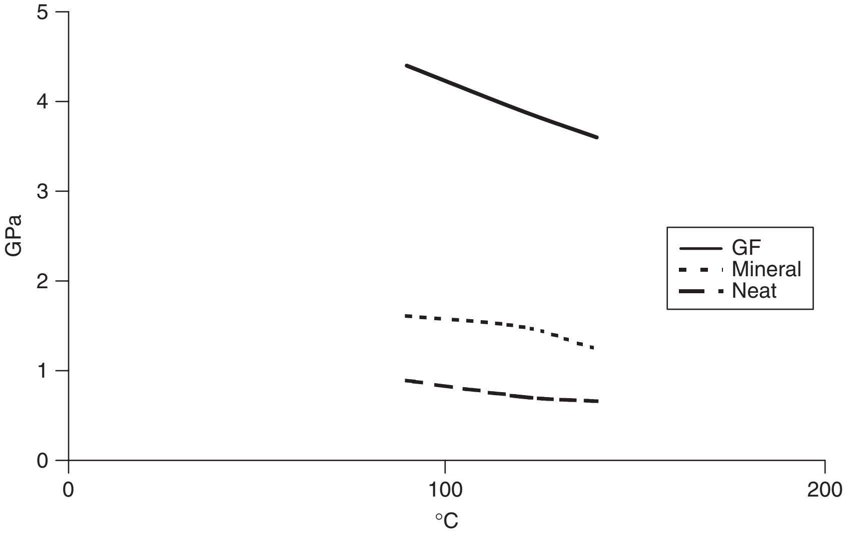


Figure 4.63. Dry PA 46 creep: examples of creep modulus (GPa) after 1000 h versus temperature (°C)

For a given grade of PA 46, Figure 4.64 displays an example of an SN or Wöhler's curve concerning flexural tests with maximum stress of ±S and pre-stress of 20 MPa.

These results are examples only and cannot be used for design purposes.

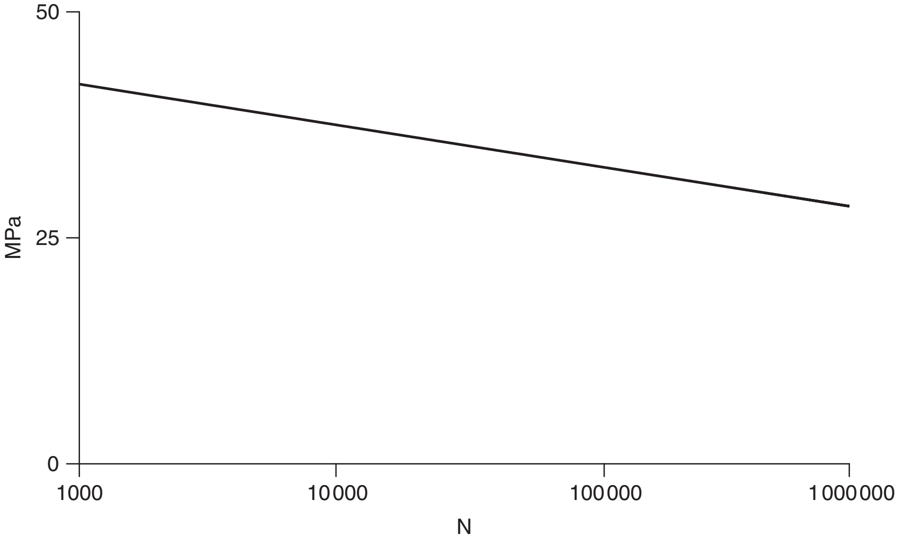


Figure 4.64. SN curve of neat PA 46, examples of maximum stress S (MPa) versus number of cycles at rupture (N) with a 20 MPa pre-stress

Chemicals

Polyamides 46 absorb water and are sensitive to it to a greater or lesser degree.

Chemical resistance is generally good to oils and greases, methanol and certain mineral salts.

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames. Moreover, polyamide drips while burning. UL94 ratings are V2 or HB.

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties. The V0 UL rating can be reached.

Electrical properties

Polyamides are fair insulators in a dry environment and at ambient temperature, with fair dielectric resistivities and rigidities, and high loss factors. Special grades are marketed for electrical applications.

In a wet environment and/or when the temperature rises, the resistivities decrease.

Trade name example

Stanyl.

Property tables

Table 4.48 relates to examples only and cannot be generalized. Data indiscriminately relate to dry or wet samples and cannot be used for design purposes.

Table 4.48 Neat and reinforced polyamides 46: examples of properties

	Neat		30% GF		40% Mineral	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.17	1.19	1.41	1.41	1.51	1.51
Shrinkage (%)	1.5	2.4	0.2	1.8	1.3	2
Absorption of water (%)	2.3	2.3	1.5	1.5	1	1
Mechanical properties						
Shore hardness, D	79	85	84	89	86	90
Rockwell hardness, R	107	123	118	120	112	122
Rockwell hardness, M	<30	50	45	65	53	71
Stress at yield (MPa)	40	100				
Tensile strength (MPa)	65	85	120	250	50	106
Elongation at break (%)	30	300	5	8	4	20
Tensile modulus (GPa)	1	3.3	4.5	9.2	2	5.8
Flexural modulus (GPa)	1	3.5	4.6	9.1	2	6.2
Notched impact strength ASTM D256 (J/m)	100	500	110	190	40	70
Thermal properties						
HDT A (1.8 MPa) (°C)	160	160	285	285	245	245
Continuous use temperature (°C)	110	150	125	150	125	140
Melting temperature (°C)	295	295	295	295	295	295
Coefficient of thermal expansion (10^{-5}/°C)	7	9	3	8	4	8
Electrical properties						
Volume resistivity (ohm.cm)	2×10^9	4×10^{15}	10^9	3×10^{15}	10^9	10^{15}
Dielectric constant	3.6	21.6	4	16.3	4	15.8
Loss factor (10^{-4})	70	8700	70	6000	80	6000
Dielectric strength (kV/mm)	16	29	24	37	24	37
Fire behaviour						
UL94 fire rating	HB	V2	HB	HB	HB	HB

4.13.5 Semi-aromatic polyamides, polyphthalamide (PPA), polyarylamide (PAA), transparent amorphous polyamide (PA-T)

Semi-aromatic PAs are copolymers of:

- an aromatic diacid and a linear diamine
- a linear diacid and an aromatic diamine.

They can be:

- Semi-crystalline, such as polyphthalamide (PPA) and polyarylamide (PAA), generally having a weak and slow absorption of water, a high rigidity, and better resistance to weathering and oils. For example, the properties of polyphthalamides are claimed to be intermediate between those of PA 66 and polyphenylene sulfide (PPS).
- Amorphous and transparent, also with good mechanical performances.

The following properties often concern engineering PAs. Transparent grades often have lower characteristics but are among the performance thermoplastics.

Applications are always technical, based on mechanical and thermal performances or on transparency and mechanical behaviour, for example:

- EE
  - connectors for electronic and electrical devices such as personal computers, digital cameras and mobile telephones; safety switches, telecommunications parts
  - use with lead-free solder especially in card connector applications for mobile telephones, personal computers and smart media
  - chassis and housings for electrical and electronic equipment, sliding parts in video recorders, disk supports in CD players . . .
  - induction motor supports . . .
- Automotive and transport
  - bearing retainers in engine compartments, gears, pivots . . .
  - bobbins for electronically controlled automatic transmission for trucks, solenoid coils in control modules for five-speed automatic truck transmissions
  - fuel pumps, cam covers, clutch parts, oil filter bodies . . .
  - vandal-proof seats, seat-adjustment parts . . .
  - mechanisms of rear-view mirror, housings . . .
  - wiper controls, headlamp controls and surrounds . . .
- Domestic appliances
  - Electric razor heads, electric iron parts, vacuum cleaner motor supports, sewing machine parts . . .
- Glass production
- Cosmetics industry
- Filter technology
- Miscellaneous
  - machine tools
  - leisure industry applications
  - medical technology . . .

There are only a few producers and the number of grades is limited:

- injection, extrusion: low, medium or high viscosity . . .
- stabilized against heat and/or oil, hydrolysis; glass or carbon fibre and/or mineral reinforced; transparent, fireproofed, low warpage . . .
- for electrical applications, self-lubricating parts . . .

Costs

The costs are higher than those of PA 6 and 66 and, as for all plastics, fluctuate greatly with the crude oil price.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at 80°C to 180°C according to the subfamily, the grade and the service conditions. For given grades, which are not representative of all semi-aromatic polyamides, maximum temperatures are:

- 155–185°C for a service life of 5000 h
- 135–165°C for a service life of 20 000 h
- 120–140°C for UL94 indices based on the electrical properties alone
- 115–130°C for UL94 indices based on the electrical and mechanical properties including impact.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

For example:

- The short-term modulus or tensile strength retention at 120°C as a percentage of the value at 20°C is roughly 30–50% for a few glass fibre reinforced grades.
- HDTs under 1.8 MPa are of the order of:

○ neat grade	80–120°C
○ 40% mineral-filled	180–220°C
○ 30% short glass fibres	220–285°C.

Figure 4.65 shows two examples of half-lives, which are not representative of all semi-aromatic polyamides.

Optical properties

The light transmittance of transparent polyamides is of the order of 85% up to more than 90% with a refractive index of 1.516, for example.

These results relate to some grades only and cannot be generalized.

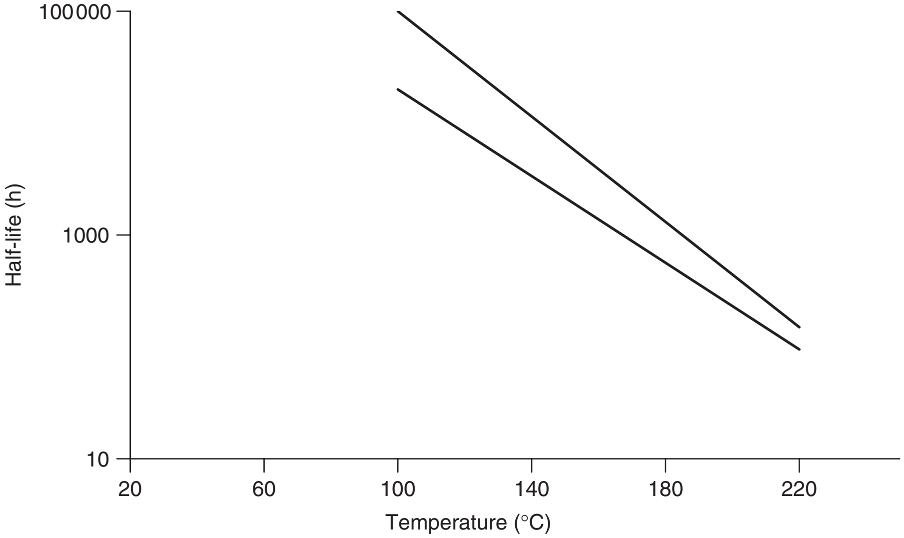


Figure 4.65. Semi-aromatic PA: examples of half-life (h) versus temperature (°C)

Mechanical properties

The mechanical properties are generally good with low elongations at break, high moduli and hardnesses, the more so as the reinforcement content rises.

Some grades are designed for tribological applications with low wear and low coefficient of friction.

Dimensional stability

Shrinkage, coefficient of thermal expansion and creep are rather low, the more so as semi-aromatic polyamides are very often reinforced. The absorption and swelling by exposure to moisture are slow and low (see Figure 4.66).

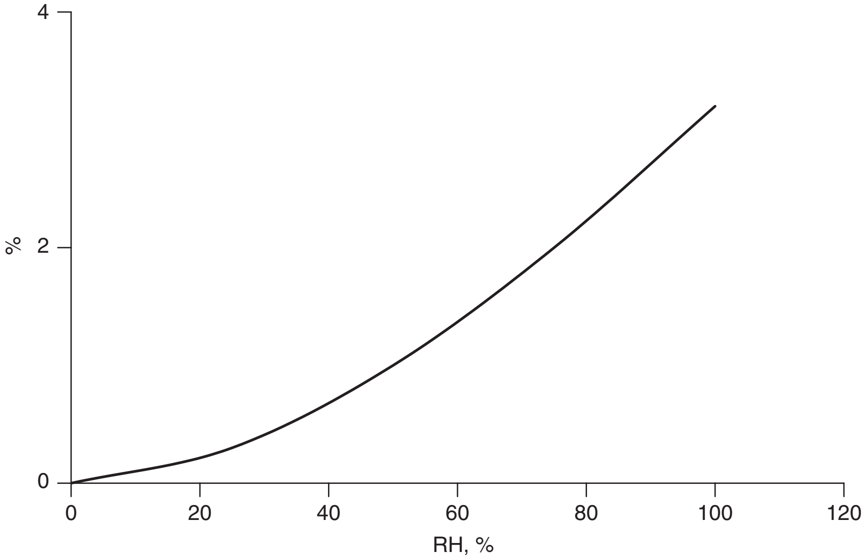


Figure 4.66. Semi-aromatic PA: moisture absorption (%) versus RH (%)

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For example, Poisson's ratios can vary from 0.28 to 0.44 according to the grade with an average value of 0.35.

These results relate to a few grades only and cannot be generalized.

Creep

Creep is rather low or very low, the more so as semi-aromatic polyamides are very often reinforced with high glass fibre contents. It changes moderately when the temperature rises.

From Figure 4.67 we can see the large differences in behaviour of transparent and highly glass fibre reinforced grades. Note that the loading of the glass fibre reinforced PAA is 30 MPa, that is, 50% higher than for the transparent PA (20 MPa).

These results relate to some grades only and cannot be generalized.

Dynamic fatigue

The dynamic fatigue can be good for well-adapted grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

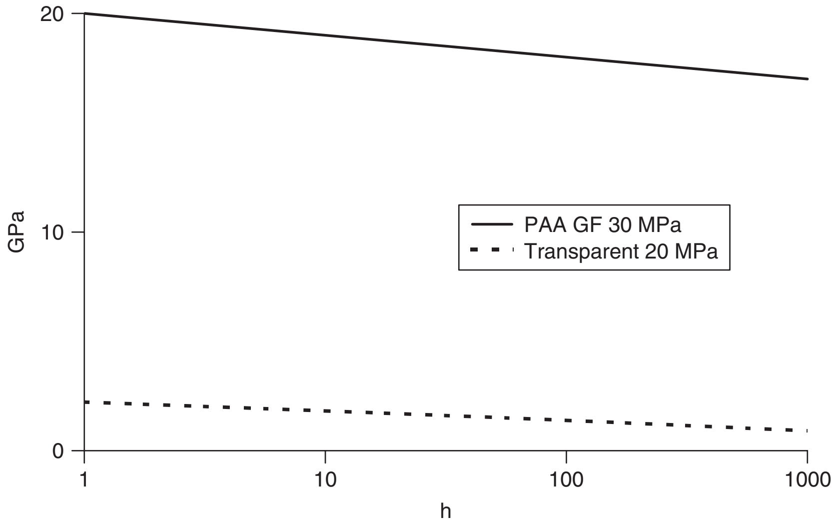


Figure 4.67. Semi-aromatic PA creep: examples of creep modulus (GPa) versus time (h) at room temperature

For two grades of reinforced semi-aromatic PA, Figure 4.68 displays examples of SN or Wöhler's curves concerning flexural tests. Note the high strength values.

These results are examples only and cannot be used for designing.

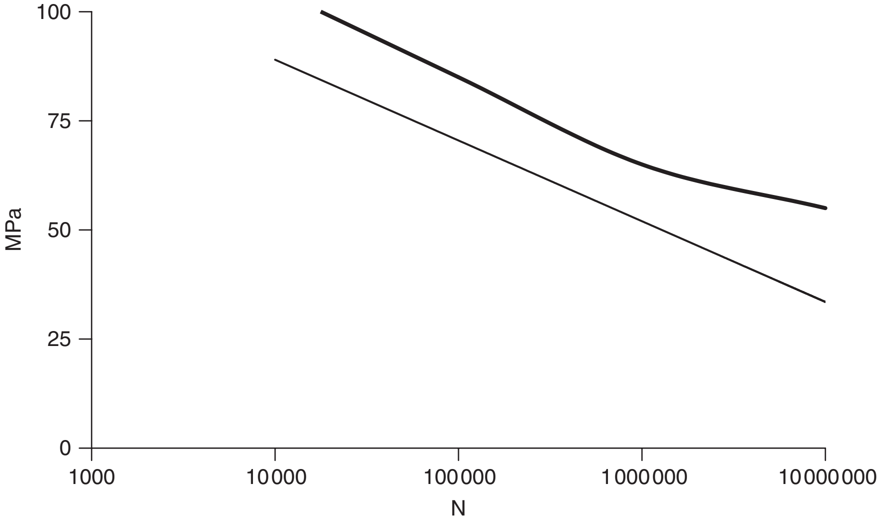


Figure 4.68. SN curves of reinforced semi-aromatic PA, examples of maximum stress S (MPa) versus number of cycles at rupture (N)

Chemicals

Semi-aromatic polyamides absorb less water than PA 6 and 66 and are less sensitive to it. Special grades are marketed for their hydrolysis resistance.

Chemical resistance is generally slightly better than for polyamides 6 and 66, but semi-aromatic polyamides are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols, formaldehyde.

Crystallinity increases impermeability and, consequently, chemical resistance.

Table 4.49 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the transparent and semi-aromatic polyamides. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames. Moreover, polyamide drips while burning. UL94 ratings are V2 or HB.

Table 4.49 Transparent PA: examples of chemical behaviour

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	⩾40	n
Acetic aldehyde	100	l
Acetone	100	l
Aniline	100	n
Benzene	100	S
Bromobenzene	100	S
Butyric acid	5–20	n
Carbon tetrachloride	100	S
Chlorobenzene	100	S
Coffee	Unknown	S
Cyclohexanone	100	S
Decaline	100	S
Diethylether	100	S
Dimethylformamide	100	n
Dioctylphthalate	100	S
Dioctylsebacate	100	S
Ethanol	96	n
Formic acid	Solution	n
Formic acid	⩾85	n
Fruit juice	Unknown	S
Hydrochloric acid	Concentrated	n
Hydrochloric acid	10	S
Hydrochloric acid	36	n
Lactic acid	90	l
Linseed oil	100	S
Liquid paraffin	100	S
Methanol	100	n
Methylene chloride	100	l
Milk	100	S
Mineral oil	100	S
Nitric acid	10	S
Nitric acid	⩾25	n
Oleic acid	Unknown	S
Oxalic acid	Unknown	S
Petrol	100	S
Petrol high-octane	100	S
Petroleum ether (ligroin)	Unknown	S
Phenol	Solution	n
Phosphoric acid	50–95	n
Potassium hydroxide	10–45	S
Pyridine	Unknown	n
Sea water	100	S
Silicone oil	100	S
Sodium hydroxide	10	S
Sugar	Solution	S
Sulfuric acid	10–25	S
Sulfuric acid	⩾96	n
Tetrachloroethylene	100	S
Tetrahydrofuran	100	n
Toluene	100	S
Tomato puree	Unknown	S
Transformer oil	100	S
Trichloroacetic acid	Unknown	S
Trichloroethylene	100	S
Tricresylphosphate	Unknown	S
Water	100	S
Xylene	100	S

S: satisfactory; l: limited; n: not satisfactory

Special formulations make it possible to improve this behaviour and to reach the V0 UL94 rating, sometimes to the detriment of other properties.

Electrical properties

Polyamides are fair insulators in a dry environment and at ambient temperature, with fair dielectric resistivities and rigidities, and high loss factors. Special grades are marketed for electrical applications.

In a wet environment and/or when the temperature rises, the resistivities decrease.

Trade name examples

Amodel, Grilamid, Ixef, Laramid, Trogamid, Zytel HTN.

Property tables

Table 4.50 relates to examples only and cannot be generalized. Data indiscriminately relate to dry or wet samples and cannot be used for design purposes.

Table 4.50 Neat and reinforced semi-aromatic polyamides: examples of properties

	PPA		Transparent PA		Lubricated PAA	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.11	1.15	1.00	1.12	1.49	1.49
Shrinkage (%)	1.3	2	0.4	1	0.4	0.8
Absorption of water (%)	0.5	0.8	0.4	1.4		
Mechanical properties						
Shore hardness, D			80	85		
Rockwell hardness, M			30	50		
Stress at yield (MPa)			60	75		
Strain at yield (%)			7	10		
Tensile strength (MPa)	62	76	50	105	135	135
Elongation at break (%)	28	30	50	300	2.2	2.2
Tensile modulus (GPa)	1.9	2.6	1.4	2.3	8.5	8.5
Flexural modulus (GPa)	2.2	2.6	1.6	2.2	7.8	7.8
Notched impact strength ASTM D256 (J/m)	960	1070	60	150	60	60
Thermal properties						
HDT B (0.46 MPa) (°C)			95	165	219	219
HDT A (1.8 MPa) (°C)	85	120	75	135		
Continuous use temperature (°C)			80	100		
Melting temperature (°C)			250	250		
Glass transition temperature (°C)			97	155		
Thermal conductivity (W/m.K)			0.21	0.23		
Specific heat (cal/g/°C)			0.33	0.34		
Coefficient of thermal expansion (10^{-5}/°C)	9	9.5	7	9		
Electrical properties						
Volume resistivity (ohm.cm)			10^{13}	10^{15}		
Dielectric constant			3	4		
Loss factor (10^{-4})			50	325		
Dielectric strength (kV/mm)			25	50		
Fire behaviour						
Oxygen index (%)			26	26		
UL94 fire rating			V2	V2		

	PAA 30% GF		PPA 33% GF		PAA 60% GF	
Miscellaneous properties						
Density (g/cm^3)	1.43	1.43	1.43	1.46	1.77	1.77
Shrinkage (%)	0.3	0.9	0.2	0.8	0.1	0.4
Absorption of water (%)	0.2	0.2	0.2	0.2	0.11	0.11
Mechanical properties						
Rockwell hardness, R			125	125		
Rockwell hardness, M	112	112			108	108
Stress at yield (MPa)	125	125	221	221		
Strain at yield (%)	2	2	2	2		
Tensile strength (MPa)	125	185	193	221	200	280

(*Continued*)

Table 4.50 (Continued)

	PAA 30% GF		PPA 33% GF		PAA 60% GF	
Elongation at break (%)	2	2.5	2.5	2	1.8	2
Tensile modulus (GPa)	10	12	11	13	18	24
Flexural modulus (GPa)	8	11	11	11	17	21
Notched impact strength ASTM D256 (J/m)	55	75	520	530	115	115
Thermal properties						
HDT B (0.46 MPa) (°C)			297	297		
HDT A (1.8 MPa) (°C)	228	228	285	285	226	226
Continuous use temperature (°C)	110	150	150	180		
Glass transition temperature (°C)	85	100	135	135		
Melting temperature (°C)	237	237	310	310		
Thermal conductivity (W/m.K)	0.15	0.15			0.55	0.55
Coefficient of thermal expansion (10^{-5}/°C)	1.5	1.5	2.4	6	1.1	1.1
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{16}	10^{16}	2×10^{15}	2×10^{15}
Dielectric constant	3	4	4	5	3	4
Loss factor (10^{-4})	700	1000	50	200	90	90
Dielectric strength (kV/mm)	28	30	21	22	23	24
Arc resistance (s)	85	85				
Fire behaviour						
Oxygen index (%)	25	25	23	23		
UL94 fire rating	HB	HB	HB	HB		

	PAA Mineral		PPA 40% Mineral		PAA 30% CF	
Miscellaneous properties						
Density (g/cm^3)	1.62	1.62	1.53	1.53	1.33	1.33
Shrinkage (%)	0.2	0.7	1	1	0.2	0.7
Absorption of water (%)	0.32	0.32	0.14	0.14		
Mechanical properties						
Shore hardness, D			87	87	>90	>90
Rockwell hardness, R			125	125	>120	>120
Rockwell hardness, M	104	104	60	60	110	110
Tensile strength (MPa)	120	185	107	107	270	270
Elongation at break (%)	2	2.5	1.6	1.6	1.3	1.3
Tensile modulus (GPa)	9	13	9	9	24	24
Flexural modulus (GPa)	8	13	7	8	21	22
Notched impact strength ASTM D256 (J/m)	70	70	48	48	60	60
Thermal properties						
HDT B (0.46 MPa) (°C)			260	260		
HDT A (1.8 MPa) (°C)	220	220	179	200	224	224
Continuous use temperature (°C)			140	160		
Thermal conductivity (W/m.K)	0.4	0.4			0.55	0.55
Coefficient of thermal expansion (10^{-5}/°C)	1	1	3	4		
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{16}	10^{16}		
Dielectric constant	4.4	4.4	4	4.2		
Loss factor (10^{-4})	90	90	6	170		
Dielectric strength (kV/mm)	28	28	22	22		
Arc resistance (s)	85	85				
Fire behaviour						
Oxygen index (%)			26	26		
UL94 fire rating			HB	HB		

4.13.6 Cast nylon

Liquid PA or cast nylon is a block copolymer of caprolactam and a prepolymer that can be processed in the liquid state, which simplifies tooling and processing machines.

Cast nylon is used for prototypes and small production runs processed by casting, rotomoulding and reaction injection moulding (RIM), possibly with structural reinforcements (SRIM) such as glass mat or fabric.

The properties are close to those of PA 6 but there is only one producer and a few grades, such as self-lubricating or FDA compliant.

Trade name example: Nyrim.

Table 4.51 relates to examples only and cannot be generalized. Data indiscriminately relate to dry or wet samples and cannot be used for design purposes.

Table 4.51 Neat, reinforced and modified cast polyamides: examples of properties

	General-purpose		Self-lubricating		SRIM glass mat or fabric reinforced	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.13	1.16	1.15	1.2	1.6	1.7
Shrinkage (%)	1.5	2				
Absorption of water (%)	0.3	0.5	0.2	0.5		
Mechanical properties						
Shore hardness, D	75	85	75	88		
Rockwell hardness, R	110	115	110	117		
Rockwell hardness, M	<10	50	<10	60		
Tensile strength (MPa)	70	84	70	80	90	114
Elongation at break (%)	20	50	20	50		
Tensile modulus (GPa)	1.7	3	2.8	3.5	9	11
Flexural modulus (GPa)	1.8	3.5	2.8	3	8	10
Notched impact strength ASTM D256 (J/m)	20	85	30	85	700	1000
Thermal properties						
HDT A (1.8 MPa) (°C)	93	93	93	177	>220	>220
Continuous use temperature (°C)	80	93	90	110		
Melting temperature (°C)	215	215	215	232		
Coefficient of thermal expansion (10^{-5}/°C)	5	7	5	10		
Electrical properties						
Volume resistivity (ohm.cm)	10^{13}	10^{14}	10^{13}	10^{14}		
Dielectric constant	3	4	3	4		
Dielectric strength (kV/mm)	20	22	16	22		
Fire behaviour						
UL94 fire rating	HB	HB	HB	HB		

4.14 Thermoplastic polyesters (PET, PBT, PETG, PCT, PTMT, PCTG, PEN, PCTA, PTT)

Thermoplastic polyesters result from the copolymerization of a diacid and a dialcohol under conditions that lead to formation of a linear macromolecule.

$$\mathrm{HOOC{-}Rb{-}COOH + HO{-}Ra{-}OH}\text{ lead to: }\mathrm{{-}(CO{-}Rb{-}COO{-}Ra{-}O)n{-}}$$

Generally:

- the diacid is terephthalic acid
- the dialcohol is:
    - ethylenediol or ethylene glycol for poly(ethylene terephthalate) (PET)
    - butenediol or butene glycol for poly(butylene terephthalate) (PBT), sometimes called poly(tetramethylene terephthalate) (PTMT).

More rarely:

- the dialcohol can be more complex or a mix of two dialcohols such as:
    - trimethylenediol or propanediol for poly(trimethylene terephthalate) (PTT)
    - cyclohexylene-dimethylenediol for poly(cyclohexylene-dimethylene terephthalate) (PCT)
    - a mix of cyclohexylene-dimethylenediol and ethyleneglycol for PETG or PCTG, according to the ratio of the two diols
- the diacid can be more complex or a mix of two diacids such as:
    - naphthalenedicarboxylic acid for poly(ethylene naphthalenedicarboxylate) (PEN)
    - a mix of terephthalic and isophthalic acids for PCTA (PCT acid).

The properties are relatively similar but differ essentially in the areas of:

- melting temperatures: 225°C for PBT, 250°C for PET, 265°C for PEN, 290°C for PCT
- crystallinity: PBT crystallizes most readily, with the usual consequences such as improvement of resistance to chemicals but higher mould shrinkage, and opacity. The most amorphous is PEN, which is transparent.

For the applications it is necessary to distinguish between:

- beverage bottles and other packaging items where polyesters compete with PVCs, and which consume more than 60% of all PET
- industrial outlets consuming the remaining PET and all PBT
- PCT is a speciality polymer for higher performance applications
- PEN is another speciality polymer mainly used for films.

Unless otherwise indicated, the following facts and figures relate to the engineering applications of PET and PBT.

4.14.1 General properties

Advantages

PET and PBT are generally chosen for their good mechanical properties and performance/cost ratios, rigidity, creep behaviour; resistance to fatigue, insulation properties, a weak moisture absorption, a broad range of service temperatures (−60°C up to 140°C), fair friction properties for special grades, good dimensional stability (except mould shrinkage for crystalline parts), possibility of food contact for special grades, aptitude for high stretching ratios.

Amorphous polyesters are used in bottle manufacturing for their transparency to light, impermeability to carbon dioxide, and possibilities for hot filling. For other packaging purposes, amorphous PET is also appreciated for its transparency to microwaves (for packaging that will be reheated).

Drawbacks

The growth of polyesters is hindered by their sensitivity to hot water above 60°C, fire behaviour except for FR grades, mould shrinkage for crystalline products, opacity (except amorphous PET), need of UV protection, limited chemical resistance, higher cost than commodities (but better performances). PET slowly crystallizes, which can slow down the production rates.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, blown film, blow moulding, co-extrusion, for thin or thick parts, high fluidity, for crosslinking . . .
- stabilized against heat, UV, hydrolysis, light and/or weathering; antistatic, conductive, high impact, reinforced, food contact, physiologically inert, fireproof, transparent, low warpage, delayed crystallization, high surface finish; 'Glass Polymers' with the look and feel of glass . . .
- for films, sheets, tubes, electrical applications, fibres, self-lubricating parts, bottles, films, packaging . . .

Costs

As for all plastics, the costs fluctuate greatly with the crude oil price, and are only given to provide a general idea. They are generally of the order of a few Euros per kilogram.

Processing

All molten-state processing methods are usable: extrusion, injection, compression, blown film, blow moulding, thermoforming, foaming, co-extrusion, machining, welding. Some rare grades can be crosslinked after shaping.

Applications

(See Chapter 2 for further information.)

Although varying according to country, for an industrialized nation the total consumption for PET and PBT can be approximately divided into:

- 55% for bottles
- 30% for films and sheets
- 5% for automotive and transport
- 5% for EE
- 5% for others.

This is an example and other data can be found elsewhere depending on the source and country.

- Transportation & automotive
  - under-the-bonnet parts . . .
  - exterior parts such as wiper arms, wiper blades, window wiper holders, exterior mirror housing, door handles . . .
  - headlamp bezels, lighting, fog lamp reflector bodies and brackets . . .
  - airflow mass meter housings and sensors . . .
  - vacuum nozzles . . .
  - valve bodies . . .
  - brake and clutch system components . . .

  - connectors, sensors, gear housings, brake booster valve bodies, tandem brake boosters . . .
  - electronics, electronics boxes (E-Boxes), fuse boxes, flex connectors, child-lock motor gear housings, ignition modules, ignition caps . . .
- Electrical & electronics
  - miniaturized electronic components . . .
  - telecoms & IT connectors, mobile phone casings, bobbins . . .
  - low voltage switch gear, electric motor parts . . .
  - lighting and lamp fittings, lamp bases of energy-saving lamps . . .
  - connectors, circuit breakers, switches . . .
  - power distribution & circuit protection . . .
  - wire and cable, optical fibre tubing . . .
- Appliances
  - housings for the home appliance market . . .
  - white goods connectors . . .
  - small appliances . . .
- Packaging
  - beverage bottles . . .
  - trays for food . . .
  - films, shrink films . . .
- Miscellaneous
  - industrial and consumer goods . . .
  - engineering applications . . .
  - textile bobbins . . .
  - meter housings . . .

4.14.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 70°C up to 140°C if the softening or melting temperatures are higher.

The UL temperature indices of specific grades can be:

- 75–155°C for the electrical properties alone
- 50–150°C for the electrical and mechanical properties excluding impact
- 50–150°C for the electrical and mechanical properties including impact.

Service temperatures are significantly lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- compared to the moduli at ambient temperature, the percentages retained at 80°C are:
  - 35% for a neat PET
  - 45–85% for a 30% glass fibre reinforced PET
- HDTs under 1.8 MPa range from:
  - 50°C up to 85°C for neat PET or PBT
  - 195°C up to 240°C for glass-reinforced PET and PBT grades
  - 220°C up to 265°C for glass-reinforced PCT grades.

Figure 4.69 displays two examples of the retention of stress at yield versus temperature for a neat and a glass fibre reinforced PBT.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially

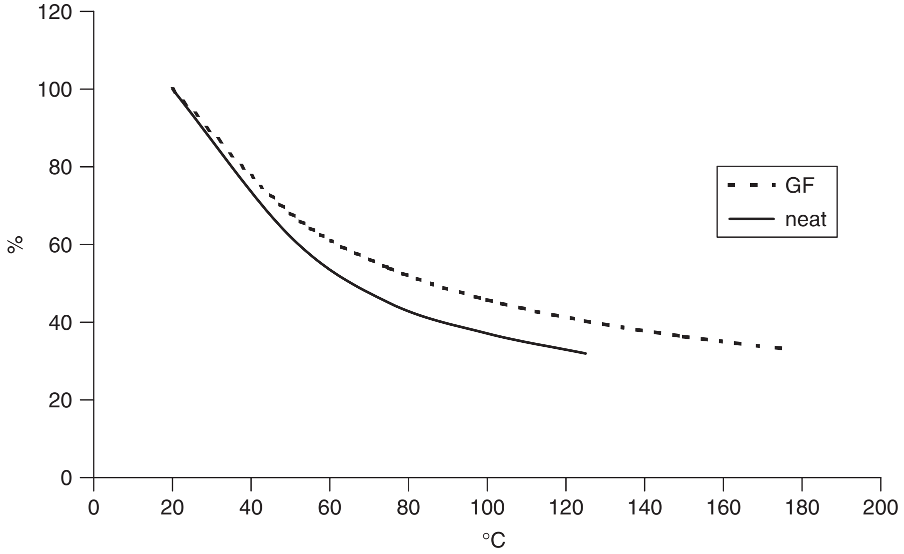


Figure 4.69. PBT examples of stress at yield retention (%) versus temperature (°C)

heat-sensitive characteristics. For given PBT grades after ageing at 180°C, tensile strength retentions are roughly:

- 100% after 4 days
- 30–80% after 40 days.

At low temperatures, the behaviour can be reasonably good down to −40°C or even −60°C according to the grades and the mechanical constraints undergone.

Rigidity slowly increases (see Figure 4.70) when the temperature decreases down to −50°C.

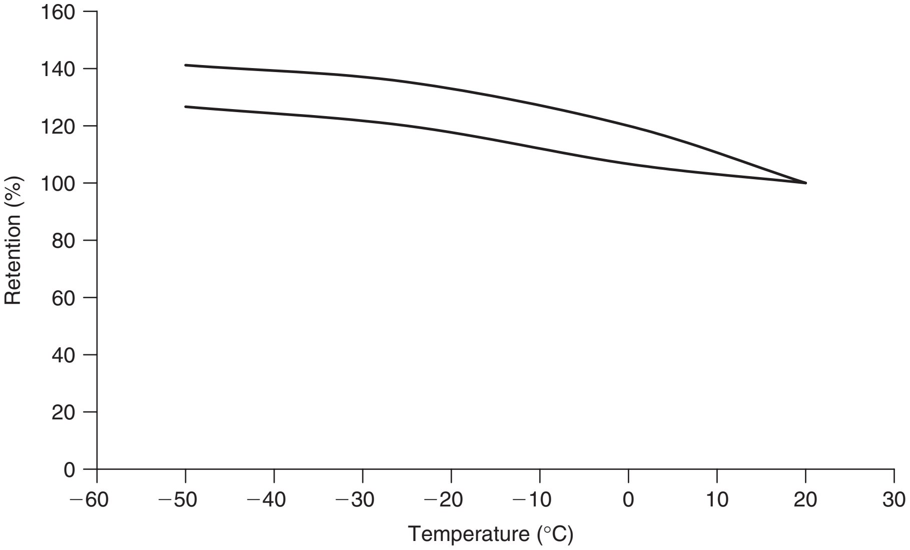


Figure 4.70. GF PBT: examples of elastic modulus retention (%) versus low temperatures (°C)

Generally, notched Izod impact strengths slowly decrease between room temperature and −30°C.

The brittle points are often of the order of −40°C down to −60°C.

Glass transition temperatures are roughly 70°C for PETs, and 60°C for PBTs.

These results relate to some grades only and cannot be generalized.

4.14.3 Optical properties

Amorphous PET is transparent with light transmittance ranging from 80% up to 92%, haze of roughly 0.3–1.3% and a refractive index of about 1.575. 'Glass Polymers' are specially designed to mimic thick glass for packaging cosmetics and healthcare products.

These results relate to some grades only and cannot be generalized.

4.14.4 Mechanical properties

The mechanical properties are generally good with sometimes high elongations at break but much more limited strains at yield. Moduli and hardnesses are rather high and impact strength is in an intermediate range. The abrasion resistance of polyester depends on the roughness, type and morphology of the opposing sliding surface. The wear resistance and coefficient of friction of special grades are suitable for tribological applications under moderate pressure.

Crystallinity and high molecular orientation improve the mechanical properties but are harmful to notched impact resistance.

Dimensional stability

Alterations by moisture exposure are weak; shrinkage and coefficient of thermal expansion depend on crystallinity; creep resistance is rather good, the more so as the glass fibre content increases.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For a given sample of 30% glass fibre reinforced PBT, it is evaluated at 0.38–0.40. This is an example only and cannot be generalized.

Creep

Neat PET or PBT have medium moduli that involve medium strains for moderate loading. Consequently, creep moduli are also in an intermediate range. Reinforcement with glass fibres leads to high moduli and, consequently, high creep moduli at room temperature. In Figure 4.71(a) we can see the broad difference between three grades tested under a load of 10 MPa. The reinforcement with 50% glass fibres leads to a modulus roughly six times that of neat PBT.

Figure 4.71(b) displays the fast decrease of creep moduli when the temperature rises.

These results relate to a few grades only and cannot be generalized.

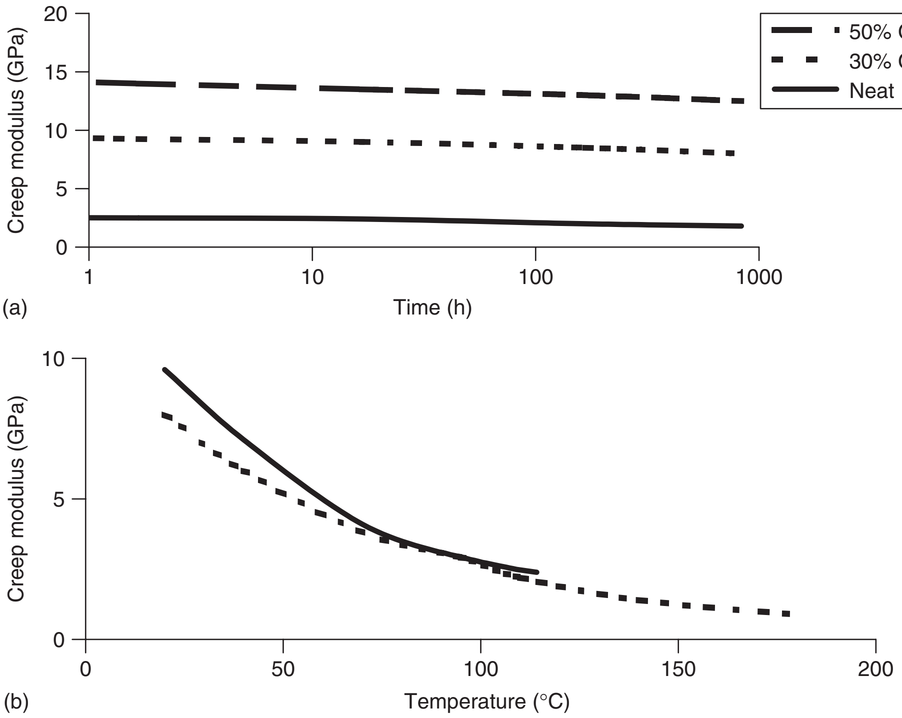


Figure 4.71 (a) PBT: examples of creep modulus (GPa) versus time (h) under 10 MPa at room temperature; (b) 30% GF PBT: examples of creep modulus (GPa) after 1000 h under 3.5 or 20 MPa versus temperature (°C)

4.14.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For a given grade of 30% glass fibre reinforced PBT, Figure 4.72 displays an example of an SN or Wöhler's curve concerning flexural tests with maximum stress of $\pm\sigma$ and average stress of 0.

Weathering

Polyesters are sensitive to hydrolysis and UV. They must be protected by addition of anti-UV and other protective agents. Generally, black grades are more resistant than neat ones. In these cases, after weathering of test bars for one year in various sunny climates, the retention of tensile strength or notched impact strength is generally good.

For three-year outdoor exposures of 3-mm-thick samples, the retention of tensile or impact strengths can be, for example:

- 50% up to 97% for natural unreinforced PBTs, depending on the UV stabilization
- 65% up to 97% for black unreinforced PBTs, depending on the UV stabilization
- 84% up to 100% for black reinforced PBTs, depending on the UV stabilization.

These results are examples only and cannot be generalized.

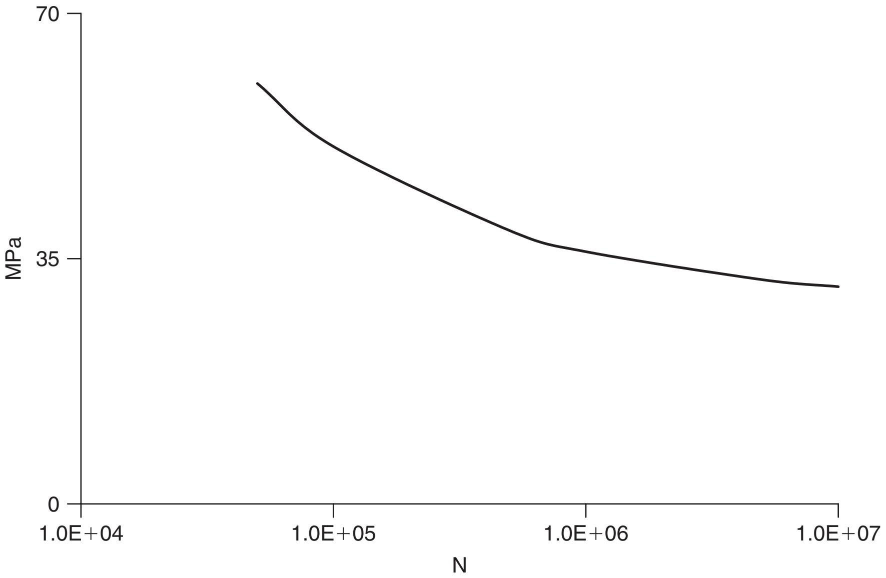


Figure 4.72. SN curve of 30% GF PBT, examples of maximum stress (MPa) versus number of cycles at rupture (N)

Chemicals

Polyesters absorb little water but are sensitive to it above 50–60°C. Stress cracking resistance is generally fair.

Suitable grades are usable in contact with food and are used for food packaging, notably beverage bottles, for example.

Chemical resistance is generally good to limited at room temperature versus dilute bases and weak acids, oils, greases, aliphatic hydrocarbons, and certain alcohols. Resistance is limited to unsatisfactory versus aromatic and halogenated hydrocarbons. Polyesters are attacked by organic and mineral acids, oxidizing agents, concentrated bases, and phenols.

Crystallinity increases impermeability and, consequently, chemical resistance.

Table 4.52 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the polyesters. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.52 Polyester: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S	Aliphatic hydrocarbons	100	S
Acetic acid	>96	l	Aluminium chloride	Solution	S
Acetic aldehyde	100	S	Aluminium sulfate	Unknown	S
Acetic anhydride	100	S	Ammonium chloride	Solution	S
Acetone	100	l	Ammonium hydroxide	30	S
Acetonitrile	100	l	Ammonium hydroxide	Dilute	n
Acetophenone	100	l	Ammonium sulfate	50	S
Acetyl chloride	100	l	Amyl acetate	100	l
Alcohols	Unknown	l	Amyl alcohol	100	S

Table 4.52 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Aniline	100	l
Aqua regia	Unknown	n
Aromatic hydrocarbons	100	l
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Benzaldehyde	100	l
Benzene	100	l
Benzoic acid	Saturated	l
Benzylchloride	100	S
Benzyl alcohol	100	l
Boric acid	Unknown	S
Brake fluid	100	S
Bromine (liquid)	100	l
Butane gas	100	S
Butanol	100	S
Butanone	100	l
Butyl acetate	100	l
Butylamine	Unknown	l
Butylchloride	100	l
Butyric acid	Unknown	S
Calcium chloride	Unknown	S
Calcium hypochlorite	Solution	l
Carbon sulfide	100	l
Carbon tetrachloride	100	S to l
Castor oil	100	S
Cellosolve	100	l
Chlorinated hydrocarbons	100	l
Chlorinated solvents	100	l
Chlorine (dry gas)	100	l
Chlorine dioxide	Unknown	l
Chlorine water	Unknown	l
Chloroacetic acid	Unknown	l
Chlorobenzene	100	l
Chlorobenzene mono	100	n
Chloroform	100	l
Chlorosulfonic acid	100	n
Chromic acid	10–50	n
Citric acid	10	S
Colza oil	100	S
Copper sulfate	Unknown	S
Cresol	100	n
Cyclohexane	100	S
Cyclohexanol	100	l
Cyclohexanone	100	l
Decaline	100	l
Dibutylphthalate	100	l
Dichloroethane	100	n
Dichloroethylene	100	l to n
Diethylamine	100	l
Diethyleneglycol	100	S
Diethylether	100	S to l
Diisopropylbenzene	100	l
Dimethylformamide	100	l
Dioctylphthalate	100	l
Dioxan	100	l
Esters	100	S
Ethanol	96	S
Ether	100	S
Ethylacetate	100	n
Ethylchloride	100	n
Ethylene glycol	100	S
Ethylhexanol	100	S
Fluorine	100	n
Formaldehyde	37	S
Formic acid	100	n
Formic acid	10–85	l
Freon 11	100	S
Freon 113	100	S
Freon 115	100	S
Freon 12	100	S
Freon 13b1	100	S
Freon 21	100	S
Freon 22	100	S
Freon 32	100	S
Furfural	100	l
Glycerol	100	S
Glycol	Unknown	S
Grease	100	S
Heptane	100	S
Hexane	100	S
Household bleach	Unknown	l
Hydraulic oil	100	S
Hydrobromic acid	48	l
Hydrochloric acid	10	S
Hydrochloric acid	36	n
Hydrofluoric acid	4–40	l
Hydrofluoric acid	60–100	n
Hydrogen peroxide	30	l
Hydrogen sulfide gas	Unknown	S
Iron(III) chloride	Unknown	S
Isobutanol	100	l
Isooctane (Fuel A)	100	S
Isopropanol	100	S to l
Kerosene	100	S
Lactic acid	10	S
Linseed oil	100	S
Liquid paraffin	100	S
Magnesium chloride	Unknown	S
Mercury	100	S
Methanol	100	l
Methylene chloride	100	n
Methylethylketone	100	l
Methylglycol	Unknown	S
Mineral oil	100	S

(*Continued*)

Table 4.52 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Monochlorobenzene	100	n
Monoethyleneglycol	100	S
Naphtha	Unknown	S
Nickel chloride	Unknown	S
Nitric acid	10–25	l
Nitric acid	⩾50	n
Nitrobenzene	100	S
Nonanol	100	S
Octane	100	S
Oleic acid	Unknown	S
Oleum @ 10%	Pure	n
Olive oil	100	S
Oxalic acid	Dilute	l
Oxalic acid	Unknown	S
Ozone	Unknown	l
Pentylacetate	100	l
Perchloroethylene	100	l
Petrol @ 10% alcohol	Unknown	S
Petrol aliphatic	100	S
Petrol high-octane	100	S
Petroleum	100	S
Petroleum ether (ligroin)	Unknown	S
Phenol	Solution	n
Phosphoric acid	<10	S
Phosphoric acid	95	n
Potassium dichromate	5	l
Potassium hydroxide	10	n
Potassium hydroxide	45	S
Potassium permanganate	1–20	S
Potassium permanganate	Solution	l
Potassium sulfate	Unknown	S
Propanol	100	S
Pyridine	Unknown	n
Sea water	100	S
Silicone oil	100	S
Silver nitrate	Unknown	S
Soap	Unknown	l
Sodium bisulfite	Solution	S
Sodium borate	Unknown	S
Sodium carbonate	10–50	S
Sodium chloride	25	S
Sodium hydroxide	10	S
Sodium hydroxide	25–40	n
Sodium hydroxide	55	l
Sodium hypochlorite	5–20	S
Sodium nitrate	Solution	S
Sparkling water	Unknown	S
Strong acids	Concentrated	n
Strong bases	Unknown	n
Sulfamic acid	Solution	S
Sulfur dioxide (gas)	Unknown	S
Sulfuric acid	2	S
Sulfuric acid	10–70	l
Sulfuric acid	96 to fuming	n
Sulfurous anhydride (gas)	Unknown	S
Tetrachloroethylene	100	l
Tetrahydrofuran	100	l
Tin chloride	Unknown	S
Toluene	100	l
Transformer oil	100	l
Trichloroacetic acid	Unknown	n
Trichloroethane	100	n
Trichloroethylene	100	l
Tricresylphosphate	Unknown	S
Triethanolamine	Unknown	l
Trimethylbenzene	100	l
Turpentine oil	100	S to l
Urea	Solution	S
Vegetable oil	100	S
Vinyl chloride	Unknown	S
Water	100	S
Weak acids	Unknown	S
Weak bases	Unknown	l
White spirit	100	S
Wine	Unknown	S
Xylene	100	l
Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: non-satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: thermoplastic polyesters have a low permeability, evaluated at 0.4 compared to the full range of 0.05 up to 400 for all tested plastics.

- Gases: thermoplastic polyesters have a low permeability, evaluated at:
  - carbon dioxide: 125 to 200 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 6 to 10 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 50 to 70 versus a full range of <1 up to 11 000 for all tested plastics
  - hydrogen: 950 versus a full range of 400 up to 20 000 for all tested plastics.

Fire resistance

Fire resistance is naturally weak. Standard grades burn easily generating flames, even after the ignition source is removed. Moreover, polyester drips while burning.

Oxygen indices are roughly 19 up to 24 with a poor UL94 rating.

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties. UL94 V0 rating can be reached for some FR grades with oxygen indices of 31 up to 34.

4.14.6 Electrical properties

Polyesters are good insulators even in wet environments with high dielectric resistivities and rigidities, and low or moderate loss factors. Special grades are marketed for electrical applications such as connectors.

PCT withstands SMT (surface mount technology) reflow soldering.

4.14.7 Joining, decoration

Welding is easy by the thermal processes and by ultrasound.

Gluing is possible with adhesives based on epoxies, polyurethanes, silicones, cyanoacrylates and hot-melts. All precautions must be taken concerning health and safety according to local laws and regulations.

Polyesters can generally be decorated by painting, metallization, printing, varnishing with compatible materials and processing.

4.14.8 Specific ISO standards concerning polyesters

ISO 15988:2003 Plastics – Film and sheeting – Biaxially oriented poly(ethylene terephthalate) (PET) films

ISO 3451-2:1998 Plastics – Determination of ash – Part 2: Poly(alkylene terephthalate) materials

4.14.9 Trade name examples

Arnite, Celanex, Corterra, Crastine, Eastar, Glass Polymer, Grilpet, Hostadur, Kodar, Orgater, Petlon, Pocan, Riteflex, Rynite, Techster, Thermx, Tribit, Ultradur, Valox, Vandar, Vestodur.

4.14.10 Property tables

Table 4.53 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.53 Polyesters: examples of properties

	Amorphous PET		PET		PBT	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.3	1.4	1.3	1.4	1.3	1.4
Shrinkage (%)	0.2	1.0	0.2	3.0	0.5	2.2
Absorption of water (%)	0.1	0.2	0.1	0.2	0.1	0.2
Mechanical properties						
Shore hardness, D			85	95	90	95
Rockwell hardness, M			50	100	70	80
Tensile strength (MPa)	40	40	45	70	40	50
Elongation at break (%)	250	300	30	70	50	200
Tensile modulus (GPa)	2.2	2.2	2.8	3.5	2	3
Flexural modulus (GPa)	2.2	2.2	2.8	3.5	2	3
Notched impact strength ASTM D256 (J/m)	10	35	15	40	35	55
Thermal properties						
HDT B (0.46 MPa) (°C)	72	72	75	115	115	150
HDT A (1.8 MPa) (°C)	70	70	65	80	50	85
Continuous use temperature (°C)	80	140	80	140	80	140
Melting temperature (°C)			220	265	220	265
Brittle point (°C)	−40	−40	−40	−40	−40	−40
Thermal conductivity (W/m.K)	0.24	0.24	0.29	0.29	0.21	0.21
Specific heat (cal/g/°C)	0.31	0.31	0.31	0.31	0.32	0.32
Coefficient of thermal expansion (10^{-5}/°C)	8	8	6	8	6	10
Electrical properties						
Volume resistivity (ohm.cm)			10^{16}	10^{16}	10^{16}	10^{16}
Dielectric constant	3	4	3	4	3	3
Loss factor (10^{-4})	20	300	20	200	10	200
Dielectric strength (kV/mm)	45	45	60	60	45	60
Arc resistance (s)	75	125	75	125		
Fire behaviour						
Oxygen index (%)					21	24
UL94 fire rating	HB	HB	HB	HB	HB	HB
	PET 30% GF		PET 30% GF Impact modified		PBT 30% GF	
Miscellaneous properties						
Density (g/cm^3)	1.5	1.6	1.5	1.5	1.5	1.6
Shrinkage (%)	0.2	1	0.2	0.9	0.2	1
Absorption of water (%)	0.1	0.1	0.1	0.3	0.1	0.1
Mechanical properties						
Shore hardness, D	95	>95	90	90	95	>95
Rockwell hardness, M	90	100	62	62	90	95
Stress at yield (MPa)	140	160	100	110	135	140
Strain at yield (%)	2	7	6	6	2	3
Tensile strength (MPa)	140	160	100	110	135	140
Elongation at break (%)	2	7	6	6	2	3
Tensile modulus (GPa)	9	12	7	9	9	11.5
Flexural modulus (GPa)	9	12	7	9	9	11.5
Notched impact strength ASTM D256 (J/m)	80	110	150	230	50	90
Thermal properties						
HDT B (0.46 MPa) (°C)	225	250	245	245	215	250
HDT A (1.8 MPa) (°C)	220	240	220	220	195	225
Continuous use temperature (°C)	100	140	100	140	100	140

Table 4.53 (Continued)

	PET 30% GF		PET 30% GF Impact modified		PBT 30% GF	
Melting temperature (°C)	245	265	245	255	220	265
Thermal conductivity (W/m.K)	0.33	0.33			0.24	0.24
Specific heat (cal/g/°C)	0.24	0.24			0.28	0.28
Coefficient of thermal expansion (10^{-5}/°C)	2	5	1.5	2	2	5
Electrical properties						
Volume resistivity (ohm.cm)					10^{16}	10^{16}
Dielectric constant	3	4			3	4
Loss factor (10^{-4})	20	160			20	120
Dielectric strength (kV/mm)	55	55			50	50
Fire behaviour						
Oxygen index (%)					19	20
UL94 fire rating	HB	HB	HB	HB	HB	HB
PBT	PBT 40% GF/mineral		PBT 20–30% Glass beads		PBT Carbon Fibres	
Miscellaneous properties						
Density (g/cm^3)	1.6	1.66	1.45	1.55	1.37	1.41
Shrinkage (%)					0.1	0.6
Mechanical properties						
Shore hardness, D	83	90				
Rockwell hardness, R	109	116				
Stress at yield (MPa)	75	120	52	55		
Strain at yield (%)	2	3	2	2.2		
Tensile strength (MPa)	70	110	45	45	135	160
Elongation at break (%)	2	3	2	4	2	3
Tensile modulus (GPa)	7.8	12	3.4	4		
Flexural modulus (GPa)					12	17
Notched impact strength ASTM D256 (J/m)					55	60
Thermal properties						
HDT B (0.46 MPa) (°C)	205	220	180	190		
HDT A (1.8 MPa) (°C)	160	200	70	90	215	220
Continuous use temperature (°C)	100	140	100	140		
Melting temperature (°C)	225	260	220	225		
Coefficient of thermal expansion (10^{-5}/°C)	2.5	2.5	10	11	1	1.5
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{15}	10^{16}	10^{2}	10^{4}
Dielectric constant	4	5.5	4	5		
Loss factor (10^{-4})	17	240	85	180		
Dielectric strength (kV/mm)	25	36	26	28		
Fire behaviour						
Oxygen index (%)	21	21	21	22		
UL94 fire rating	HB	HB	HB	HB	HB	HB
PCT	30% GF PCT		30% GF HI PCT		30% GF FR PCT	
Miscellaneous properties						
Density (g/cm^3)	1.43	1.46	1.41	1.43	1.63	1.63
Shrinkage (%)	0.1	0.8			0.1	0.8
Mechanical properties						
Shore hardness, D	90	92	83	85		
Rockwell hardness, R	115	>120	113	113		
Rockwell hardness, M	70	79	40	50		

(*Continued*)

Table 4.53 (Continued)

PCT	30% GF PCT		30% GF HI PCT		30% GF FR PCT	
Tensile strength (MPa)	117	130	97	97	120	120
Elongation at break (%)	2.3	2.3	3.1	3.1	2	2
Flexural modulus (GPa)	8.3	8.5	6.8	6.8	9.6	9.6
Notched impact strength ASTM D256 (J/m)	75	75	150	150	90	90
Thermal properties						
HDT B (0.46 MPa) (°C)	280	280	268	268	276	276
HDT A (1.8 MPa) (°C)	262	263	221	221	255	255
Continuous use temperature (°C)	110	150	110	150	110	150
Melting temperature (°C)	295	310	295	310	295	310
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}			10^{15}	10^{16}
Dielectric constant	3	3.3			3	3.1
Loss factor (10^{-4})	70	180			20	140
Dielectric strength (kV/mm)	16	17			20	21
Arc resistance (s)	150	163			175	182
Fire behaviour						
UL94 fire rating	HB	HB	HB	HB	V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers are needed
Weak acids	Good to limited behaviour
Strong acids	Unsatisfactory
Weak bases	Good to limited behaviour
Strong bases	Limited to unsatisfactory behaviour
Solvents	Chemical resistance is generally good to limited at room temperature versus dilute bases and weak acids, oils, greases, aliphatic hydrocarbons, certain alcohols Limited to unsatisfactory resistance to aromatic and halogenated hydrocarbons. Polyesters are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols
Food contact	Possible for special grades

4.15 Acrylics (PMMA, PMI, SMMA, MBS)

PMMA or poly(methyl methacrylate) is the basic, main and most representative member of the acrylics but there are also:

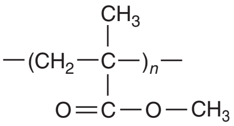
- copolymers with styrenics: SMMA (styrene-methyl methacrylate) and MBS (terpolymer of methyl methacrylate-butadiene-styrene)
- a copolymer with imides: PMI or poly(methacrylimide), which is more heat resistant.

PMMA (see Figure 4.73) is an amorphous and highly transparent thermoplastic copolymerized from methyl methacrylate according to two possible methods:

- in suspension: the polymer is then injected or extruded as with the other thermoplastics
- by direct casting of the monomer or a mix of the monomer and a prepolymer. Cast goods are isotropic, free from orientation and have excellent optical properties. Molecular weights can be as high as 1 000 000 g/mol.

The backbone is identical to that of the polyolefins but the ester pendant groups are different with a polar character.

Unless otherwise indicated, the following facts and figures relate to the engineering applications of PMMA.



$$-(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle O{=}C-O-CH_3}{C}}-)_n-$$

Figure 4.73. PMMA formula

4.15.1 General properties

Advantages

The optical properties, transparency, brightness, stability of colours and outstanding weathering resistance are the basic motivations for the choice of PMMA for optics and transparent parts for technical and aesthetic applications. Fair mechanical properties at room temperature, rigidity, rather low water absorption, good creep resistance, excellent electric properties (notably the arc resistance), ease of machining, and possibilities of food contact for specific grades are complementary advantages. Direct casting of the monomer or its mix with prepolymer is one of the rare liquid processing possibilities for thermoplastics.

PMI: more heat-resistant and suitable for foam manufacture.

Drawbacks

PMMA is handicapped by a low impact resistance, limited heat behaviour (except for the acrylic imides), inherent flammability, sensitivity to environmental stress cracking in the presence of certain chemicals, chemical attack by certain current solvents. For some grades, processing can be more difficult than for some other current thermoplastics.

Special grades

They can be classified according to the type of processing, specific properties or targeted applications:

- casting, extrusion, injection, for thin or thick parts, high fluidity . . .
- high transparency, impact modified, heat and/or detergent stabilized; high molecular weight, better resistance to stress cracking, plasticized, high rigidity, resistant to gamma rays, food contact, physiologically inert, low warpage, abrasion-resistant, reinforced, antistatic . . .
- for optics, clocks and watches, food industry, films, sheets, electrical applications, optical fibres . . .

Costs

As for all plastics, the costs fluctuate widely with the crude oil price and are only given to provide a general idea. They are generally of the order of a few Euros per kilogram.

Processing

Casting, continuous sheet casting between stainless-steel belts, pouring and several methods in the molten state are usable: extrusion, injection, compression, thermoforming, co-injection, machining, welding. Specific grades of PMI can be foamed.

Applications

(See Chapter 2 for further information.)

Although varying from country to country, for an industrialized nation the total PMMA consumption can be approximately divided into:

- 25% for casting
- 38% for extruded sheets
- 37% for moulding.

This is an example and other data can be found elsewhere depending on the source and the country.

The main application areas are:

- Optical components for automotive, electronics, photography, binoculars, sunglasses, watch glasses, lenses, magnifying glasses, camera lenses . . .
- Transparent and decorative parts for automotive and transport:
  - lenses for taillights and parking lights, rear lights . . .
  - instrument panels, dials, indicators, tachometer covers . . .
  - nameplates, medallions . . .
  - warning triangles . . .
- Lighting, lights, lighting diffusers, light-control lenses in lighting fixtures . . .
- Signs: internally illuminated outdoor signs, indoor and outdoor signs, diffusers, side-lit signs, very thin illuminated displays, fluorescent signs.
- Glazing applications, shatter-resistant glazing: buildings, aircraft, boats, mass transit, architectural, and protective glazing, windows and skylights, sight glasses, sight gauges . . .
- Transparent thermoformed products, store fixtures and displays . . .
- Electrical engineering: lamp covers, switch parts, dials, control buttons, embedment of components . . .
- Optoelectronics: covering of displays, from small LCDs in cellular phones to large rear-projection television sets or screens designed for audiovisual presentations . . .
- Optical fibres . . .
- Office equipment: writing and drawing instruments, pens, leaflet dispensers, shower cubicles, minor office or drawing equipment, squares, rulers, telephone dials . . .
- Transparent technical parts: indicators, dials, inspection holes, peepholes, portholes, domes, panes, caps, casings, hoods and electrical parts . . .
- Civil engineering: acoustic screens . . .
- Transparent and decorative parts for vending machines, appliance panels, knobs and housings, housewares, piano keys, medical instruments, dust covers for hi-fi equipment, microwave oven doors . . .
- Furniture, knobs, small furniture . . .
- Arts and fashion: embedment of items, sculptures, decorative inclusions, jewels, knick-knacks . . .
- Medicine:
  - packaging for tablets, pills, capsules, suppositories, urine containers, sterilizable equipment . . .
  - implants . . .
  - hip prostheses . . .
  - percutaneous (through-the-skin) poly(methyl methacrylate) (PMMA) vertebroplasty . . .
  - intraocular lenses . . .
  - membranes for continuous haemodiafiltration . . .
  - composite cements for orthopaedic surgery . . .

- Miscellaneous: transparent pipelines, toys, moulds, models, gauges, product prototypes, demonstration models; special UV-absorbing grades for document preservation in museums and for various photographic applications; aesthetic objects; hairbrushes . . .
- Cast and extruded sheets, cell-cast sheets, stretched sheets, films down to 50 microns used in automotive, construction, electronics, leisure, protection, communications and sports; laminated protective surfaces on ABS, PVC or other plastic sheets that are thermoformed into parts requiring resistance to outdoor weathering: motorcycle shrouds, recreational vehicle panels, residential siding and transformer housings.
- Deeply formed components subsequently backed with glass fibre reinforced polyester: tub-shower units, camper tops, furniture and recreational vehicle bodies.
- Polymethacrylimide (PMI) rigid foams as core material for composites used in aerospace launch vehicles, commercial and military airplanes, unmanned aerial vehicles, helicopters, ships, high-speed trains, X-ray tables, Formula One racing cars, high-performance bicycles, cross-country skis . . .

4.15.2 Thermal behaviour

Provided the softening temperatures are higher, the continuous use temperatures in an unstressed state are generally estimated at:

- from 60°C up to 95°C for PMMA
- from 120°C up to 150°C for PMI.

For PMMA, the UL temperature indices can be as low as 50°C.

Service temperatures are noticeably lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- the percentage of tensile strength retained at 80°C compared to the tensile strength at ambient temperature is roughly 32% for a PMMA grade
- HDTs under 1.8 MPa range from:
  - ○ 70°C up to 100°C for PMMA
  - ○ 130°C up to 160°C for PMI.

At low temperatures, the behaviour can be reasonably good, allowing applications in the automotive, civil engineering and building sectors.

Tensile strength increases by 34% when the temperature decreases from 20°C down to −20°C.

Glass transition temperatures are roughly:

- 90°C up to 135°C for PMMA
- 143°C up to 168°C for PMI.

These results relate to some grades only and cannot be generalized.

4.15.3 Optical properties

Amorphous PMMA and PMI are transparent with light transmittance ranging from 80% up to 92%, haze of less than 3% for a 3 mm thickness and a refractive index of about 1.49.

For SMMA and MBS, refractive indices are higher, 1.52 up to 1.56 for example, with a light transmittance of the order of 87–91% and a haze from 0.7% up to 3%.

These results relate to some grades only and cannot be generalized.

4.15.4 Mechanical properties

The mechanical properties are generally good with a fair rigidity as long as the temperature does not rise too much. However, general-purpose grades have a low impact resistance and a certain propensity to crazing under loading, which can occur in a few days under loading of about 20 MPa, for some grades. Special impact-modified grades avoid this crazing.

The abrasion resistance of PMMA depends on the roughness, type and morphology of the opposing sliding surface. Scratch resistance can be good, notably for specific grades designed for this property. PMMA are not intended for tribological applications.

Dimensional stability

Alterations by moisture exposure are weak; shrinkage and coefficients of thermal expansion are low, as for other amorphous polymers; creep resistance is rather good at room temperature.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular orientation. For given samples, Poisson's ratios are evaluated at 0.35–0.40. This is an example only and cannot be generalized.

Creep

PMMA has medium moduli that involve medium strains for moderate loading. Consequently, creep moduli are also in an intermediate range at room temperature. When the temperature rises moderately, the creep modulus decreases significantly, as we can see in Figure 4.74: the difference is slightly more than 40% for a temperature increase from 20°C to 50°C.

These results relate to a few grades only and cannot be generalized.

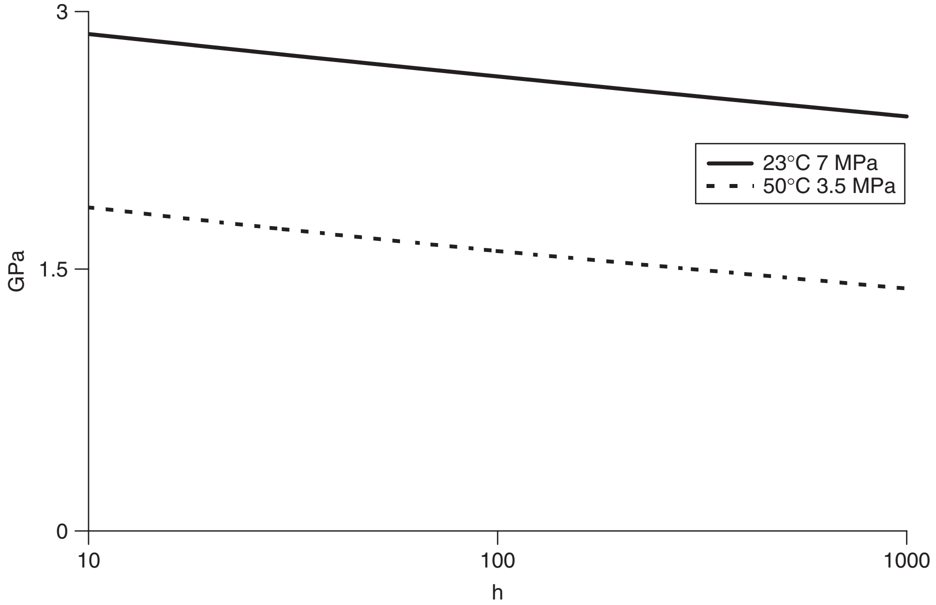


Figure 4.74. PMMA examples of creep modulus (GPa) versus time (h) under 3.5 or 7 MPa at 23°C or 50°C

4.15.5 Ageing

Weathering

The weathering resistance is one of the most interesting features of PMMA, along with its transparency. PMMA is inherently UV resistant and this characteristic can be further improved by addition of protective agents.

Optical properties are not greatly affected by long outdoor exposures. For example, after three-years' exposure in a sunny climate, the light transmittance of given grades is superior to 90%, and the yellowing and haze are slight.

For 3-mm-thick samples exposed in the same conditions, the retention of mechanical performances can be, for example:

- 70–85% for tensile strengths
- 40–70% for elongations at break
- 70–90% for impact strengths.

These results are examples only and cannot be generalized.

Chemicals

PMMA absorbs little water and shows fair resistance at ambient and moderate temperatures. Generally, PMMA has a certain propensity to stress cracking but special grades are marketed.

Suitable grades are usable in contact with food.

Chemical resistance is generally good to limited at room temperature versus weak acids and bases, oils, greases, aliphatic hydrocarbons.

PMMAs are attacked by strong acids, strong and concentrated bases, esters, ethers, ketones, aldehydes, aromatic and halogenated hydrocarbons, certain alcohols, oxidizing agents, and phenols.

Table 4.54 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily

Table 4.54 PMMA: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S	Ammonium hydroxide	30	S
Acetic acid	>96	n	Ammonium nitrate	Unknown	S
Acetic aldehyde	40–100	n	Ammonium sulfate	50	S
Acetic anhydride	100	l	Amyl acetate	100	n
Acetone	100	n	Amyl alcohol	100	n
Acetonitrile	100	n	Aniline	100	n
Acetophenone	100	n	Antimony chloride	10	S
Acetyl chloride	100	n	Aqua regia	Unknown	n
Alcohols	Unknown	n to l	Aromatic hydrocarbons	100	n
Allyl alcohol	96	n	ASTM1 oil	100	S
Alum	Solution	S	ASTM2 oil	100	S
Aluminium chloride	Solution	S	ASTM3 oil	100	S
Aluminium sulfate	Unknown	S	Barium chloride	Saturated	S
Ammonia liquid	100	n	Barium hydroxide	Saturated	S
Ammonium chloride	Solution	S	Beer	Unknown	S

(*Continued*)

Table 4.54 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Benzaldehyde	100	n	Dioctylphthalate	100	l
Benzene	100	n	Dioctylsebacate	100	l
Benzylchloride	100	n	Dioxan	100	n
Benzyl alcohol	100	n	Epichlorhydrin	Unknown	n
Boric acid	Unknown	S	Esters	100	n
Bromine (liquid)	100	n	Ethanol	30–96	l
Bromine water	Solution	l	Ethylacetate	100	n
Butanol	100	n	Ethylchloride	100	n
Butanone	100	n	Ethylene dibromide	100	n
Butyl acetate	100	n	Ethylene glycol	100	l to S
Butylamine	Unknown	n	Ethylene oxide	100	l
Butylchloride	100	n	Ethylenebromide	100	n
Butyraldehyde	100	n	Fluorine	100	n
Butyric acid	5	l	Fluosilicic acid	Unknown	S
Butyric acid	100	n	Formaldehyde	37	S
Butyrylchloride	100	n	Formic acid	10	S
Calcium chloride	Unknown	S	Formic acid	85–100	n
Calcium hypochlorite	Solution	S	Freon 11	100	l
Carbon dioxide	100	S	Freon 113	100	l
Carbon oxide	Unknown	S	Freon 12	100	l
Carbon sulfide	100	n	Freon 21	100	n
Carbon tetrachloride	100	l to n	Freon 22	100	n
Castor oil	100	S	Freon 32	100	l
Cellosolve	100	n	Fruit juice	Unknown	S
Chlorinated hydrocarbons	100	n	Fuel without benzene	100	l
Chlorinated solvents	100	n	Furfural	100	n
Chlorine (dry gas)	100	l	Glycerol	100	S
Chlorine (wet)	Unknown	l	Heptane	100	S
Chlorine water	Unknown	l	Hexane	100	S
Chloroacetic acid	Unknown	n	Household bleach	Unknown	S
Chlorobenzene	100	n	Hydrobromic acid	20–48	S
Chloroform	100	n	Hydrochloric acid	10	S
Chlorosulfonic acid	100	n	Hydrofluoric acid	40–100	n
Chromic acid	10–20	S	Hydrogen peroxide	30	S
Chromic acid	Saturated	n	Hydrogen peroxide	10 V	S
Citric acid	10	S	Hydrogen peroxide	90	n
Coffee	Unknown	S	Hydrogen sulfide gas	Unknown	S
Colza oil	100	S	Iron(III) chloride	Unknown	S
Copper sulfate	Unknown	S	Iron sulfate	Saturated	S
Cresol	100	n	Isobutanol	100	n
Cyclohexane	100	n	Isooctane (Fuel A)	100	S
Cyclohexanol	100	n	Isopropanol	100	S
Cyclohexanone	100	n	Isopropanol	10	l
DDT	Unknown	S	Kerosene	100	S
Decaline	100	n	Lactic acid	10–90	S
Diacetone alcohol	100	n	Lanoline	Unknown	S
Dibutylphthalate	100	n	Lead acetate	10	S
Dibutylsebacate	100	l	Lead tetraethyl	Unknown	S
Dichloroethane	100	n	Linseed oil	100	S
Dichloroethylene	100	n	Liqueurs	Unknown	S
Dichloromethylene	100	n	Liquid paraffin	100	S
Diethylamine	100	n	Magnesium chloride	Unknown	S
Diethyleneglycol	100	S	Magnesium hydroxide	Unknown	S
Diethylether	100	n	Magnesium sulfate	Unknown	S
Diisopropylbenzene	100	n	Manganese sulfate	Unknown	S
Dimethylformamide	100	n	Mercury	100	S

Table 4.54 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Mercury chloride	Unknown	S
Methane	100	S
Methanol	5–10	S
Methanol	50	l
Methanol	100	n
Methylamine	<32	S
Methylbenzoate	100	n
Methylbutylketone	100	n
Methylene chloride	100	n
Methylethylketone	100	n
Milk	100	S
Mineral oil	100	S
Monochlorobenzene	100	n
Monoethyleneglycol	100	S
Naphtha	Unknown	n
Naphthalene	100	l
Nickel chloride	Unknown	S
Nitric acid	10	S
Nitric acid	65–100	n
Nitrobenzene	100	n
Octane	100	l
Oleic acid	Unknown	S
Oleum @ 10%	Pure	n
Olive oil	100	S
Oxalic acid	Saturated	S
Oxygen	Unknown	S
Ozone	Unknown	l
Pentanol	100	n
Pentylacetate	100	n
Perchloroethylene	100	n
Petrol aliphatic	100	l
Petroleum	100	S
Petroleum ether (ligroin)	Unknown	l
Phenol	90	n
Phosphoric acid	≤10	S
Phosphoric acid	85–95	n
Picric acid	Unknown	S
Picric acid	Solution	n
Polish	100	S
Potassium carbonate	Saturated	S
Potassium cyanide	Unknown	S
Potassium dichromate	10	S
Potassium ferrocyanide	Saturated	S
Potassium fluoride	Unknown	S
Potassium hydroxide	10	S to l
Potassium hydroxide	10–45	S
Potassium hydroxide	50	n
Potassium nitrate	Saturated	S
Potassium permanganate	20	S
Potassium sulfite	Saturated	S
Potassium sulfate	Unknown	S
Propanol	100	l
Propylene oxide	100	n
PVC plasticized	Unknown	n
PVC rigid	100	S
Pyridine	100	n
Silicone oil	100	l
Silver nitrate	Saturated	S
Sodium bisulfite	Solution	S
Sodium borate	Unknown	S
Sodium carbonate	10	S
Sodium carbonate	50	l
Sodium chlorate	Saturated	S
Sodium chloride	25	S
Sodium fluoride	Saturated	S
Sodium hydroxide	10	S to l
Sodium hydroxide	20–55	S
Sodium hydroxide	50	n
Sodium hypochlorite	5–20	S
Sodium nitrate	Solution	S
Soft rubber	Unknown	n
Stearic acid	Unknown	S
Strong acids	Concentrated	l to n
Strong bases	Unknown	l to n
Styrene	100	n
Sulfur dioxide (gas)	Unknown	S
Sulfuric acid	2–30	S
Sulfuric acid	50	l
Sulfuric acid	70 to fuming	n
Sulfurous anhydride	100	S
Sulfurous anhydride (gas)	Unknown	S
Tartaric acid	Solution	S
Tetrachloroethane	100	n
Tetrachloroethylene	100	n
Tetrahydrofuran	100	n
Tin chloride	Unknown	S
Toluene	100	n
Town gas (benzene-free)	100	S
Transformer oil	100	l
Trichloroacetic acid	10	l
Trichloroethane	100	n
Trichloroethylene	100	n
Tricresylphosphate	Unknown	n
Triethanolamine	Unknown	l
Trimethylbenzene	100	n
Turpentine oil	100	S to l
Urea	Solution	S
Vegetable oil	100	S
Vinyl chloride	Unknown	n
Vinyl acetate	100	l
Water	100	S
Weak acids	Unknown	l
Weak bases	Unknown	l
White spirit	100	l
Wine	Unknown	S
Xylene	100	n
Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory; V: by volume representative of all the acrylics. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Fire resistance

Fire resistance is naturally weak. Standard grades burn, generating flames, even after the ignition source is removed. Moreover, acrylics drip while burning.

Oxygen indices are roughly 18 up to 20 with a poor UL94 rating.

4.15.6 Electrical properties

Acrylics are good insulators even in wet environments, with high dielectric resistivities and moderate loss factors. Special grades are marketed for electrical applications.

4.15.7 Joining, decoration

PMMA is prone to stress cracking and contact with plasticized PVC, rubber seals and silicone sealants must be avoided or carefully studied.

Welding is possible for certain grades by the thermal processes, high frequencies, induction and by ultrasound. The strength of the joints can be 10–40% of the PMMA used. Gluing generally gives better results.

Gluing is possible with pure solvents, monomer or chloroform for example, or with PMMA dissolved in solvents. Preliminary tests are essential. The strength of joints can be 60–70% of the PMMA used.

All precautions must be taken concerning health and safety according to local laws and regulations.

PMMA can generally be decorated by painting, varnishing, metallization, printing with compatible materials and processing.

4.15.8 Foams

'Rohacell', a closed-cell PMI foam developed by Röhm of Germany to be used as cores in lightweight sandwich composites for transport, has specific advantages:

- a density range from 30 to 300 kg/m^3
- a high resistance to the solvents used for processing the composites
- excellent mechanical properties and high thermal stability
- high specific tensile strength and elastic modulus (specific properties are engineering properties divided by density)
- a low thermal conductivity
- excellent damping properties and shock absorption
- a low X-ray absorption.

On the other hand, oxygen indices are low: roughly 19 to 20.

Table 4.55 displays some examples of performances.

Examples of applications:

- aeronautics: parts for Airbus, ATR, Eurocopter, Dassault, McDonnell Douglas, radomes . . .
- automobile: parts for Matra, Volvo . . .
- railways: two-floor TGV (high-speed train), front end of the Italian Pendolino . . .

Table 4.55 Examples of polymethacrylimide foam properties

Density (kg/m^3)	32	75	110	190
Density (g/cm^3)	0.032	0.075	0.110	0.190
Tensile strength (MPa)	1	2.8	3.5	8.5
Flexural strength (MPa)	0.8	2.5	4.5	12
Compression strength (MPa)	0.4	1.5	3	3–8
Elongation at break (%)	3.5	4.5	4.5	6
Elastic modulus (GPa)	0.036	0.092	0.160	0.380
Dimensional stability (°C)	180	180	180	130
Thermal conductivity (W/m.K)	0.031	0.030	0.032	
Specific properties: engineering properties divided by density				
Specific tensile strength (MPa)	31	37	32	45
Specific elastic modulus (GPa)	1.1	1.2	1.5	2

- medical: radiography table (low X-ray absorption) . . .
- naval: racing boats, yachts, catamarans . . .
- sports and leisure: parts for skis, rackets . . . (Head, Dynastar, Atomic), wheels and frames for racing bikes . . .

4.15.9 Specific ISO standards concerning acrylics

ISO 1628-6:1990 Plastics – Determination of viscosity number and limiting viscosity number – Part 6: Methyl methacrylate polymers

ISO 7823-1:2003 Plastics – Poly(methyl methacrylate) sheets – Types, dimensions and characteristics – Part 1: Cast sheets

ISO 7823-2:2003 Plastics – Poly(methyl methacrylate) sheets – Types, dimensions and characteristics – Part 2: Extruded sheets

ISO 7823-3:2003 Plastics – Poly(methyl methacrylate) sheets – Types, dimensions and characteristics – Part 3: Continuous cast sheets

ISO 8257-1:1998 Plastics – Poly(methyl methacrylate) (PMMA) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 8257-2:2001 Plastics – Poly(methyl methacrylate) (PMMA) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 12017:1995 Plastics – Poly(methyl methacrylate) double- and triple-skin sheets – Test methods

4.15.10 Trade name examples

Acrylite, Altuglas, Altulite, Cyrolite, Diakon, Hesalite, Oroglas, Perspex, Plexiglas, RTP acrylics, Vedril . . .

PMI: Kamax, Rohacell

SMMA, MBS: NAS, Zylar . . .

4.15.11 Property tables

Table 4.56 relates to examples only and cannot be generalized. Data cannot be used for design purposes. See also Table 4.55 for PMI foam properties.

Table 4.56 Acrylics: examples of properties

	Cast PMMA		Moulded PMMA		Impact PMMA	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.17	1.2	1.17	1.2	1.1	1.2
Shrinkage (%)			0.2	0.8	0.2	0.8
Absorption of water (%)	0.2	0.4	0.1	0.4	0.2	0.8
Mechanical properties						
Shore hardness, D	95	>95	90	>95	83	95
Rockwell hardness, M	80	100	70	105	40	80
Stress at yield (MPa)	55	77	38	70		
Strain at yield (%)	2	7	2	10		
Tensile strength (MPa)	55	77	38	70	35	65
Elongation at break (%)	2	7	2	10	4	70
Tensile modulus (GPa)	2.5	5	2.5	3.5	1.5	3.5
Flexural modulus (GPa)	2.5	5	2.5	3.5	1.5	3.5
Notched impact strength ASTM D256 (J/m)	15	25	10	25	20	130
Thermal properties						
HDT B (0.46 MPa) (°C)	75	115	80	110	75	100
HDT A (1.8 MPa) (°C)	70	100	70	100	70	95
Continuous use temperature (°C)	50	95	50	90	50	90
Glass transition temperature (°C)	90	135	90	110	90	110
Thermal conductivity (W/m.K)	0.15	0.25	0.15	0.25		
Specific heat (cal/g/°C)	0.35	0.35	0.35	0.35		
Coefficient of thermal expansion (10^{-5}/°C)	5	9	5	9	5	9
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{14}	10^{16}		
Dielectric constant	2	5	2	5		
Loss factor (10^{-4})	200	600	200	2000		
Dielectric strength (kV/mm)	15	22	15	22		
Fire behaviour						
Oxygen index (%)	18	20	18	20	18	20
UL94 fire rating	HB	HB	HB	HB	HB	HB

	SMMA MBS		Heat-stabilized PMMA		PMI	
Miscellaneous properties						
Density (g/cm^3)	1.09	1.13	1.15	1.25	1.2	1.22
Shrinkage (%)	0.2	0.6	0.2	0.8	0.2	0.8
Absorption of water (%)	0.15	0.24	0.2	0.4	0.2	0.4
Mechanical properties						
Shore hardness, D	90	95	95	>95	95	>95
Rockwell hardness, M	75	85	90	100	90	100
Stress at yield (MPa)			65	79	77	79
Strain at yield (%)			2	10	4	4
Tensile strength (MPa)	53	70	65	79	77	79
Elongation at break (%)	2	27	2	10	4	4
Tensile modulus (GPa)	2.8	3.6	2.5	4.3	3.6	4.3
Flexural modulus (GPa)	2.4	3.2	2.5	4.3	3.6	4.3
Notched impact strength ASTM D256 (J/m)	20	50	10	25	10	25
Thermal properties						
HDT B (0.46 MPa) (°C)			90	170	140	170
HDT A (1.8 MPa) (°C)	84	99	85	160	132	160
Continuous use temperature (°C)			100	150	120	150
Glass transition temperature (°C)			100	168	143	168
Thermal conductivity (W/m.K)					0.15	0.15
Coefficient of thermal expansion (10^{-5}/°C)			4	9	4	7

Table 4.56 (Continued)

	SMMA MBS		Heat-stabilized PMMA		PMI	
Electrical properties						
Volume resistivity (ohm.cm)			10^{14}	10^{16}	10^{16}	10^{16}
Dielectric constant			2	5	3	3.2
Loss factor (10^{-4})					100	100
Dielectric strength (kV/mm)					17	17
Fire behaviour						
Oxygen index (%)			18	20	19	20
UL94 fire rating			HB	HB	HB	HB

	Antistatic clear acrylic		30% GF reinforced acrylic	
Miscellaneous properties				
Density (g/cm^3)	1.15	1.15	1.42	1.42
Shrinkage (%)	0.5	0.7	0.1	0.2
Absorption of water (%)			0.2	0.2
Mechanical properties				
Shore hardness, D			85	90
Rockwell hardness, R			120	120
Rockwell hardness, M			50	80
Tensile strength (MPa)	38	38	103	103
Elongation at break (%)	10	>10	1	1
Tensile modulus (GPa)	1.4	1.4	10.3	10.4
Flexural modulus (GPa)	1.7	1.7	10.3	10.4
Notched impact strength ASTM D256 (J/m)	53	53	53	53
Electrical properties				
Volume resistivity (ohm.cm)	10^{9}	10^{9}	10^{16}	10^{17}
Fire behaviour				
Oxygen index (%)	18	20	18	20
UL94 fire rating	HB	HB	HB	HB

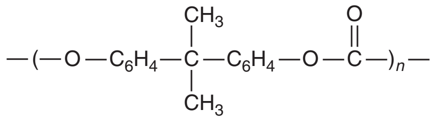
General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV resistant
Weak acids	Good to limited behaviour
Strong acids	Good to unsatisfactory behaviour according to the concentration
Weak bases	Good behaviour
Strong bases	Good to unsatisfactory behaviour according to the concentration
Solvents	Chemical resistance is generally good to limited at room temperature versus oils, greases, aliphatic hydrocarbons PMMAs are attacked by esters, ethers, ketones, aldehydes, aromatic and halogenated hydrocarbons, certain alcohols, oxidizing agents, phenols
Food contact	Possible for special grades

4.16 Polycarbonates (PC)

Polycarbonates are polyesters resulting from the polycondensation of carbonic anhydride (furnished by phosgene) and a bisphenol.

The most-common polycarbonates are based on bisphenol A (see Figure 4.75) but, more recently, 'heat resistant' grades were launched based on other bisphenols, possibly blended with bisphenol A.



$$-(-\mathrm{O}-\mathrm{C_6H_4}-\underset{\mathrm{CH_3}}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}}-\mathrm{C_6H_4}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-)_n-$$

Figure 4.75. Polycarbonate formula

Polycarbonates are amorphous and highly transparent thermoplastics like acrylics, but with excellent impact strength, a higher price and lower resistance to UV and weathering.

Unless otherwise indicated, the following facts and figures relate to the engineering applications of polycarbonates based on bisphenol A.

4.16.1 General properties

Advantages

Polycarbonates are used in optics, transparent technical parts, aesthetic applications and protection devices for their transparency, mechanical properties, impact resistance, rigidity, good creep behaviour, fatigue resistance, insulating properties, dimensional stability, low moisture uptake, broad range of service temperatures (−100°C up to +135°C), food contact and sterilization possibilities for suitable grades.

Drawbacks

Polycarbonates are handicapped by their sensitivities to light and hydrolysis, requiring efficient protection for outdoor exposure; fire behaviour, except for FR grades; sensitivity to environmental stress cracking and attacks by chemicals such as bases, oils, chlorinated solvents, ketones. The cost, which is justified by the performances, is higher than that of PMMA and, of course, the commodities.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, blow moulding, thermoforming, structural foam, blown film, for thin or thick parts; low, medium or high fluidity . . .
- high transparency, impact-modified, heat and/or hydrolysis stabilized; better resistance to stress cracking, high rigidity, food contact, physiologically inert, low warpage, abrasion-resistant, reinforced, antistatic, conductive . . .
- for optics, CDs, lenses, automotive lenses, food packaging, films, sheets, electrical applications, medical uses . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide some idea. They are generally of the order of several Euros per kilogram, higher than those of PMMAs.

Processing

All the molten-state processing methods are usable: extrusion, injection, blowing, compression, thermoforming, co-injection, machining, welding. Specific grades can be used for structural foam.

Consumption

The total polycarbonate consumption varies according to the country. For example, in Europe (according to APME data), it can be approximately divided into:

- 32% for glazing and sheets
- 22% for E&E
- 18% for CDs
- 9% for automotive & transport
- 6% for appliances and consumer goods
- 3% for medical and health care
- 3% for bottles and packaging
- 3% for leisure and safety
- 4% for miscellaneous.

This is an example and other data can be found elsewhere depending on the source and the country.

Applications

(See Chapter 2 for further information.)

The main applications for polycarbonates are:

- Glazing
  - architectural glazing, roofs of verandas, stations, stadiums, sheeting applications . . .
  - protective glazing, vandal-proof windows, shatter-resistant glazing, windows and skylights . . .
  - aircraft, boats, mass transit . . . .
  - sight glasses, sight gauges, portholes . . .
- Films
  - technical uses: keyboards, instrument panels, control boards, insulating layers and cards . . .
  - aesthetic applications . . .
  - in-mould decoration . . .
- Electrical & electronics (E&E) and optical media
  - optical media, computer and audio compact discs . . .
  - internal components and current-carrying devices, brush holders, coil bobbins & forms . . .
  - power distribution, connectors, insulators, relay components, meter housings and covers, casket hardware . . .
- Electrical household appliances
  - telecommunications, mobile phones, housing for GSM phones . . .
  - electrical chargers, battery boxes . . .
  - electric portable tool housings; computer and business machine parts . . .

- Lighting
  - light globes, lighting diffusers, light-control lenses . . .
  - outdoor lighting fixtures . . .
- Optical components
  - automotive, electronics, photography, binocular, camera lenses . . .
  - sunglasses, magnifying glasses . . .
- Automotive & transportation
  - automotive lighting: head and fog lamp lenses, interior lighting covers and exterior lighting applications . . .
  - interior cladding, dashboards, instrument panel retainers, knee bolsters, glove box doors, steering column covers, defroster/demister grilles, speaker grilles . . .
  - exterior parts, large parts, bumpers, body panels . . .
  - card guides . . .
  - nameplates and bezels . . .
- Industrial equipment
  - transparent technical parts: indicators, dials, inspection holes, peepholes, portholes, domes, panes, caps, casings, hoods and electrical parts . . .
  - transparent and decorative parts for vending machines, appliance panels, knobs and housings, housewares . . .
  - assembly line cogs . . .
  - equipment housings . . .
  - brackets, structural parts, covers, handles, rollers, machine guards, fittings . . .
  - power tools . . .
  - high-temperature and -pressure windows, portholes in pressure chambers . . .
  - jet pump impellers and diffusers . . .
- Packaging
  - baby bottles, water dispensers, water bottles . . .
- Medical applications
  - lenses, lenses for eyeglasses . . .
  - dialysis equipment parts, compact heart-lung systems . . .
  - medical tubing . . .
  - gamma-sterilizable reusables . . .
  - instrument covers, handles, machine guards, fittings . . .
- Safety
  - face shields, safety helmets
  - high-temperature and -pressure glazing . . .
- Miscellaneous
  - aircraft & missile components . . .
  - cash dispensers . . .
  - traffic lights . . .
  - garden equipment . . .
  - furniture, office & institutional furniture . . .
  - sporting goods . . .
  - static dissipative grades: covers, guards, access panels, machine windows and doors, static control shields, glove boxes, electronic equipment, process instrumentation, conveyor line covers, cleanroom windows and doors, partitions, and pass-through modules . . .

4.16.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 90°C up to 125°C for general-purpose grades and up to 140°C for heat-resistant polycarbonates if the softening or melting temperatures are higher.

The UL temperature indices of specific grades can range from 65°C up to 130°C for the electrical and mechanical properties including impact.

Service temperatures are noticeably lower under loading because of modulus decay, strain, creep, relaxation. . . For example:

- Compared to the value at ambient temperature, the percentage of stress retention at yield is roughly 85–90% at 100°C for given reinforced or neat grades.
- For a glass fibre reinforced polycarbonate with an engineering tensile strength of 80 MPa, the creep strengths for failure after 1 h are:
- ○ 85% of the engineering tensile strength at 23°C
- ○ 69% of the engineering tensile strength at 60°C
- ○ 57% of the engineering tensile strength at 100°C.
- HDTs under 1.8 MPa range from:
- ○ 125°C up to 140°C for neat polycarbonates
- ○ 140°C up to 180°C for heat-resistant grades
- ○ 135°C up to 150°C for glass-reinforced grades.

Figure 4.76 displays two examples of modulus retention versus temperature for a neat and a glass fibre reinforced polycarbonate; the two curves are practically intermingled with an abrupt fall at roughly 140–145°C.

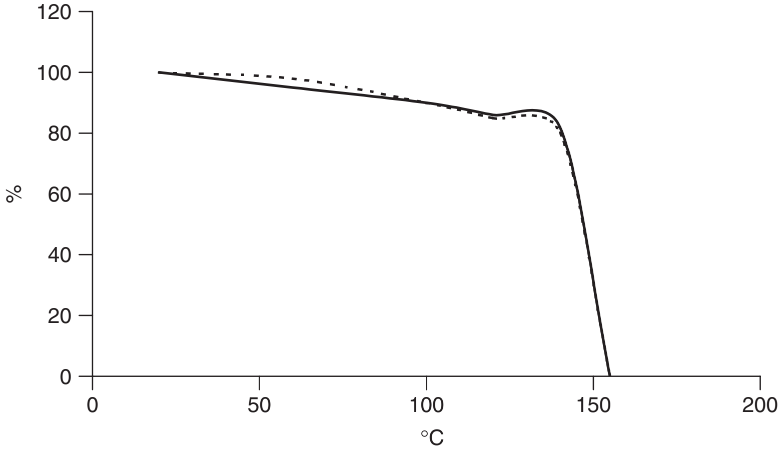


Figure 4.76. PC examples of modulus retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially heat-sensitive characteristics.

At low temperatures, the behaviour can be reasonably good down to −20°C or even less according to the grades and the mechanical constraints undergone.

Rigidity slowly increases (see Figure 4.77) when the temperature decreases down to −60°C.

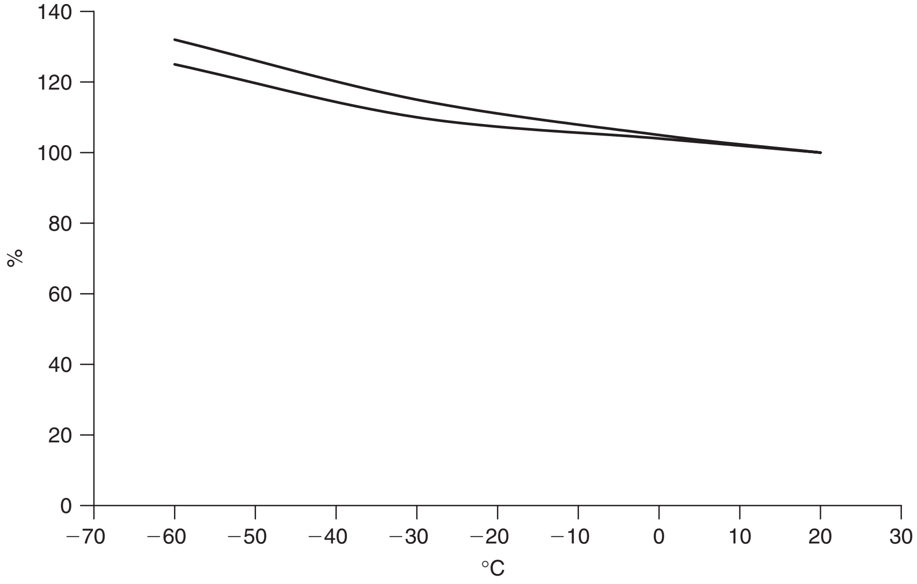


Figure 4.77. PC examples of elastic modulus retention (%) versus sub-zero temperatures (°C)

Generally, notched Izod impact strengths slowly decrease between room temperature and −15°C/−20°C and then fall but are still fair (see Figure 4.78).

Glass transition temperatures are high, roughly 150°C for general-purpose grades and 160–200°C for heat-resistant grades.

These results relate to some grades only and cannot be generalized.

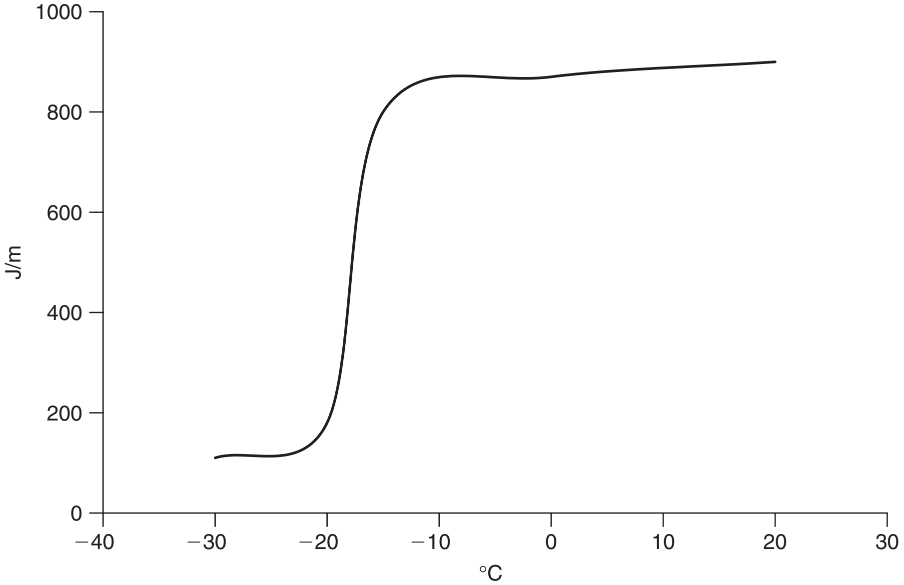


Figure 4.78. PC examples of notched impact strength (J/m) versus low temperatures (°C)

4.16.3 Optical properties

Amorphous polycarbonate is transparent with light transmittance ranging from 80% up to 91%, a haze of roughly 0.7–1.5% and a refractive index of about 1.58–1.586.

These results relate to some grades only and cannot be generalized.

4.16.4 Mechanical properties

The mechanical properties are generally good with rather high elongations at break but much more limited strains at yield. Moduli and hardnesses are in a medium range and impact strengths are excellent. The abrasion resistance of polycarbonates depends on the roughness, type and morphology of the opposing sliding surface. The wear resistance and coefficient of friction of special grades are suitable for tribological applications.

Friction

Some self-lubricating grades of polycarbonate are marketed, containing specific additives and reinforced with glass or carbon fibres. The coefficients of friction are in a good range, from 0.1 up to 0.21. Wear resistance is not as good as for PA 66.

These results relate to a few grades only and cannot be generalized.

Dimensional stability

Alterations by moisture exposure are weak; the shrinkage and coefficient of thermal expansion are rather low, typical of amorphous thermoplastics; creep resistance is good, the more so as the glass fibre content increases.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For given samples of neat and reinforced polycarbonates, it is evaluated at 0.38–0.39. This is only an example and cannot be generalized.

Creep

Neat polycarbonates have medium moduli that involve medium strains for moderate loading. Consequently, creep moduli are also in an intermediate range. Reinforcement with glass fibres leads to high moduli and, consequently, high creep moduli at room temperature. From Figure 4.79(a) we can see the broad difference between two grades tested under a load of 21 MPa. The reinforcement with 20% glass fibres leads to a modulus roughly twice that of neat polycarbonate.

For a neat polycarbonate, Figure 4.79(b) displays an example of the decrease in creep modulus as the temperature rises.

For a neat polycarbonate with an engineering tensile strength of 67 MPa, the creep strengths for failure after 10 000 h are:

- 15 MPa at 120°C, namely 22% of the engineering tensile strength.
- 20 MPa at 100°C, namely 30% of the engineering tensile strength.
- 30 MPa at 80°C, namely 45% of the engineering tensile strength.
- 38 MPa at 60°C, namely 57% of the engineering tensile strength.
- 45 MPa at 23°C, namely 67% of the engineering tensile strength.

These results relate to a few grades only and cannot be generalized.

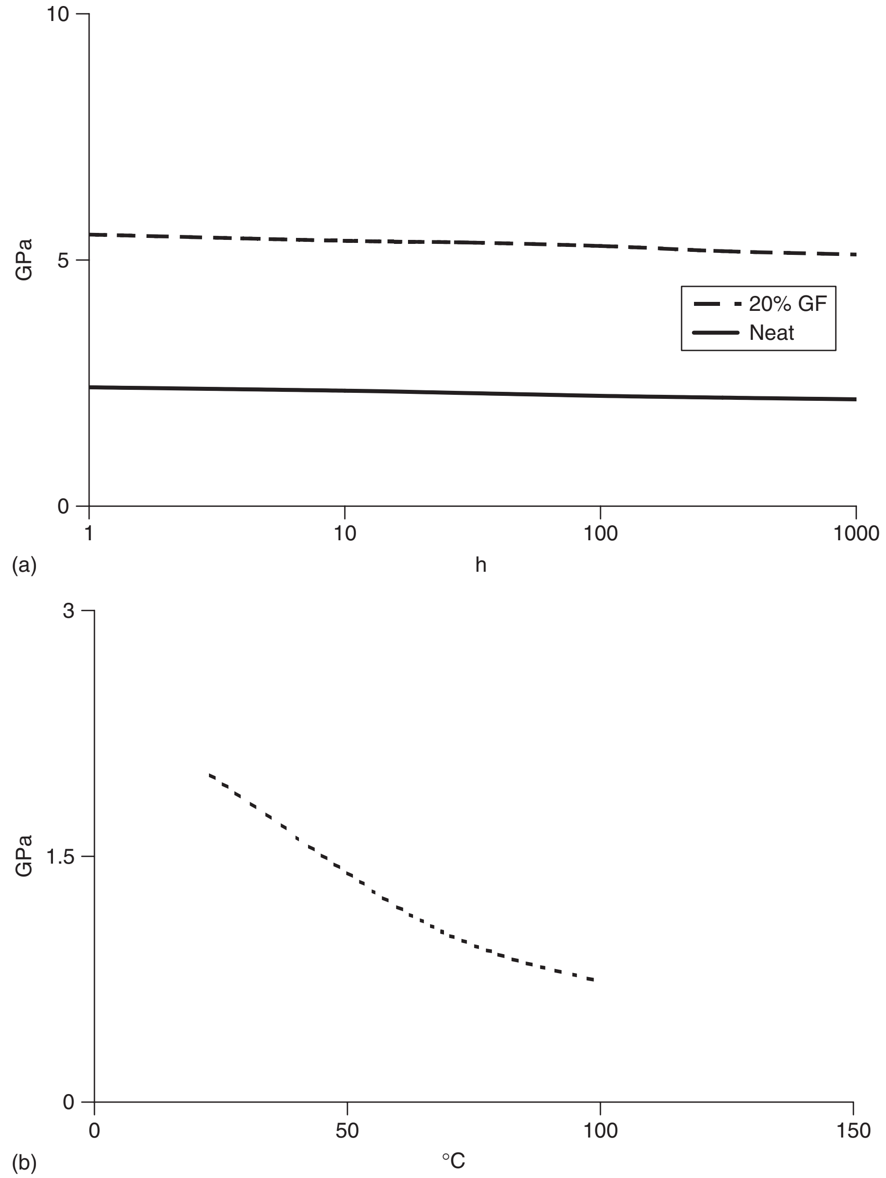


Figure 4.79. (a) PC examples of creep modulus (GPa) versus time (h) under 21 MPa at room temperature; (b) Neat PC: examples of creep modulus (GPa) after 1000 h under 7 MPa versus temperatures (°C)

4.16.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For a given grade of a 20% glass fibre reinforced polycarbonate and a neat grade, Figure 4.80 displays examples of SN or Wöhler's curves concerning flexural tests.

These results are examples only and cannot be generalized.

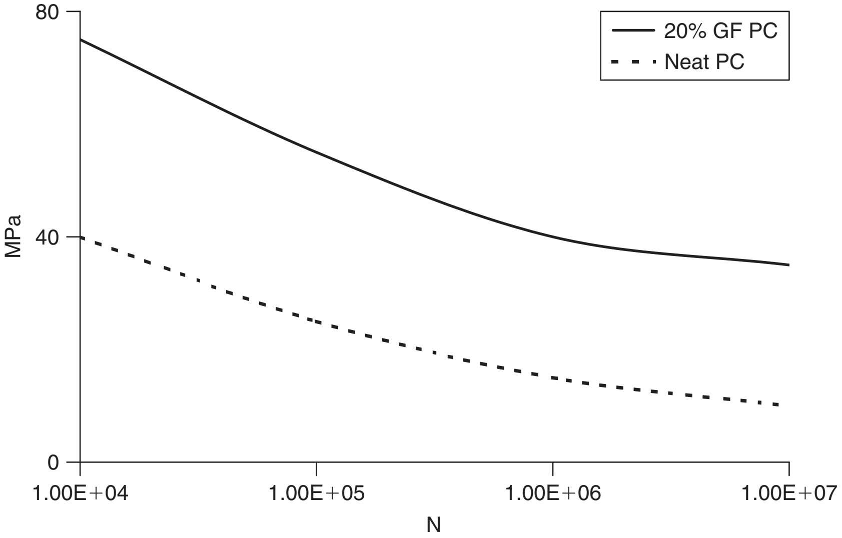


Figure 4.80. SN curve of neat and 20% GF PC, examples of maximum stress (MPa) versus number of cycles at rupture (N)

Weathering

Polycarbonates are inherently sensitive to hydrolysis and UV. They must be protected by addition of anti-UV and other protective agents. Generally, black grades are more resistant than neat ones. In these cases, after weathering test bars for one year in various sunny climates, the retention of tensile strength or notched impact strength is generally good.

For a two-year outdoor exposure of transparent polycarbonates, the retention of impact strengths can be, for example:

- 4% for a non-stabilized grade
- 100% for a UV-stabilized grade.

Under the same conditions, the optical properties after exposure are:

- non-stabilized grade: 82% for transmittance, 20% for the haze, 20 for the yellowing index
- UV-stabilized grade: 87% for transmittance, 15% for the haze, 6 for the yellowing index.

Very different data can be obtained with other grades under different conditions. These results are examples only and cannot be generalized.

Chemicals

Polycarbonates absorb little water but are sensitive to it when the temperature rises.

Suitable grades are usable in contact with food and are used for food packaging, notably baby bottles and water dispensers, for example.

Chemical resistance is generally good to limited at room temperature versus dilute acids, oils, greases, aliphatic hydrocarbons, certain alcohols.

Polycarbonates are attacked by aldehydes, ketones, esters, ethers, aromatic and halogenated hydrocarbons, organic and mineral concentrated acids, concentrated bases, amines, phenols.

Table 4.57 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the polycarbonates. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.57 Polycarbonates: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S
Acetic acid	>96	n
Acetic aldehyde	100	n
Acetic anhydride	100	n
Acetone	100	n
Acetonitrile	100	n
Acetophenone	100	n
Acetyl chloride	100	n
Acrylic acid	100	S
Ajax detergent	Unknown	S
Aliphatic hydrocarbons	100	S
Allyl alcohol	96	l
Alum	Solution	S
Aluminium chloride	Solution	S
Aluminium oxalate	Unknown	S
Aluminium sulfate	Unknown	S
Ammonia gas	100	n
Ammonium chloride	Solution	l
Ammonium fluoride	20	n
Ammonium hydroxide	Dilute, 30	n
Ammonium nitrate	Unknown	S
Ammonium sulfate	50	S
Ammonium sulfide	Solution	n
Amyl acetate	100	l
Amyl alcohol	100	n
Aniline	100	n
Antimony chloride	10–90	S
Antistatic	Unknown	l to n
Aqua regia	Unknown	n
Aromatic hydrocarbons	100	n
Arsenic acid	20	S
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Bacterol disinfectant	5	S
Barium chloride	Saturated	S
Battery acid	Unknown	S
Beer	Unknown	S
Benzaldehyde	100	n
Benzene	100	n
Benzoic acid	Saturated	n
Benzylchloride	100	n
Benzyl alcohol	100	n
Borax	Saturated	S
Boric acid	Unknown	S
BP Energol EM 100	100	S
BP Energol HL 100	100	S
BP HLR 65	100	S
Brake fluid	100	n
Bromine (liquid)	100	n
Bromobenzene	100	n
Butane gas	100	S
Butanol	100	S
Butanone	100	n
Butter	100	S
Butyl acetate	100	n
Butylamine	Unknown	n
Butylchloride	100	n
Butyric acid	20	n
Calcium chloride	Unknown	S
Calcium hypochlorite	Solution	S
Camphor oil	100	n
Carbon oxide	Unknown	S
Carbon sulfide	100	n
Carbon tetrachloride	100	S
Castor oil	100	S
Cellosolve	100	S
Cement	Unknown	S
Chlorinated hydrocarbons	100	n
Chlorinated solvents	100	n
Chlorine (dry gas)	100	n
Chlorine (wet)	Unknown	n
Chlorine dioxide	Unknown	n
Chlorine water	Unknown	S
Chlorobenzene	100	n
Chloroform	100	n
Chlorosulfonic acid	100	n
Chromic acid	20	S
Citric acid	10	S
Clove	Unknown	n
Coffee	Unknown	S
Cognac	Unknown	S
Colza oil	100	S
Copper sulfate	Unknown	S
Cresol	100	n
Cyclohexane	100	l
Cyclohexanol	100	l
Cyclohexanone	100	n
DDT	Unknown	n
Decaline	100	S
Developer (photographic)	Unknown	S
Diacetone alcohol	100	n
Dibutylphthalate	100	n
Dichloroethane	100	n

Table 4.57 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Dichloroethylene	100	n	Isopropanol	100	S to l
Diethylamine	100	n	Kerosene	100	l
Diethylether	100	n	Lactic acid	10	S
Diisopropylbenzene	100	n	Lanoline	Unknown	S
Dimethylformamide	100	n	Lead acetate	10	S
Dioctylphthalate	100	l to n	Lead tetraethyl	10	l
Dioxan	100	n	Linseed oil	100	S
Ethanol	96	S	Liqueurs	Unknown	S
Ethylacetate	100	n	Liquid paraffin	100	S
Ethylamine	100	n	Magnesium chloride	Unknown	S
Ethylbromide	100	n	Magnesium sulfate	Unknown	S
Ethylchloride	100	n	Margarine	100	S
Ethylene glycol	100	S	Mercury	100	S
Ethylenechloride	100	n	Mercury chloride	Unknown	S
Ethylhexanol	100	S	Methane	100	S
Fluorine	100	n	Methanol	100	l
Fluosilicic acid	32	S	Methylamine	<32	n
Formaldehyde	37	S	Methylbutylketone	100	n
Formic acid	10	l	Methylene chloride	100	n
Formic acid	85	n	Methylethylketone	100	n
Freon 11	100	l	Methylglycol	Unknown	S
Freon 113	100	S	Milk	100	S
Freon 115	100	l	Mineral oil	100	l
Freon 12	100	l	Monochlorobenzene	100	n
Freon 13b1	100	l	Monoethyleneglycol	100	S
Freon 21	100	l	Mustard	Unknown	S
Freon 22	100	l	Naphtha	Unknown	S
Freon 32	100	l	Nickel chloride	Unknown	S
Freon TF, TWD 602	100	S	Nitric acid	10	S
Fruit juice	Unknown	S	Nitric acid	⩾25	n
Furfural	100	n	Nitrobenzene	100	n
Glycerol	100	l	Nitromethane	100	n
Glycol	Unknown	S	Nitrous gas	Concentrated	n
Grease	100	S	Nonanol	100	S
Heptane	100	S	Oleic acid	Unknown	S
Hexane	100	S	Oleum @ 10%	Pure	n
Hydraulic oil	100	S	Olive oil	100	S
Hydrobromic acid	48	l	Oxalic acid	Unknown	S
Hydrochloric acid	Concentrated	n	Oxygen	Unknown	S
Hydrochloric acid	10–20	S	Ozone	Unknown	S
Hydrofluoric acid	4	S	Pentane	100	S
Hydrofluoric acid	⩾40	n	Pentanol	100	l
Hydrogen peroxide	30	S	Pentylacetate	100	n
Hydrogen sulfide	Unknown	S	Perchloric acid	10	S
Hydrogen sulfide gas	Unknown	S	Perchloric acid	70	l
Ink	Unknown	S	Perchloroethylene	100	n
Iodine (alcoholic solution)	Unknown	l	Petrol aliphatic	100	l
Iodine (solid)	100	n	Petrol high-octane	100	n
Iodine tincture	Unknown	l	Petroleum	100	l
Iron(III) chloride	Unknown	S	Petroleum ether (ligroin)	Unknown	l
Iron sulfate	Saturated	S	Phenol	90	n
Isobutanol	100	S	Phosphoric acid	85	l
Isooctane (Fuel A)	100	l	Potassium carbonate	Saturated	S

(*Continued*)

Table 4.57 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Potassium cyanide	Unknown	n
Potassium dichromate	5 to saturated	S
Potassium fluoride	Unknown	S
Potassium hydroxide	Solution	n
Potassium hydroxide	10	S
Potassium hydroxide	⩾45	n
Potassium nitrate	Saturated	S
Potassium perchlorate	10	S
Potassium permanganate	1–20	S
Potassium persulfate	10	S
Potassium sulfate	Unknown	S
Propanol	100	l
Propionic acid	20	S
Propionic acid	100	n
Propylene oxide	100	n
PVC plasticized	Unknown	l
PVC rigid	100	S
Pyridine	100	n
Sea water	100	S
Silicone oil	100	S
Silver nitrate	Unknown	S
Soap	Unknown	l
Sodium bisulfite	Solution	S
Sodium borate	Unknown	S
Sodium carbonate	10	S
Sodium carbonate	50	l
Sodium chlorate	Saturated	S
Sodium chloride	25	S
Sodium hydroxide	10	S
Sodium hydroxide	⩾40	n
Sodium hypochlorite	2–20	S
Sodium nitrate	Solution	S
Starch	100	S
Strong acids	Concentrated	l
Strong bases	Unknown	l
Styrene	100	n
Sugar	Solution	S
Sulfur dioxide (gas)	Unknown	l
Sulfuric acid	2–25	S
Sulfuric acid	50–70	l
Sulfuric acid	⩾85	n
Sulfurous acid	Solution	n
Sulfurous anhydride	100	l
Sulfurous anhydride (gas)	Unknown	l
Sun lotion	100	S
Tallow	100	S
Tannic acid	Solution	n
Tartaric acid	Solution	n
Tea	Unknown	S
Tetrachloroethane	100	n
Tetrachloroethylene	100	n
Tetrahydrofuran	100	n
Tin chloride	Unknown	S
Toluene	100	n
Tomato puree	Unknown	S
Town gas (benzene-free)	100	S
Transformer oil	100	S
Trichloroacetic acid	Unknown	n
Trichloroacetic acid	10	l
Trichloroethane	100	n
Trichloroethylene	100	n
Tricresylphosphate	Unknown	n
Triethylamine	Unknown	n
Trimethylbenzene	100	n
Turpentine oil	100	l
Urea	Solution	S
Varnish dissolver	100	n
Vegetable oil	100	S
Vinegar	Unknown	S
Vinyl chloride	Unknown	n
Vodka	Unknown	S
Washing powder	5	l
Water	100	S
Weak acids	Unknown	S
Weak bases	Unknown	l
White spirit	100	l
Wine	Unknown	S
Xylene	100	n
Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: polycarbonate has a medium permeability, evaluated at 2.5 compared to a full range of 0.05 up to 400 for all tested plastics.

- Gases: polycarbonate has a high permeability, evaluated at:
  - carbon dioxide: 9100 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 425 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 2500 versus a full range of <1 up to 11 000 for all tested plastics
  - hydrogen: 13 750 versus a full range of 400 up to 20 000 for all tested plastics.

Fire resistance

Fire resistance is naturally weak. For general-purpose grades, oxygen indices are roughly 25 up to 27 with a V2 UL94 rating.

Special formulations make it possible to improve this behaviour, sometimes to the detriment of other properties. UL94 V0 rating can be reached for some FR grades with oxygen indices of 36–41.

4.16.6 Electrical properties

Polycarbonates are good insulators even in wet environments, with high dielectric resistivities, fair rigidities, and low or moderate loss factors. Special grades are marketed for electrical applications.

4.16.7 Joining, decoration

Welding is easy by the thermal processes and by ultrasound.

Gluing is possible with:

- solvents (methylene chloride, for example), either pure or with dissolved polycarbonate
- adhesives based on epoxies, polyurethanes, silicones, cyanoacrylates.

Preliminary tests are essential.

All precautions must be taken concerning health and safety according to the local laws and regulations.

Polycarbonates can generally be decorated by painting, metallization, printing, varnishing with compatible materials and processing.

4.16.8 Specific ISO standards concerning polycarbonates

ISO 1628-4:1999 Plastics – Determination of the viscosity of polymers in dilute solution using capillary viscometers – Part 4: Polycarbonate (PC) moulding and extrusion materials

ISO 7391-1:1996 Plastics – Polycarbonate (PC) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 7391-2:1996 Plastics – Polycarbonate (PC) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

ISO 11963:1995 Plastics – Polycarbonate sheets – Types, dimensions and characteristics.

4.16.9 Trade name examples

Acrylite, Apec, Calibre, Lexan, Makrolon, Sinvet, Xantar.

4.16.10 Property tables

Table 4.58 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.58 Polycarbonates: examples of properties

Neat grades	General-purpose		Heat-resistant		FR V0	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.2	1.2	1.15	1.2	1.2	1.2
Shrinkage (%)	0.5	0.7	0.7	1.0	0.5	0.7
Absorption of water (%)	0.1	0.2	0.1	0.2	0.15	0.15
Mechanical properties						
Shore hardness, D	85	95	90	95	85	90
Rockwell hardness, R	114	>120	118	>120	118	123
Rockwell hardness, M	50	85	70	90	59	62
Stress at yield (MPa)	50	65	60	70	61	62
Strain at yield (%)	7	7	7	7	6	7
Tensile strength (MPa)	55	77	55	77	60	67
Elongation at break (%)	100	150	50	120	100	120
Tensile modulus (GPa)	2.1	2.5	2.2	2.5	2.3	2.5
Flexural modulus (GPa)	2.1	2.5	2.2	2.5	2.4	2.5
Notched impact strength ASTM D256 (J/m)	650	950	80	650	540	950
Thermal properties						
HDT B (0.46 MPa) (°C)	130	145	150	190		
HDT A (1.8 MPa) (°C)	130	140	150	180	125	135
Continuous use temperature (°C)	90	125	90	140	90	125
Glass transition temperature (°C)	150	150	160	200		
Brittle point (°C)	−25	−25				
Thermal conductivity (W/m.K)	0.2	0.2				
Specific heat (cal/g/°C)	0.3	0.3			0.3	0.3
Coefficient of thermal expansion (10^{-5}/°C)	6	7	7	9	6	7
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{15}	10^{16}		
Dielectric constant	3	3	3	3	3	3
Loss factor (10^{-4})	7	100	8	100	10	10
Dielectric strength (kV/mm)	15	30	35	38	17	18
Arc resistance (s)	10	120				
Fire behaviour						
Oxygen index (%)	24	25	24	24	36	41
UL94 fire rating	V2	V2	V2	V2	V0	V0
	20–40% GF		20–30% GF FR		20% GF heat-resistant FR	
Miscellaneous properties						
Density (g/cm^3)	1.35	1.52	1.4	1.5	1.3	1.3
Shrinkage (%)	0.1	0.5	0.1	0.5	0.3	0.4
Absorption of water (%)	0.1	0.2	0.1	0.4		
Mechanical properties						
Shore hardness, D	90	>95	90	>95		
Rockwell hardness, M	70	95	70	95		
Stress at yield (MPa)	90	160	90	140	100	100
Strain at yield (%)	2	4	2	4	3	3
Tensile strength (MPa)	90	160	90	140	95	100
Elongation at break (%)	2	4	2	4	3	4
Tensile modulus (GPa)	6	10	7	8	6	6
Flexural modulus (GPa)	6	10	7	8	5	6
Notched impact strength ASTM D256 (J/m)	90	200	90	110		
Thermal properties						
HDT B (0.46 MPa) (°C)	140	150	145	155	184	184
HDT A (1.8 MPa) (°C)	135	150	140	150	178	178

Table 4.58 (Continued)

	20–40% GF		20–30% GF FR		20% GF heat-resistant FR	
Continuous use temperature (°C)	90	125	110	125		
Glass transition temperature (°C)	150	150	150	150		
Thermal conductivity (W/m.K)	0.22	0.22				
Coefficient of thermal expansion (10^{-5}/°C)	2	4	2	4	2	3
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{15}	10^{16}	10^{16}	10^{16}
Dielectric constant	3	3.5	3	3	3	3
Loss factor (10^{-4})	9	75	9	75	14	85
Dielectric strength (kV/mm)	20	20	20	20	38	38
Fire behaviour						
UL94 fire rating			V0	V0	V0	V0

	20–30% CF		Self-lubricating 20% PTFE		Structural foam	
					Foaming ratio	
					10%	15%
Miscellaneous properties						
Density (g/cm^3)	1.26	1.32	1.35		1.1	1.05
Shrinkage (%)	0.1	0.2	0.4	0.5	0.7	0.4
Mechanical properties						
Stress at yield (MPa)					52	45
Strain at yield (%)					4	4
Tensile strength (MPa)	155	175	50	50		
Elongation at break (%)	2	3	70	70	6	6
Tensile modulus (GPa)					2.5	2.3
Flexural modulus (GPa)	12	14	1.9	2	2.9	2.8
Notched impact strength ASTM D256 (J/m)	100	100	120	120		
Thermal properties						
HDT B (0.46 MPa) (°C)					141	143
HDT A (1.8 MPa) (°C)	142	146	128	128	134	133
Specific heat (cal/g/°C)					0.28	0.28
Coefficient of thermal expansion (10^{-5}/°C)	1.7	2.3	7	7		
Electrical properties						
Volume resistivity (ohm.cm)	10^{3}	10^{6}			$>10^{15}$	$>10^{15}$
Dielectric strength (kV/mm)					15	14
Fire behaviour						
UL94 fire rating	V1	V1	V2	V1		

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV-protection is needed
Weak acids	Good to limited behaviour
Strong acids	Good to unsatisfactory behaviour according to the concentration
Weak bases	Good behaviour
Strong bases	Good to unsatisfactory behaviour according to the concentration
Solvents	Chemical resistance is generally good to limited at room temperature versus oils, greases, aliphatic hydrocarbons, certain alcohols PC is attacked by aldehydes, esters, ethers, ketones, aromatic and halogenated hydrocarbons, certain alcohols, amines, phenols
Food contact	Possible for special grades

4.17 Polyoxymethylene, polyacetal, acetal or polyformaldehyde (POM)

Polyacetal is marketed under two forms:

- homopolymer of oxymethylene: $-(-CH_2-O-)_n-$
- copolymer of oxymethylene with a minor level of another comonomer.

Properties, although quite similar, can slightly differ in:

- mechanical performances
- glass transition temperature
- HDT.

Unless otherwise indicated, the following facts and figures relate indiscriminately to homo- or co-polymers.

4.17.1 General properties

Advantages

Acetals are appreciated for their good mechanical properties, elasticity, fatigue and wear resistances, low coefficient of friction, good dimensional stability (except mould shrinkage and coefficient of thermal expansion), fair heat resistance at moderate temperatures, low-temperature behaviour, chemical resistance versus essential fluids such as water, oils, greases, solvents and oil products, excellent performance/cost ratios, high impact strength of super-tough grades.

Drawbacks

Acetals are handicapped by an inherent sensitivity to UV and weathering (but UV-resistant grades are marketed), opacity or slight translucence, flammability (but FR grades are marketed), chemical attack by strong acids and sometimes weak acids and bases, rather high density, higher cost than commodities though justified by their performance. The high crystallinity induces a high coefficient of thermal expansion and high mould shrinkage. Heat resistance is somewhat limited.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, thermoforming, blown film, blow moulding, for thin or thick parts, high fluidity . . .
- impact-modified (Super-Tough); stabilized against heat, UV, light, hydrolysis and/or detergent; high molecular weight, high rigidity, food contact, low warpage, antifriction, abrasion-resistant, reinforced, antistatic, conductive, low odour, laser markable . . .
- for household appliances; food, electrical, plumbing applications. There are multiple grades for antifriction applications filled with molybdenum disulfide, PTFE, glass or aramid and carbon fibres, silicone oil . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide an idea. Acetal costs are generally of the order of a few Euros per kilogram.

Processing

All the molten-state methods are usable: extrusion, injection, compression, thermoforming, co-injection, blow moulding, machining, welding.

Consumption

Varying with the country and the source, the following consumption data for acetals can be found for the main outlets (0 signifies that the sector is not taken into account by certain sources and its consumption is added to another market):

• automotive and transport	27–35%
• electric household appliances	20–40%
• industry	6–19%
• consumer goods	0–15%
• building	0–10%
• sports and leisure	0–9%
• medical	0–2%
• packaging	0–1%
• miscellaneous	8–16%

This is an example and other data can be found elsewhere depending on the source and country.

Applications

(See Chapter 2 for further information.)
The main applications for acetals are:

- Automotive & transportation
  - control cables . . .
  - heater and air conditioner control system components, functional parts in the heating, ventilation and coolant sectors . . .
  - snap fittings and fixing parts for interior linings . . .
  - door handles, styling strips, housings and seat belt components, steering columns, window-support brackets, window cranks . . .
  - automotive under-the-hood components, fuel pumps and other fuel system components, ball cocks and caps for gasoline systems, gears, cams, bushings, clips, lugs . . .
  - windscreen washer parts, windscreen wipers . . .
- Household goods, office equipment
  - control dials, pump and timer parts, valves, gears . . .
  - TV tuner arms . . .
  - vapour pumps and distributors for domestic irons, shock-proof kettles . . .
  - parts of timers and projectors of slides, housings of portable tools . . .
  - general business machine parts, spring and screen parts . . .
  - coils, rewind rollers for radio and videocassettes, stereo cassette parts, tape desks . . .
  - precision parts for measurement and control technology . . .
  - heating appliance insulation . . .
  - telephone components . . .
- Mechanical engineering
  - rollers, bearings, bushings, conveyor plates, wear pads . . .
  - timing screws . . .
  - washers . . .
  - housing parts, handles and knobs . . .

  - couplings, pump impellers . . .
  - gears, sprocket wheels, gearwheels, cams, springs . . .
  - small pressure vessels, coil formers . . .
  - nuclear engineering components, gears, cams . . .
  - packaging machinery star wheels . . .
  - poultry processing parts, valve stems . . .
  - clips, lugs, conveyor links valves . . .
  - aerosol components, aerosol valves and heads . . .
- Plumbing and installation sector
  - small pressure vessels, sound-damping mountings for WCs and bathrooms, toilet cistern valves . . .
  - ball cocks, faucets, faucet cartridges, faucet underbodies, valve stems . . .
  - irrigation equipment and valves . . .
  - pump and filter housings, impellers, plumbing systems . . .
  - fittings, hinges, showerheads . . . .
- Consumer goods
  - clock and watch parts, watch gears . . .
  - quality toys . . .
  - butane lighter bodies, disposable cigarette lighters . . .
  - zippers . . .
  - mechanical pen and pencil parts . . .
  - garden sprayers . . .
  - ski bindings, shoe components, sole plates for golf shoes . . .
- Food industry
  - milk pumps . . .
  - coffee spigots . . .
  - filter housings . . .
  - food conveyors, poultry processing parts . . .
- Antifriction parts
  - Bearings, bushings, rods, zippers . . .

4.17.2 Thermal behaviour

If the softening temperatures are higher, the continuous use temperatures in an unstressed state are generally estimated from 80°C up to 110°C.

The UL temperature indices of specific grades can be:

- 95–110°C for the electrical properties alone
- 80–105°C for electrical and mechanical properties excluding impact
- 75–95°C for electrical and mechanical properties including impact.

Service temperatures are noticeably lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- the percentage retention of tensile strength at 80°C compared to the tensile strength at ambient temperature is roughly 62% for a general-purpose grade
- the percentage retention of moduli at 100°C compared to the moduli at ambient temperature are roughly:
  - 22–25% for given general-purpose grades
  - 35–40% for given glass fibre reinforced grades

- HDTs under 1.8 MPa range from:
  - ○ 110°C up to 136°C for neat POM
  - ○ 64°C up to 90°C for a super-tough grade.

Figure 4.81 displays two examples of stress at yield retention versus temperatures for general-purpose (GP) and self-lubricating grades.

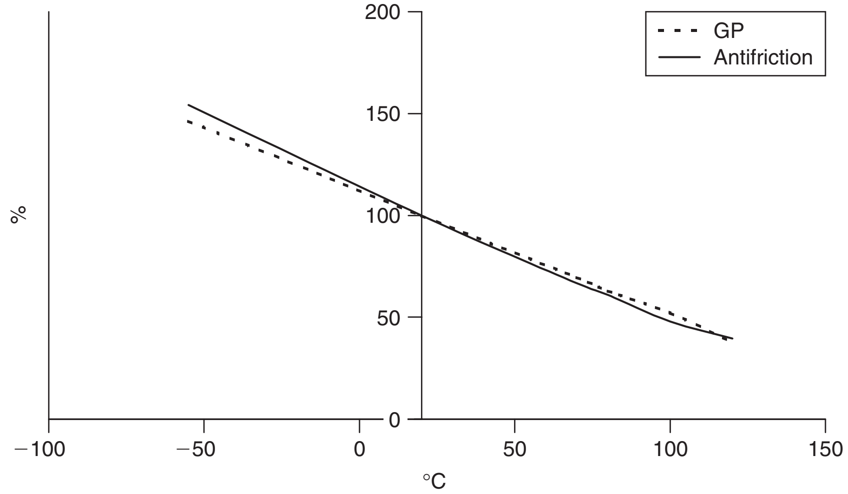


Figure 4.81. POM examples of stress at yield retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially heat-sensitive characteristics.

At low temperatures, the behaviour can be reasonably good down to −40°C or even −60°C, according to the grades and the mechanical constraints undergone.

At −55°C, the elastic modulus is 39% higher than the value at +20°C for some neat grades.

At −40°C, notched Izod impact strengths are:

- 64 J/m versus 80 J/m at 20°C for a general-purpose grade
- 96 J/m versus 133 J/m at 20°C for a semi-impact grade.

Glass transition temperatures are roughly between −50°C and −60°C.

These results relate to some grades only and cannot be generalized.

4.17.3 Optical properties

Acetals are whitish and translucent to opaque according to the grade, crystallinity and thickness.

Refractive index is roughly 1.48.

These results relate to some grades only and cannot be generalized.

4.17.4 Mechanical properties

The mechanical properties are generally good with a fair rigidity as long as the temperature does not rise too much. However, general-purpose grades can have a low impact resistance. Special impact-modified grades are marketed with an excellent notched impact strength.

The abrasion resistance, generally fair, depends on the roughness, type and morphology of the opposing sliding surface. POMs are often used for antifriction applications.

Friction

A broad choice of lubricating and reinforcing additives leads to a good range of coefficients of friction, from 0.1 up to 0.3 for the static coefficients, and low wear from excellent to good.

For example, static and dynamic coefficients of friction are, respectively:

- 0.1 and 0.08 with addition of PTFE and silicone oil
- 0.13 and 0.08 with addition of PTFE only
- 0.16 and 0.11 with addition of silicone oil only.

Dimensional stability

Alterations by moisture exposure are weak but shrinkage and coefficients of thermal expansion are high, as for other crystalline polymers; creep resistance is good at room temperature.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular orientation. For a given sample, Poisson's ratio is evaluated at 0.35. This is an example only and cannot be generalized.

Creep

POM has medium moduli that involve medium strains for moderate loading. Consequently, creep moduli are also in an intermediate range at room temperature, as we can see in Figure 4.82(a).

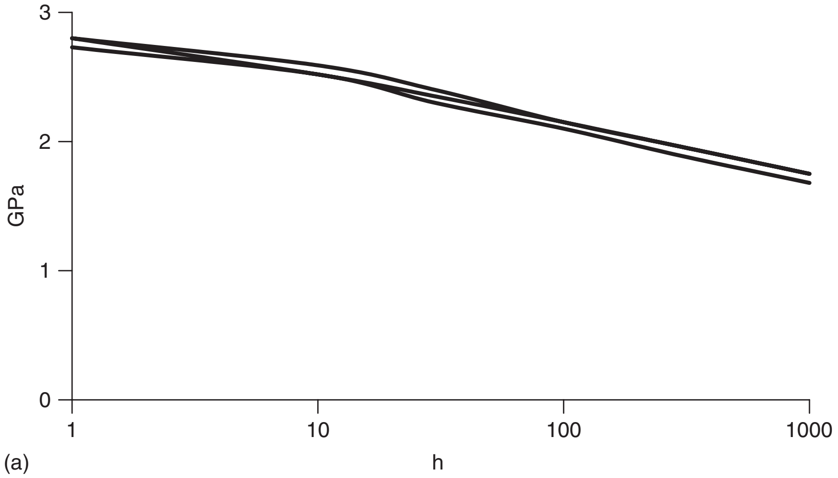


Figure 4.82 (a) Neat POM creep: examples of creep modulus (GPa) versus time (h) for loading from 3.5 up to 10.5 MPa

When the temperature rises moderately, the creep modulus decreases significantly (see Figure 4.82(b)). The decrease is roughly:

- 50% for a temperature increasing from 20°C to 60°C
- 70% for a temperature increasing from 20°C to 100°C.

These results relate to a few grades only and cannot be generalized.

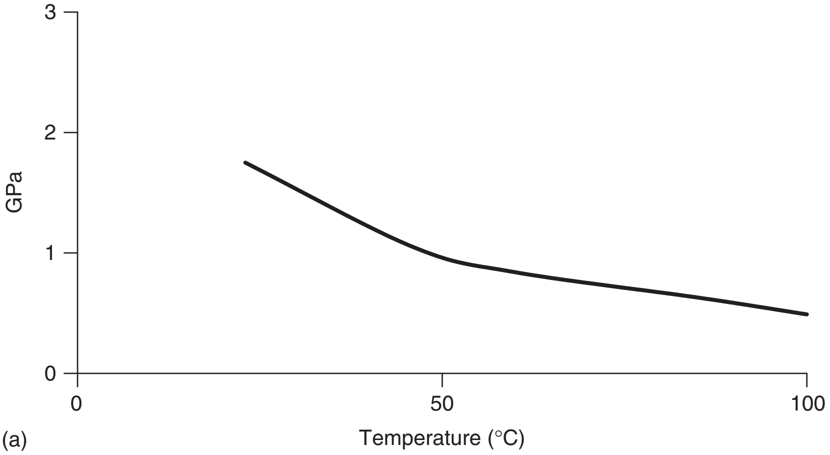


Figure 4.82. (b) Neat POM creep: examples of creep modulus (GPa) after 1000 h versus temperature (°C) under 3.5 MPa

4.17.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For two given grades of neat and 30% glass fibre reinforced POM, Figure 4.83 displays examples of SN or Wohler's curves concerning flexural tests.

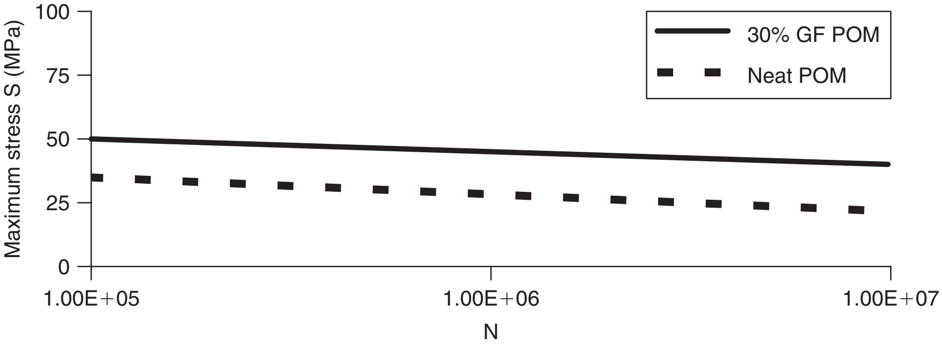


Figure 4.83. SN curve of neat and 30% GF POM, examples of maximum stress S (MPa) versus number of cycles at rupture (N)

Weathering

Polyacetals are UV sensitive and must be protected by addition of anti-UV and other protective agents. Generally, black grades are more resistant than natural ones. In these cases, after weathering test bars for one year in various sunny climates, the retention of tensile strength or notched impact strength is generally good.

For three- and ten-year outdoor exposures of 3-mm-thick samples, retentions of tensile strength and elongation at break can be, for example:

- nearly 100% of tensile strength for UV-stabilized acetals
- 45% up to 75% for elongation at break, depending on the UV stabilization.

These results are examples only and they cannot be generalized.

High-energy radiation

Polyacetals are sensitive to high-energy radiation and sterilization by this process can only be used if high mechanical properties are not required; impact resistance in particular is altered. Exposure to doses exceeding 30 kJ/kg causes yellowing and a decrease of the impact resistance.

Chemicals

Polyacetals absorb little water but are sensitive to boiling water. For a given grade, the loss of tensile strength in boiling water is 25% after two years but then accelerates strongly.

Suitable grades are usable in contact with food.

Chemical resistance is generally good to limited at room temperature versus oils, greases, aliphatic hydrocarbons, insecticides, fertilizers, and certain alcohols.

Resistance is limited to aldehydes, ketones, aromatic and halogenated hydrocarbons, weak acids and bases, and dilute strong bases.

Resistance is unsatisfactory versus strong acids, hot oxidizing agents, concentrated bases and phenols.

Crystallinity increases impermeability and, consequently, chemical resistance.

Table 4.59 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the polyacetals. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: polyacetal has a medium permeability, evaluated at 2.5 for a full range of 0.05 up to 400 for all tested plastics.
- Gases: polyacetal has a low permeability, evaluated at:
    - Carbon dioxide: 96 versus a full range of 30 up to 59 000 for all tested plastics.
    - Nitrogen: 10 versus a full range of 1 up to 3500 for all tested plastics.
    - Oxygen: 50 versus a full range of <1 up to 11 000 for all tested plastics.
    - Hydrogen: 420 versus a full range of 400 up to 20 000 for all tested plastics.

Acetals are used for cigarette lighters thanks to their imperviousness to butane.

Table 4.59 POM: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S
Acetic acid	⩾50	l
Acetic aldehyde	100	S
Acetic anhydride	100	n
Acetone	100	l
Acetonitrile	100	n
Acetophenone	100	l
Acetyl chloride	100	n
Acetylene tetrabromide	100	l
Acrylic acid	100	n
Aldehydes	Unknown	l
Aliphatic hydrocarbons	100	S
Aluminium chloride	Solution	l
Aluminium sulfate	Unknown	l
Ammonium chloride	Solution	S
Ammonium hydroxide	30	S
Ammonium sulfate	50	l
Amyl acetate	100	S
Amyl alcohol	100	S
Antimony chloride	10	n
Aqua regia	Unknown	n
Aromatic hydrocarbons	100	l
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Benzaldehyde	100	S
Benzene	100	S
Benzylchloride	100	S
Benzyl alcohol	100	S
Boric acid	Unknown	S
Bromine (liquid)	100	n
Butanol	100	S
Butanone	100	l
Butyl acetate	100	S
Butylamine	Unknown	S
Butylchloride	100	S
Butyraldehyde	100	l
Butyric acid	100	l
Calcium chloride	Unknown	S
Carbon sulfide	100	S
Carbon tetrachloride	100	S
Castor oil	100	S
Cellosolve	100	S
Chlorinated hydrocarbons	100	l
Chlorinated solvents	100	l
Chlorine (dry gas)	100	n
Chlorine water	Unknown	l
Chloroacetic acid	Unknown	n
Chlorobenzene	100	S
Chlorobenzene mono	100	l
Chloroform	100	n
Chlorosulfonic acid	Unknown	n
Chromic acid	Unknown	l
Citric acid	10	S
Coffee	Unknown	S
Colza oil	100	S
Copper sulfate	Unknown	S
Cresol	100	n
Cyclohexane	100	S
Cyclohexanol	100	S
Cyclohexanone	100	S
Decaline	100	S
Developer (photographic)	Unknown	S
Diacetone alcohol	100	S
Dibutylphthalate	100	S
Dibutylsebacate	100	S
Dichloroethane	100	l
Dichloroethylene	100	l to n
Diethylamine	100	n
Diethyleneglycol	100	S
Diethylether	100	S
Diisopropylbenzene	100	S
Dimethylformamide	100	S
Dioctylphthalate	100	l
Dioctylsebacate	100	S
Dioxan	100	l
Esters	100	l
Ethanol	96	S
Ether	100	S
Ethylacetate	100	S
Ethylchloride	100	l
Ethylene glycol	Unknown	S to l
Ethylhexanol	100	S
Fixing solution pH 5.4	Unknown	S
Fluorine	100	n
Formaldehyde	37	S
Formic acid	10	S
Formic acid	⩾40	n
Freon 11	100	S
Freon 113	100	S
Freon 115	100	S
Freon 12	100	S
Freon 13b1	100	S
Freon 21	100	S
Freon 22	100	S
Freon 32	100	S
Fuel JP1	100	S
Fuel (benzene-free)	100	S
Furfural	100	S
Glycerol	100	S
Grease	100	S
Heptane	100	S
Hexane	100	S
Household bleach	Unknown	l
Hydrazine	100	S
Hydrobromic acid	48	n
Hydrochloric acid	10	l

(*Continued*)

Table 4.59 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Hydrochloric acid	⩾20	n
Hydrofluoric acid	40	n
Hydrogen peroxide	30	l to n
Hydrogen peroxide	90	n
Hydrogen sulfide gas	Unknown	S
Ink	Unknown	S
Iron(III) chloride	Unknown	l
Isobutanol	100	S
Isooctane (Fuel A)	100	S
Isopropanol	100	l
Kerosene	100	S
Lactic acid	10	S
Lactic acid	90	l
Lavender water	Unknown	S
Lead acetate	10	S
Linseed oil	100	S
Liquid paraffin	100	S
Magnesium chloride	Unknown	S
Manganese sulfate	Unknown	S
Methanol	100	S
Methylbromide	100	n
Methylbutylketone	100	S
Methylene chloride	100	n
Methylethylketone	100	l
Methylglycol	Unknown	l
Mineral oil	100	S
Molasses	Unknown	S
Monochlorobenzene	100	l
Monoethanolamine	Unknown	S
Monoethyleneglycol	100	l
Naphtha	Unknown	S
Nickel chloride	Unknown	S
Nitric acid	⩾10	n
Nitrobenzene	100	l
Nonanol	100	S
Oil of cloves	Unknown	S
Oleic acid	Unknown	S
Olive oil	100	S
Oxalic acid	Unknown	l
Ozone	Unknown	n
Perchloroethylene	100	S
Petrol aliphatic	100	S
Petrol high-octane	100	S
Petroleum	100	S
Phenol	Solution	n
Phosphoric acid	<10	l
Phosphoric acid	⩾85	n
Potassium cyanide	Unknown	S
Potassium dichromate	10	S
Potassium fluoride	Unknown	S
Potassium hydroxide	10–45	S
Potassium permanganate	10–20	S
Potassium permanganate	Solution	l
Potassium sulfate	Unknown	S
Propanol	100	l
Propionic acid	100	n
Propylene oxide	100	l
Pyridine	Unknown	S to l
Sea water	100	S
Silicone oil	100	l
Silver nitrate	Unknown	S
Sodium bisulfite	Solution	n
Sodium borate	Unknown	S
Sodium carbonate	10	S
Sodium chloride	25	S
Sodium cyanide	Unknown	S
Sodium hydroxide	10	S
Sodium hydroxide	20	l
Sodium hydroxide	55	S
Sodium hypochlorite	13	l
Sodium hypochlorite	20	n
Sodium nitrate	Solution	S
Soya oil	100	S
Strong acids	Concentrated	n
Strong bases	Unknown	l
Styrene	100	S
Sulfur dioxide (gas)	Unknown	n
Sulfuric acid	2	S
Sulfuric acid	10	l
Sulfuric acid	⩾25	n
Sulfurous anhydride (gas)	Unknown	n
Tetrachloroethylene	100	S
Tetrahydrofuran	100	l
Thionyl chloride	100	n
Tin chloride	Unknown	S
Toluene	100	S
Transformer oil	100	S
Trichloroacetic acid	Unknown	n
Trichloroethane	100	S
Trichloroethylene	100	n
Tricresylphosphate	Unknown	S
Triethanolamine	Unknown	S
Triethylamine	Unknown	S
Trimethylbenzene	100	S
Turpentine oil	100	S
Urine	Unknown	S
Vegetable oil	100	S
Vinyl chloride	Unknown	S
Washing powder	5	S
Water	100	S
Weak acids	Unknown	l
Weak bases	Unknown	l
White spirit	100	S
Wine	Unknown	S
Xylene	100	S
Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Fire resistance

Fire resistance is naturally weak. Standard grades burn generating flames, even after the ignition source is removed. Moreover, acetals drip while burning.

Oxygen indices are roughly 18 up to 20 with a poor UL94 rating.

4.17.6 Electrical properties

Acetals are good insulators even in wet environments, with fair dielectric resistivities and low loss factors. Special grades usable up to 110°C are marketed for electrical applications.

4.17.7 Joining, decoration

Welding is possible for certain grades by all processes except high frequencies.

Gluing is difficult because of the resistance to solvents. The rare types suitable for joining by diffusion and treatment of the surfaces to be assembled are highly toxic and must be used only with stringent precautions and after in-depth information has been studied. Preliminary tests are essential. All precautions must be taken concerning safety and hygiene according to local laws and regulations.

Acetals can generally be decorated by painting and varnishing after surface treatment. Metallization is very often used with specific grades marketed for this process. Printing is possible with compatible materials and processing.

4.17.8 Specific ISO standards concerning acetals

ISO 9988-1:2004 Plastics – Polyoxymethylene (POM) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 9988-2:1999 Plastics – Polyoxymethylene (POM) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

4.17.9 Trade name examples

Celcon, Delrin, Duracon, Hostaform, Iupital Acetal, Kematal, Lucel, Sniatal, Ultraform. . .

4.17.10 Property tables

Table 4.60 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.60 Acetals: examples of properties

Neat grades	Homopolymer		Copolymer		Impact-resistant	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.42	1.42	1.41	1.41	1.3	1.39
Shrinkage (%)	1.8	2.2	2	2	1	2.5
Absorption of water (%)	0.25	0.4	0.11	0.22	0.3	0.5
Mechanical properties						
Shore hardness, D	85	95	80	93	80	90
Rockwell hardness, R	120	120	120	120	105	117
Rockwell hardness, M	75	94	78	80	35	79
Stress at yield (MPa)	67	72				

(*Continued*)

Table 4.60 (Continued)

Neat grades	Homopolymer		Copolymer		Impact-resistant	
	Min.	Max.	Min.	Max.	Min.	Max.
Strain at yield (%)	5	15			20	75
Tensile strength (MPa)	64	70	61	80	42	60
Elongation at break (%)	15	75	45	75	60	200
Tensile modulus (GPa)	3.1	3.1	3	3.7	1.4	2.3
Flexural modulus (GPa)	2.8	2.8	3.1	3.7	1.4	2.3
Notched impact strength ASTM D256 (J/m)	70	80	50	75	130	910
Thermal properties						
HDT B (0.46 MPa) (°C)	170	172	158	160	145	169
HDT A (1.8 MPa) (°C)	130	136	110	132	64	90
Continuous use temperature (°C)	80	110	80	110	80	100
Glass transition temperature (°C)	−60	−50	−60	−50		
Melting temperature (°C)	175	175	164	172	164	175
Brittle point (°C)	−40	−40	−40	−40	−50	−40
Thermal conductivity (W/m.K)	0.3	0.4	0.3	0.4		
Specific heat (cal/g/°C)	0.35	0.38	0.35	0.38		
Coefficient of thermal expansion (10^{-5}/°C)	10	15	11	12	12	13
Electrical properties						
Volume resistivity (ohm.cm)	10^{13}	10^{14}	10^{14}	10^{16}	2×10^{14}	10^{16}
Dielectric constant	3.7	4	3.7	4	3.7	4
Loss factor (10^{-4})	50	70	10	95	70	160
Dielectric strength (kV/mm)	20	32	20	70	16	19
Arc resistance (s)	200	220			120	120
Fire behaviour						
Oxygen index (%)	18	19	18	19	18	19
UL94 fire rating	HB	HB	HB	HB	HB	HB
	25–30% Glass fibre reinforced		Mineral-filled		Self-lubricating	
Miscellaneous properties						
Density (g/cm^3)	1.56	1.59	1.5	1.6	1.42	1.54
Shrinkage (%)	0.5	1.8	1.5	2	1.8	3
Absorption of water (%)	0.2	0.3	0.2	0.5	0.2	0.27
Mechanical properties						
Shore hardness, D	90	>95	90	95	83	>95
Rockwell hardness, R	>120	>120	>120	>120	118	>120
Rockwell hardness, M	85	95	83	90	58	94
Stress at yield (MPa)					43	57
Strain at yield (%)					5	14
Tensile strength (MPa)	130	140	50	75	48	70
Elongation at break (%)	3	12	1	55	10	70
Tensile modulus (GPa)	10	10.5	4.5	8.5	1.8	3.1
Flexural modulus (GPa)	9.5	10.5	4.5	8	2	3
Notched impact strength ASTM D256 (J/m)	50	100	34	65	25	78
Thermal properties						
HDT B (0.46 MPa) (°C)	165	174	158	175	168	172
HDT A (1.8 MPa) (°C)	145	163	110	150	118	136
Continuous use temperature (°C)	80	110	80	105	80	105
Melting temperature (°C)	164	169	164	175	164	175
Brittle point (°C)	−40	−40			−40	−40
Thermal conductivity (W/m.K)	0.41	0.41			0.31	0.31

Table 4.60 (Continued)

	25–30% Glass fibre reinforced		Mineral-filled		Self-lubricating	
Specific heat (cal/g/°C)	0.31	0.31			0.35	0.38
Coefficient of thermal expansion (10^{-5}/°C)	2	3	5	9	10	12
Electrical properties						
Volume resistivity (ohm.cm)	10^{14}	10^{16}	10^{14}	10^{15}	5×10^{12}	10^{16}
Dielectric constant	3.9	5			3	4
Loss factor (10^{-4})	20	80			20	90
Dielectric strength (kV/mm)	19	23			16	19
Arc resistance (s)	170	170			126	183
Fire behaviour						
Oxygen index (%)	18	19	18	19	18	19
UL94 fire rating	HB	HB	HB	HB	HB	HB

	Glass bead filled		Carbon fibre reinforced		Antistatic	
Miscellaneous properties						
Density (g/cm^3)	1.59	1.59	1.48	1.48	1.42	1.42
Shrinkage (%)	1.3	1.7	0.2	1	1.8	2.1
Absorption of water (%)	0.2	0.3	0.2	0.4	0.3	0.3
Mechanical properties						
Shore hardness, D	93	95	>95	>95		
Rockwell hardness, R	120	120	>120	>120		
Rockwell hardness, M	83	85	97	99		
Strain at yield (%)			1	1		
Tensile strength (MPa)	63	65	120	160	50	50
Elongation at break (%)	10	10	2	4	7	10
Flexural modulus (GPa)	3.6	4	10	17	2.8	2.8
Notched impact strength ASTM D256 (J/m)	50	70	38	38	30	30
Thermal properties						
HDT B (0.46 MPa) (°C)	162	163	166	168	160	160
HDT A (1.8 MPa) (°C)	135	150	160	163	110	110
Continuous use temperature (°C)	80	110	80	110		
Coefficient of thermal expansion (10^{-5}/°C)	9	9	4	5	10	10
Electrical properties						
Volume resistivity (ohm.cm)	10^{14}	10^{14}	<10	100	<50	<50
Dielectric strength (kV/mm)	20	21				
Fire behaviour						
Oxygen index (%)	18	19				
UL94 fire rating	HB	HB	HB	HB		

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV-protection is needed
Weak acids	Limited behaviour
Strong acids	Unsatisfactory behaviour except for very low concentrations
Weak bases	Limited behaviour
Strong bases	Good to unsatisfactory behaviour according to the concentration
Solvents	Chemical resistance is generally good to limited at room temperature versus oils, greases, aliphatic hydrocarbons, certain alcohols, insecticides, fertilizers. Resistance is limited to aldehydes, ketones, aromatic and halogenated hydrocarbons, weak acids and bases, dilute strong bases POM is attacked by strong acids, hot oxidizing agents, concentrated bases, phenols
Food contact	Possible for special grades

4.18 Polyphenylene oxide, polyphenylene ether (PPO, PPE)

Polyphenylene oxide and polyphenylene ether are oxides or ethers like polyoxymethylene but an aromatic unit replaces the methylene group leading to $-(-C_6H_4-O-)_n-$

Polyphenylene ether has too high a glass transition temperature to be easily processed and is marketed in the form of alloys with other resins, such as:

- high-impact polystyrene (HIPS), which is the most used
- polyamides for specific applications that are developing, particularly in exterior automotive applications
- polyetherimide, a development targeting niche under-the-hood applications
- thermoplastic polyester. These alloys don't appear to be developing well.

Unless otherwise indicated, the following facts and figures relate to alloys with HIPS. This alloy enhances processing but alters thermal behaviour. The average PPE level is often roughly 45% but can vary broadly from 30% up to 75% to optimize the set of properties according to the targeted application.

4.18.1 General properties

Advantages

PPEs are used in technical parts because of the good price/performance ratios for mechanical and electrical properties; creep behaviour, low moisture uptake, heat and low-temperature behaviour, resistance to moisture and hot water; good dimensional stability.

PPE/PA alloys are more heat-resistant allowing in-line paintability. Surface appearance reaches Class A for automotive parts.

Drawbacks

PPEs are handicapped by an inherent sensitivity to fire and to common chemicals, such as hydrocarbons, chlorinated solvents and concentrated mineral acids. They have rather high coefficients of friction and are slightly attacked by UV and weathering, requiring UV protection. The number of producers is limited.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, thermoforming, blow moulding, for thin or thick parts, high fluidity, structural foam . . .
- impact-modified; stabilized against heat, UV, light, hot water and/or detergent; high molecular weight, high rigidity, food contact, low warpage, reinforced, antistatic, conductive, laser markable . . .
- for the automotive industry; household appliances; food, electrical, plumbing applications . . .

Costs

As for all plastics, costs fluctuate with the crude oil price and are only given to provide a rough idea. They are generally of the order of a few Euros per kilogram.

Processing

All molten-state methods are usable: extrusion, injection, compression, thermoforming, co-injection, blow moulding, machining, welding.

Consumption

Global consumption of PPEs is estimated at 350 000–500 000 t/year, mainly in the automotive, electrical & electronics, business machine & appliance markets.

Depending on the country and the source, the following data can be found for the main outlets (0 signifies that the sector is not taken into account by certain sources and its consumption is added to another market):

automotive & transport	30%
E&E	40%
appliances, consumer goods	20%
machinery, building, packaging	0–10%

This is an example and other data can be found elsewhere according to the source and country.

Applications

(See Chapter 2 for further information.)

- Automotive & transportation
  - heater and air conditioner control system components, functional parts in the heating, ventilation and coolant sectors . . .
  - instrument panels, interior mirror housings . . .
  - seat backs . . .
  - grilles, spoilers, exterior mirror housings, wheel trims . . .
  - large parts such as body panels, fenders . . .
  - under-the-hood components, impellers for water pumps in engine cooling . . .
  - PA/PPE for motorcycle fairings, bumpers and static structural components – Nissan X Trail front guards and Renault, Toyota side kit panels . . .
  - foamed PPE: automotive door padding, knee bolsters, pillar trims, sun visors, instrument panel retainers, top covers, centre-stacks . . .
- Electrical & electronics
  - electrical terminal housings, distributor cabinets and large capacitor cases . . .
  - relay sockets, cable connectors, bulb sockets, coil formers . . .
  - high-tolerance electrical switch boxes and connectors . . .
  - sensors and circuits . . .
- Appliances, household goods, office equipment
  - general business machine parts, brackets and structural components of office products, business machine chassis, frames & housings; large computer and printer housings (painted, foamed) . . .
  - internal appliance components, heating appliance insulation, insulators . . .
  - power tool, portable mixers, hairdryer housings . . .
  - coffee pots, drink vending machines and washing machine parts . . .
  - microwave components . . .
  - telecommunications frames and chassis, cell phone battery covers . . .

  - ○ TV backplates & deflection yokes . . .
  - ○ structural and interior components . . .
  - ○ foamed PPE: computers, business equipment, electrical/electronic appliances, telecommunications . . .
- Mechanical engineering
  - ○ housing parts, handles and knobs . . .
  - ○ machine housings, pump housings and impellers, fluid and material handling components, water-pump housings and impellers in machinery and engineering . . .
  - ○ frames, ventilating parts . . .
  - ○ water purification equipment parts . . . .
  - ○ gears . . .
- Plumbing and installation sector
  - ○ pump and filter housings, impellers, plumbing systems . . .
  - ○ plastic parts in central heating systems . . .
  - ○ microwaveable food packaging . . .

4.18.2 Thermal behaviour

Provided the softening temperatures are higher, the continuous use temperatures in an unstressed state are generally estimated from 80°C up to 110°C.

The UL temperature indices of specific grades can be:

- 50–110°C for the electrical properties alone
- 50–110°C for the electrical and mechanical properties excluding impact
- 50–105°C for the electrical and mechanical properties including impact.

Service temperatures are noticeably lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- the percentage retention of moduli at 100°C compared to the moduli at ambient temperature are roughly:
  - ○ 65–80% for given general-purpose grades
  - ○ 75–85% for given glass fibre reinforced grades
- HDTs under 1.8 MPa are roughly:
  - ○ 77°C for a structural foam
  - ○ from 90°C up to 130°C for neat PPE
  - ○ from 134°C up to 144°C for 30% glass fibre reinforced grades
  - ○ 225°C for a 30% glass fibre reinforced PPE/PA
- Vicat B/120 temperatures are roughly:
  - ○ from 120°C up to 135°C for neat general-purpose PPE/PS
  - ○ from 170°C up to 195°C for neat PPE/PA
  - ○ 150°C for a 30% glass fibre reinforced general-purpose PPE/PS
  - ○ 240°C for a 30% glass fibre reinforced PPE/PA.

Figure 4.84 displays two examples of modulus retention versus temperature for a neat general-purpose PPE/PS and a 30% glass fibre reinforced grade.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially heat-sensitive characteristics.

At low temperatures, the behaviour can be reasonably good down to −40°C or even more, according to the grades and the mechanical constraints imposed.

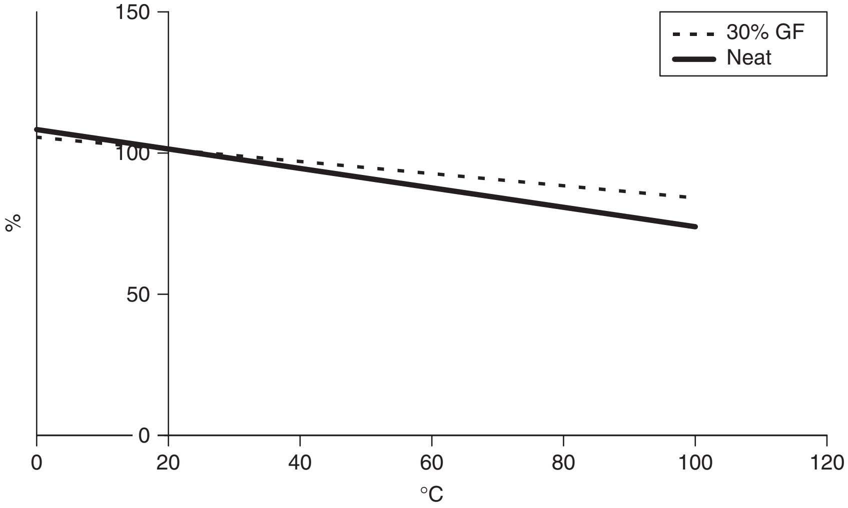


Figure 4.84. PPE examples of modulus retention (%) versus temperature (°C)

At −40°C, notched Izod impact strengths are:

- 75–140 J/m versus 150–250 J/m at 20°C for given general-purpose grades
- 70 J/m versus 80 J/m at 20°C for a 30% glass fibre reinforced PPE/PS.

Glass transition temperatures are high, 100–150°C for example, or even 210°C.

These results relate to some grades only and cannot be generalized.

4.18.3 Optical properties

PPEs are opaque.

4.18.4 Mechanical properties

The mechanical properties are generally good with a fair rigidity even when the temperature rises to 100°C. General-purpose grades have fair impact resistance.

PPE has a high coefficient of friction and is generally not suitable for self-lubricating parts.

Dimensional stability

Moisture uptake, shrinkage and coefficients of thermal expansion are low; creep resistance is good at room temperature. Consequently, dimensional stability is good.

Poisson's ratio

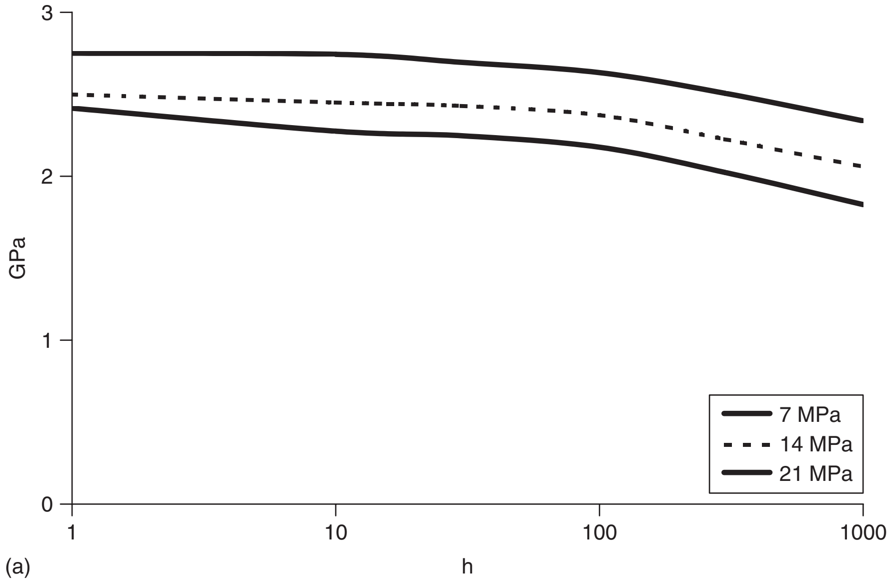
Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular orientation. For given samples, Poisson's ratios are evaluated at:

- 0.31–0.38 for PPE
- 0.27–0.28 for glass fibre reinforced PPE.

These are examples only that cannot be generalized.

Creep

PPE has medium moduli that involve medium strains for moderate loading. Consequently, creep moduli are also in a medium range at room temperature, as we can see in Figure 4.85(a).



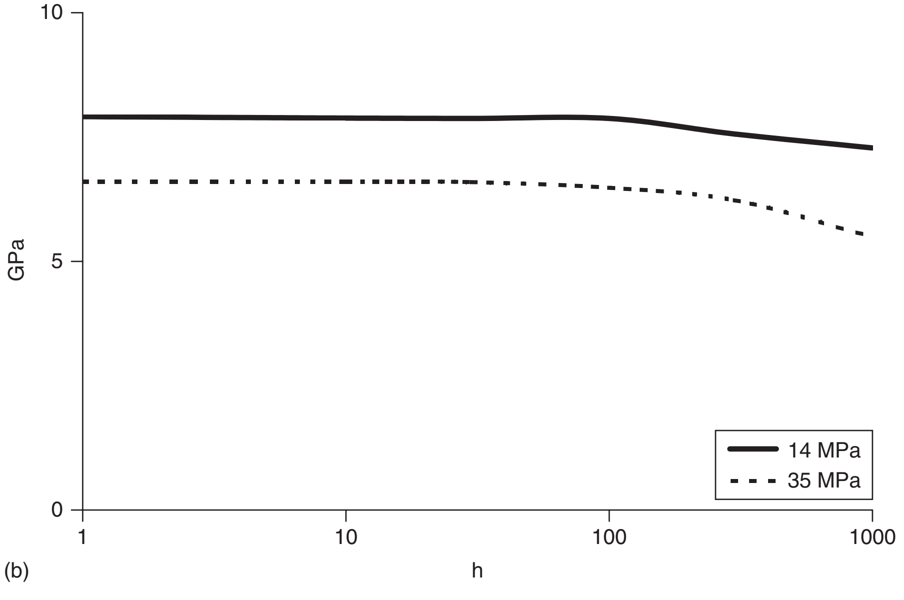


Figure 4.85. (a) Neat PPE creep: examples of creep modulus (GPa) versus time (h) for loading from 7 up to 21 MPa; (b) 30% GF PPE creep: examples of creep modulus (GPa) versus time (h) for loading from 14 up to 35 MPa

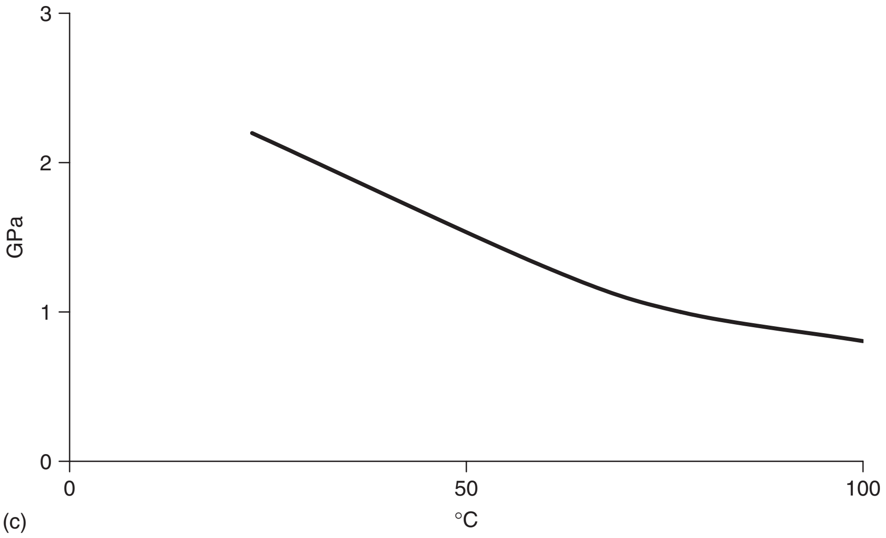


Figure 4.85. (c) Neat PPE creep: examples of creep modulus (GPa) after 1000 h versus temperature (°C) under 10.5 MPa

As for the other thermoplastics, reinforcement with 30% glass fibres strongly enhances creep moduli, as seen in Figure 4.85(b), in which the modulus scale is more than three times that of Figure 4.85(a).

When the temperature rises moderately, the creep modulus decreases significantly, as we can see in Figure 4.85(c). The decrease is roughly:

- 40% for a temperature rise from 20°C up to 60°C
- 60% for a temperature rise from 20°C up to 100°C.

These results relate to a few grades only and cannot be generalized.

4.18.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For two given grades of neat and 30% glass fibre reinforced PPE, Figure 4.86 displays examples of SN or Wöhler's curves concerning flexural tests.

Weathering

PPE is moderately UV-sensitive but must be protected by addition of anti-UV and other protective agents. Generally, black grades are more resistant than natural ones.

Chemicals

PPE absorbs little water and isn't very sensitive to it, even at boiling temperature.

Suitable grades are usable in contact with food.

Hydrolysis resistance is generally good versus hot water, weak acids and bases. Versus strong and concentrated acids and bases, PPE has a good to limited resistance.

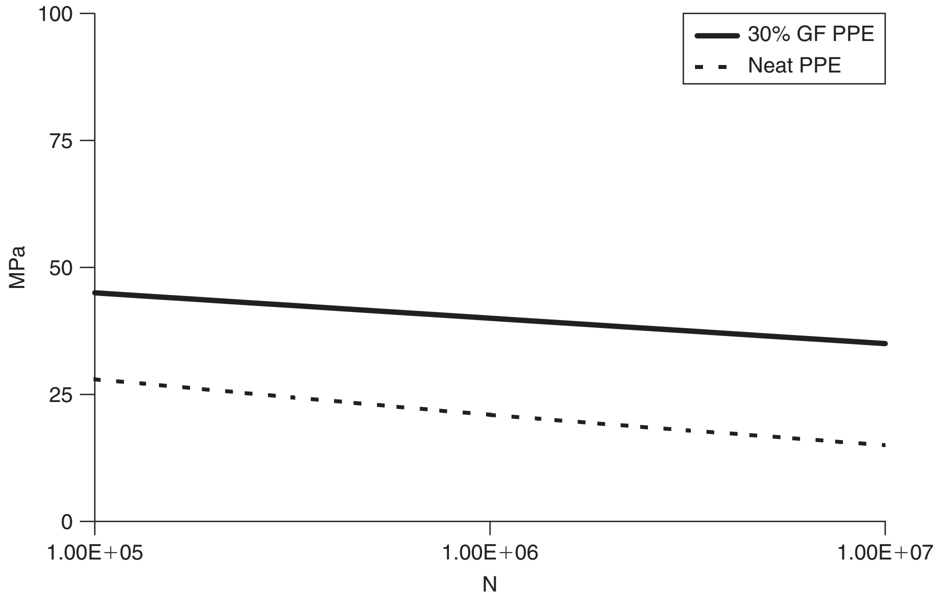


Figure 4.86. SN curve of neat and 30% GF PPE, examples of maximum stress S (MPa) versus number of cycles at rupture (N)

Chemical resistance at room temperature is generally good to limited versus oils, greases, aliphatic hydrocarbons and alcohols.

Resistance is poor versus ketones, esters, ethers, aromatic and halogenated hydrocarbons, amines, and phenols.

Table 4.61 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the polyphenylene ethers. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Fire resistance

Fire resistance is naturally weak. Standard grades burn generating flames, even after the ignition source is removed. Moreover, PPE drips while burning.

Oxygen indices are less than 20 with a poor UL94 rating.

FR grades are marketed that can reach oxygen indices of 36 and a V0 UL94 rating.

4.18.6 Electrical properties

PPE are good insulators even in wet environments, with fair dielectric resistivities and low loss factors. Special grades usable up to 110°C are marketed for electrical applications.

4.18.7 Joining, decoration

Welding is possible for certain grades by all processes except high frequencies.

Gluing is possible with:

- Solvents (trichloroethylene or methylene chloride, for example), pure or with dissolved PPE.
- Certain adhesives such as cyanoacrylates, silicones, urethanes, epoxies.

Table 4.61 PPE: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	⩾10	S
Acetone	100	n
Acetophenone	100	n
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonium chloride	Solution	l
Ammonium hydroxide	30	S
Ammonium sulfate	50	S
Amyl acetate	100	n
Amyl alcohol	100	l
Aniline	100	n
Antimony chloride	10	S
Aqua regia	Unknown	l
Aromatic hydrocarbons	100	n
Arsenic acid	Unknown	S
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Benzaldehyde	100	n
Benzene	100	n
Benzyl alcohol	100	l
Boric acid	Unknown	S
Brake fluid	100	l
Bromine (liquid)	100	n
Butanol	100	S
Butanone	100	n
Butyl acetate	100	n
Butylamine	Unknown	n
Butylchloride	100	n
Calcium chloride	Unknown	S
Carbon sulfide	100	n
Carbon tetrachloride	100	n
Castor oil	100	l
Cellosolve	100	n
Chlorinated hydrocarbons	100	n
Chlorinated solvents	100	n
Chlorine (dry gas)	100	n
Chlorine dioxide	Unknown	n
Chlorine water	Unknown	l
Chlorobenzene	100	n
Chloroform	100	n
Chlorosulfonic acid	Unknown	n
Chromic acid	20	S
Chromic acid	50	l
Citric acid	10	S
Colza oil	100	S
Cyclohexane	100	n
Cyclohexanol	100	n
Cyclohexanone	100	n
Diacetone alcohol	100	n
Dibutylphthalate	100	n
Dichloroethane	100	n
Dichloroethylene	100	n
Diethylamine	100	n
Diethyleneglycol	100	S
Diethylether	100	n
Diisopropylbenzene	100	n
Dimethylamine	100	n
Dimethylformamide	100	n
Dioctylphthalate	100	n
Dioxan	100	n
Ethanol	Unknown	S
Ethanol	96	l
Ethylacetate	100	n
Ethylchloride	100	n
Ethylene glycol	100	S
Ethylhexanol	100	S
Fluorine	100	n
Formaldehyde	35	S to l
Formic acid	85	S
Freon 11	100	n
Freon 113	100	n
Freon 115	100	n
Freon 12	100	n
Freon 13b1	100	n
Freon 21	100	n
Freon 22	100	n
Freon 32	100	n
Furfural	100	n
Glycerol	100	S
Grease	100	l
Hexane	100	S
Hydrobromic acid	48	S
Hydrochloric acid	10–36	S
Hydrofluoric acid	40	S
Hydrogen peroxide	3–30	S
Hydrogen sulfide gas	Unknown	S
Iron(III) chloride	Unknown	S
Isobutanol	100	S
Isooctane (Fuel A)	100	n
Isopropanol	100	l
Kerosene	100	l
Linseed oil	100	S
Liquid paraffin	100	n
Magnesium chloride	Unknown	S
Methanol	100	l
Methylbutylketone	100	n
Methylene chloride	100	n
Methylethylketone	100	n
Methylglycol	Unknown	S
Mineral oil	100	l
Monochlorobenzene	100	n
Monoethyleneglycol	100	S
Naphtha	Unknown	l
Nickel chloride	Unknown	n

(*Continued*)

Table 4.61 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Nitric acid	10	S	Sodium hydroxide	55	l
Nitric acid	65	l	Sodium hypochlorite	20	S
Nitric acid	⩾75	n	Sodium nitrate	Solution	S
Nitrobenzene	100	n	Strong acids	Concentrated	l
Nonanol	100	S	Strong bases	Unknown	S
Oleic acid	Unknown	S	Styrene	100	n
Oleum @ 10%	Pure	n	Sulfur dioxide (gas)	Unknown	l
Olive oil	100	S	Sulfuric acid	10–70	S
Ozone	Unknown	S	Sulfuric acid	96	l
Perchloroethylene	100	n	Sulfuric acid	Fuming	n
Petrol aliphatic	100	n	Sulfurous anhydride (gas)	Unknown	l
Petrol high-octane	100	n	Tetrachloroethane	100	n
Petroleum	100	n	Tetrachloroethylene	100	n
Phenol	90	n	Tetrahydrofuran	100	n
Phosphoric acid	85	S	Toluene	100	n
Potassium cyanide	Unknown	S	Transformer oil	100	l
Potassium fluoride	Unknown	S	Trichloroethane	100	n
Potassium hydroxide	45	S	Trichloroethylene	100	n
Potassium permanganate	20	S	Triethylamine	Unknown	n
Potassium sulfate	Unknown	S	Trimethylbenzene	100	n
Propanol	100	l	Turpentine oil	100	n
Propylene oxide	100	n	Urea	Solution	S
Pyridine	Unknown	n	Vegetable oil	100	S
Sea water	100	S	Water	100	S
Silver nitrate	Unknown	S	Weak acids	Unknown	S
Sodium borate	Unknown	S	Weak bases	Unknown	S
Sodium carbonate	10	S	White spirit	100	l
Sodium chloride	25	S	Wine	Unknown	S
Sodium cyanide	Unknown	S	Xylene	100	n
Sodium hydroxide	10	S	Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

The choice of adhesive can be made only after thorough research and preliminary tests. The parts should not be subjected to high stresses.

All precautions must be taken concerning safety and hygiene according to the local laws and regulations.

PPE can generally be decorated by painting and varnishing after surface treatment. Metallization is very often used with specific grades marketed for this process. Printing is possible with compatible materials and processing.

4.18.8 Specific ISO standards concerning PPE

ISO 15103-1:2000 Plastics – Poly(phenylene ether) (PPE) moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 15103-2:2000 Plastics – Poly(phenylene ether) (PPE) moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

4.18.9 Trade name examples

Luranyl, Noryl, Prevex, Ultranyl, Vestoran.

4.18.10 Property tables

Table 4.62 relates to examples only and cannot be generalized. Data cannot be used for design purposes.

Table 4.62 PPE: examples of properties

PPE	General-purpose		Impact-modified		FR V0	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.04	1.1	1	1.11	1.06	1.1
Shrinkage (%)	0.5	0.8	0.6	1	0.6	1
Absorption of water (%)	0.06	0.12	0.06	0.12	0.08	0.12
Mechanical properties						
Shore hardness, D	85	90	85	90	85	90
Rockwell hardness, M	50	70	50	70	50	70
Stress at yield (MPa)	45	65	50	56	45	65
Strain at yield (%)	2	7			2	7
Tensile strength (MPa)	45	60	45	55	45	55
Elongation at break (%)	45	60	40	60	30	50
Tensile modulus (GPa)	2.1	2.8	2.1	2.8	2.4	2.5
Flexural modulus (GPa)	2.1	2.8	2.1	2.8	2.4	2.5
Notched impact strength ASTM D256 (J/m)	130	300	150	400	200	300
Thermal properties						
HDT B (0.46 MPa) (°C)	110	138	100	120	100	150
HDT A (1.8 MPa) (°C)	90	130	90	120	90	150
Continuous use temperature (°C)	80	110	80	110	80	110
Glass transition temperature (°C)	100	210	130	150		
Brittle point (°C)	−50	−40				
Thermal conductivity (W/m.K)	0.16	0.22			0.16	0.22
Specific heat (cal/g/°C)	0.32	0.32				
Coefficient of thermal expansion (10^{-5}/°C)	3	7	4	8	3	7
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}			10^{15}	10^{16}
Dielectric constant	2.7	2.7			2.7	2.7
Loss factor (10^{-4})	4	9			7	31
Dielectric strength (kV/mm)	20	22			16	25
Arc resistance (s)	53	80				
Fire behaviour						
Oxygen index (%)	18	19	18	19		
UL94 fire rating	HB	HB	HB	HB	V0	V0
PPE	20% Glass fibre FR V1		30% Glass fibre		Mineral-filled	
Miscellaneous properties						
Density (g/cm^3)	1.2	1.2	1.26	1.28	1.2	1.25
Shrinkage (%)	0.3	0.4	0.1	0.4	0.3	0.7
Absorption of water (%)			0.06	0.1	0.06	0.12
Mechanical properties						
Shore hardness, D			85	90	85	90
Rockwell hardness, M			50	60	60	70
Stress at yield (MPa)	90	90	100	130	65	75
Strain at yield (%)	2	2	3	3		
Tensile strength (MPa)	80	80	100	130	65	75

(*Continued*)

Table 4.62 (Continued)

PPE	20% Glass fibre FR V1		30% Glass fibre		Mineral-filled	
Elongation at break (%)	3	3	3	3	20	40
Tensile modulus (GPa)	6.5	6.5	7	9	2.9	3.5
Flexural modulus (GPa)			7	9	2.9	3.5
Notched impact strength ASTM D256 (J/m)			80	130	150	200
Thermal properties						
HDT B (0.46 MPa) (°C)	140	140	138	154	100	120
HDT A (1.8 MPa) (°C)	135	135	134	144	90	110
Continuous use temperature (°C)	80	110	80	110	80	110
Glass transition temperature (°C)			100	150	100	150
Thermal conductivity (W/m.K)	0.22	0.22	0.28	0.28		
Coefficient of thermal expansion (10^{-5}/°C)	3	4	1.5	2.5	2	5
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{15}	10^{15}	10^{16}		
Dielectric constant	3	3	2.9	2.9		
Loss factor (10^{-4})	20	20	10	15		
Dielectric strength (kV/mm)			22	22		
Fire behaviour						
UL94 fire rating	V1	V1	HB	HB	HB	HB

PPE/PA alloys	Unfilled		10% GF		30% GF	
Miscellaneous properties						
Density (g/cm^3)	1.1	1.1	1.16	1.16	1.31	1.31
Shrinkage (%)	1.2	1.6	0.5	0.7	0.3	0.5
Absorption of water (%)	0.4	0.4				
Mechanical properties						
Stress at yield (MPa)	54	60				
Strain at yield (%)	5	7				
Tensile strength (MPa)	56	57	90	90	160	160
Elongation at break (%)	50	100	15	15	3	3
Tensile modulus (GPa)	2.1	2.2	4.5	4.5	9	9
Notched impact strength ASTM D256 (J/m)	175	250	80	80	85	85
Thermal properties						
HDT A (1.8 MPa) (°C)			175	175	225	225
Thermal conductivity (W/m.K)	0.23	0.23	0.24	0.24	0.26	0.26
Coefficient of thermal expansion (10^{-5}/°C)	9	9	4.5	4.5	2.3	2.3
Fire behaviour						
Oxygen index (%)	18	19	26	26	29	29
UL94 fire rating	HB	HB	HB	HB	HB	HB

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV-protection is needed
Weak acids	Good behaviour
Strong acids	Good to limited behaviour
Weak bases	Good behaviour
Strong bases	Good to limited behaviour
Solvents	Chemical resistance is generally good to limited at room temperature versus oils, greases, aliphatic hydrocarbons, alcohols Poor resistance versus ketones, esters, ethers, aromatic and halogenated hydrocarbons, hot oxidizing agents, amines, phenols
Food contact	Possible for special grades

4.19 Fluorinated thermoplastics: fully perfluorinated thermoplastics (PTFE or TFE, PFA, FEP), copolymers (ETFE), partially fluorinated (PVDF, PVF), chlorofluoroethylene (PCTFE) and copolymer (ECTFE)

All these thermoplastics have some similarities but also important differences explained by their chemical structure and physical characteristics.

- Polytetrafluorethylene or PTFE (sometimes called TFE) is the most commonly used, the best known and, perhaps, has the highest performance, with excellent performance/cost ratios. Its main drawback is the impossibility of processing it by conventional molten-state methods. All the hydrogen atoms of polyethylene are replaced by fluorine, leading to the following formula:

  $$-(-CF_2-CF_2-)_n-$$

  The fluorine content is theoretically 76%. Crystallinity is very high, 95% for example.
- Perfluoroalkoxy (PFA) is very like PTFE with very similar fluorine content and properties, but it is melt processable and more expensive.
- FEP is a copolymer of tetrafluoroethylene and hexafluoropolypropylene and has a fluorine content of the same order as PTFE.
- ETFE is a copolymer of tetrafluoroethylene and ethylene. The TFE/ethylene ratio is greater than 75%, leading to fluorine contents of about 60% or more.
- PCTFE is monochlorotrifluoroethylene containing 49% fluorine but also 30% chlorine, that is, a halogen total of 79%.
- ECTFE is a copolymer of monochlorotrifluoroethylene and ethylene and has, of course, a lower halogen content depending on the monomer ratio.
- PVDF is a difluoro derivative leading to the following formula $-(-CH_2-CF_2-)_n-$ and a fluorine content of 59%.
- PVF is a monofluoro derivative leading to the following formula $-(-CH_2-CHF-)_n-$ and a fluorine content of 41%.

These fluoropolymers also differ in their crystallinity, molecular weight and, possibly, a minor comonomer. Consequently, each has its set of properties. To try to shed light on this 'jungle', Figure 4.87(a) to (f) displays their relative positions versus some of the essential properties relating to their main applications:

- anticorrosion
- high service temperature
- low service temperature
- low friction parts.

Chemical behaviour

It is difficult to make a comparison because each material can be sensitive to different chemicals but, generally, within the service temperatures range, the chemical resistance increases with the amount of fluorine, or halogen total for PCTFE and ECTFE.

Arbitrarily, we suggest the following rating:

- PTFE, the most resistant
- PFA, FEP
- PCTFE
- ECTFE

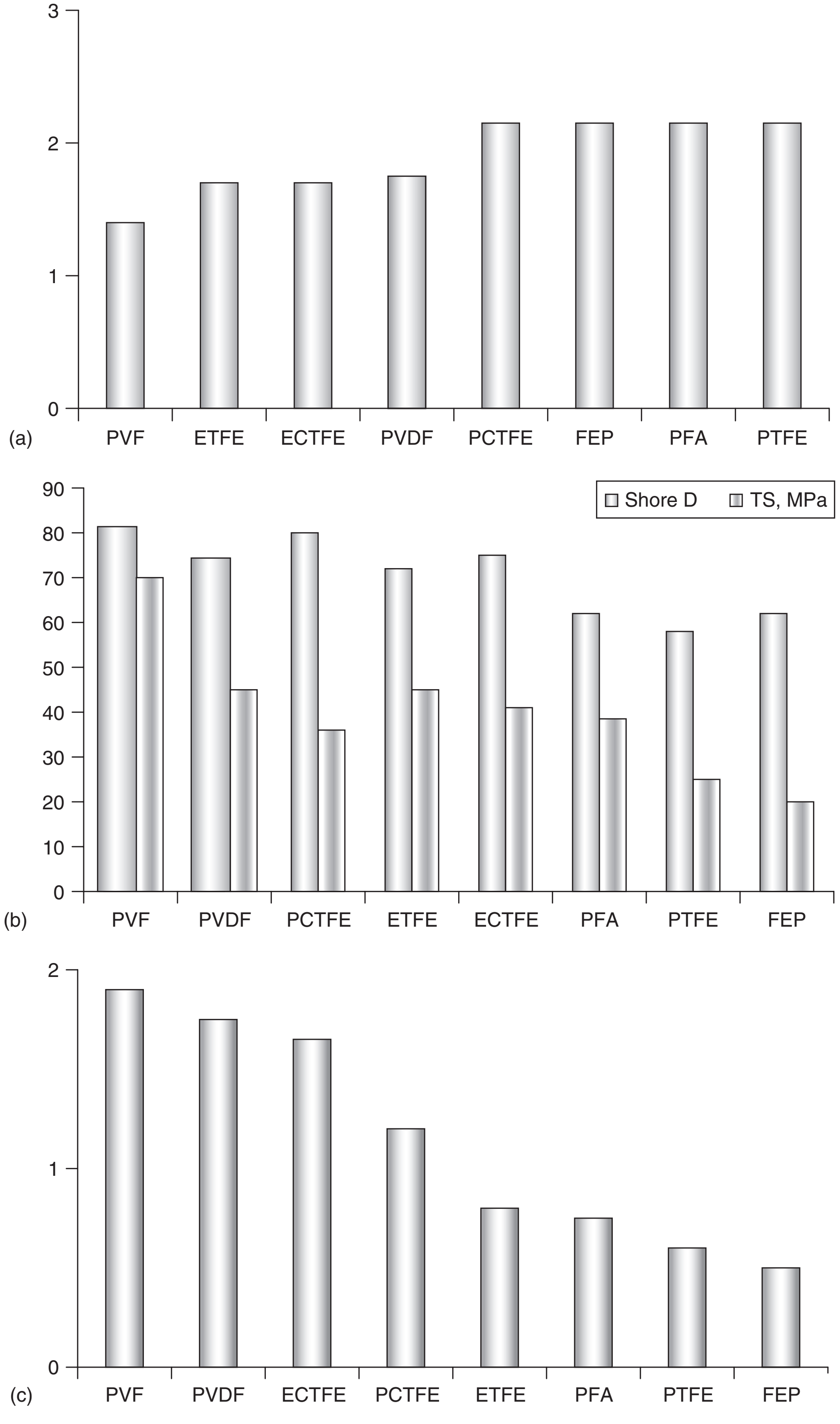


Figure 4.87. (a) Fluoropolymers: density examples (g/cm^3); (b) Fluoropolymers: hardness (Shore D) and tensile strength (MPa) examples; (c) Fluoropolymers: tensile modulus (GPa) examples

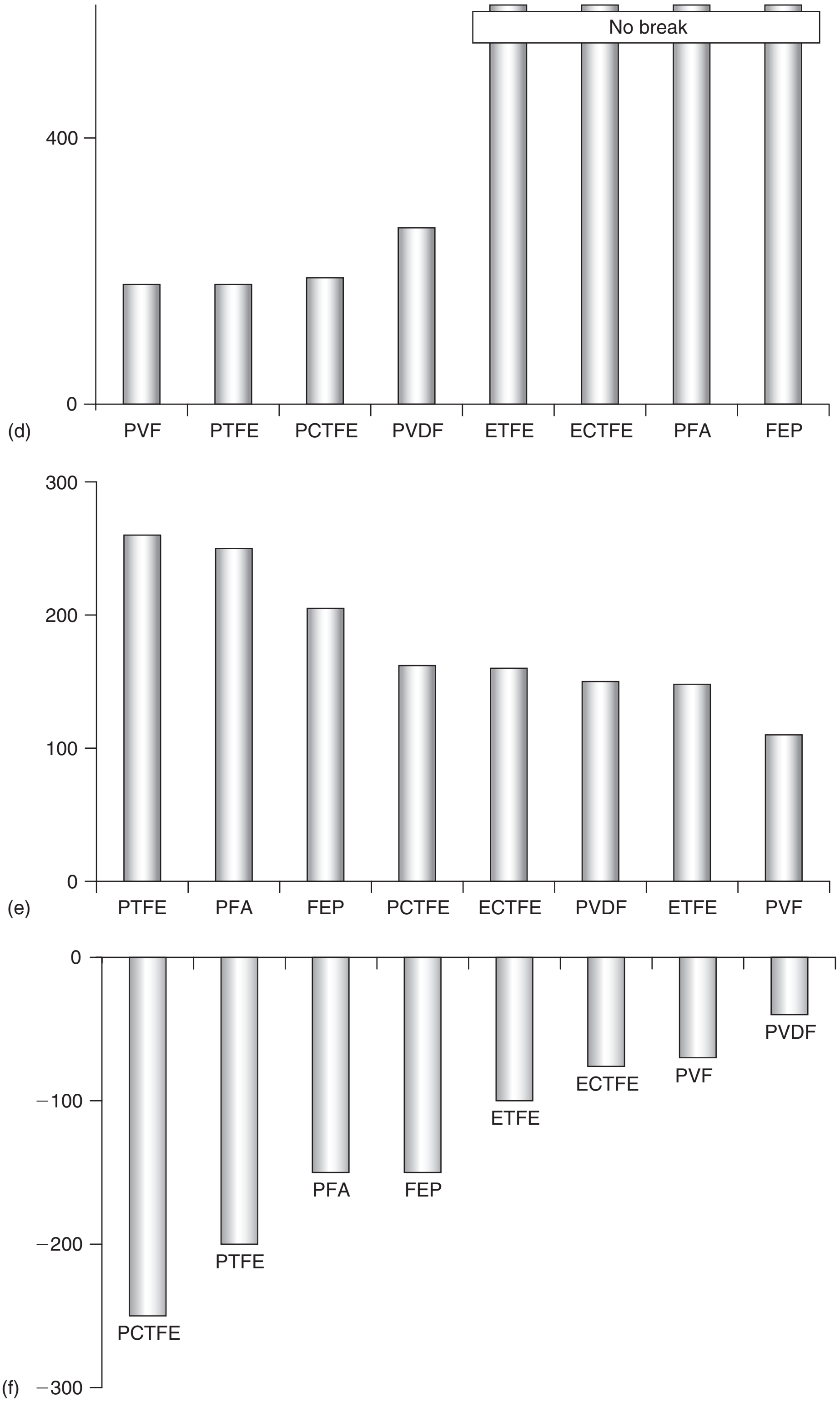


Figure 4.87. (d) Fluoropolymers: notched impact (J/m) examples; (e) Fluoropolymers: continuous use temperature (°C) examples; (f) Fluoropolymers: minimum service temperature (°C) examples

- ETFE
- PVDF
- PVF.

Densities

These increase with the fluorine content, or the halogen content for PCTFE and ECTFE (see Figure 4.87(a)).

Mechanical properties

- Tensile strengths (see Figure 4.87(b)) vary from 15 MPa to 70 MPa.
- The tensile moduli (see Figure 4.87(c)) of some fluoropolymers are in the same range as common structural thermoplastics and the others are flexible with moduli similar to LDPE.
- Notched impact strength (see Figure 4.87(d)) is good to excellent (no break).

Service temperatures

- Continuous use temperatures in an unstressed state (see Figure 4.87(e)) vary from 107°C up to 250°C.
- Minimum service temperatures (see Figure 4.87(f)) vary from −250°C up to −40°C.

Electrical properties

All the fluoropolymers are insulating but:

- resistivities vary from 10^{12} up to 10^{18}
- PVDF and PVF have high dielectric constant and loss factors
- PVDF has piezoelectric properties.

Coefficient of friction

This property can be modified by additives and a rating is inevitably arbitrary. We suggest the following rating but others can be valid:

- PTFE
- PFA
- FEP
- ETFE
- ECTFE
- PCTFE
- PVF.

Specific ISO standards concerning fluorinated polymers

ISO 12086-1:1995 Plastics – Fluoropolymer dispersions and moulding and extrusion materials – Part 1: Designation system and basis for specifications

ISO 12086-2:1995 Plastics – Fluoropolymer dispersions and moulding and extrusion materials – Part 2: Preparation of test specimens and determination of properties

4.19.1 Perfluorinated thermoplastics (PTFE or TFE, PFA, FEP)

Polytetrafluorethylene or PTFE (sometimes called TFE) is the most commonly used, the best known and, perhaps, has the highest performance, with excellent performance/cost ratios. Its main drawback is the impossibility of processing it by conventional molten-state methods.

The fluorine content is theoretically 76%. Crystallinity is very high, 95%, for example.

PFA and FEP are very like PTFE with very similar fluorine content and properties, but are melt processable and more expensive.

Advantages

PTFE is appreciated for its: exceptional chemical resistance, very good resistance to heat and low temperature; very good electrical insulating properties even in hot and wet environments, good resistance to light, UV and weathering; low coefficient of friction, strong anti-adhesion properties; flexibility, good fatigue resistance under low stresses, fire resistance but beware of toxic fumes; food, medical and high-purity grades; very low water absorption.

FEP can be processed by injection and extrusion and offers the same advantages as PTFE, but to a lesser degree. The upper service temperature is not so good, inferior by roughly 50°C.

PFA can also be processed by injection and extrusion and offers the same advantages as PTFE.

Drawbacks

All these polymers contain significant amounts of fluorine.

PTFE is handicapped by the impossibility of using the conventional molten-state processing methods and the difficulty and cost of the suitable specific methods. Additional disadvantages are the sensitivity to creep and abrasion; significant dimensional variation around the glass transition temperature (about 19°C); the price (justified by the high performances); density; difficulties of joining; corrosive and toxic fumes in the event of fire.

FEP: the disadvantages are similar to those of PTFE, except that injection and extrusion are possible, but the cost is higher.

PFA: the disadvantages are similar to those of PTFE, except that injection and extrusion are possible, but the price is higher than that of FEP.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, sintering, compression, isostatic moulding, coating, spreading, impregnation, powders for lubrication, thin or thick parts, granular, fine powder, aqueous dispersion and micropowder . . .
- high molecular weight, glass-graphite-bronze filled, food contact, low warpage, reinforced, antistatic, conductive, transparent, high purity . . .
- for E&E, food, anticorrosion, self-lubricating, semiconductor applications . . .

Costs

As for all plastics, the costs fluctuate greatly with the crude oil price, and are only given to provide a general idea. They are generally of the order of ten or a few tens of Euros per kilogram for PTFE, twice as much as PTFE for FEP and three times as much as PTFE for PFA.

Processing

PTFE: sintering, pressing, ram or paste extrusion, compression moulding or isostatic moulding, machining, hot stamping, extrusion of pre-sintered powders on special machines.

Dispersion: metal coatings, coating, pulverization, impregnation, cast (for thin films), fibre spinning.

FEP, PFA: conventional molten-state processing methods are usable, such as injection, extrusion, compression; machining is also suitable.

Consumption

The global consumption is roughly estimated at 70 000 t/year, mainly in industrial and electrical & electronics applications. FEP and PFA consumptions are, perhaps, ten times inferior to that of PTFE.

Varying with the country and the source, the following data can be found for the main outlets:

• Industry	65–75%
• E&E	10–20%
• Others	10–20%.

This is an example and other data can be found elsewhere depending on the source and country.

Applications

(See Chapter 2 for further information.)

Fluorinated thermoplastics are only used for high-performance applications related to their high heat, low temperature, chemical inertness, high purity, non-stick and self-lubricating properties. High-purity grades are appreciated by the semiconductor, pharmaceutical and other similar sectors.

- Industry
  - washers, flanges, baffles . . .
  - gaskets, seals, rings, O-rings, D-rings, U-seals, V-seals, cup seals . . .
  - encapsulated O-rings and other parts, lined products . . .
  - self-lubricating components . . .
  - lantern rings for pumps, bellow-type seals for centrifugal pumps; hydraulic, pneumatic, earthmoving equipment; cylinder valves for O_2, CO_2, refined gases, chlorine, ammonia . . .
  - bellows for glass columns, glass valves, pipelines . . .
  - valve and pump components, balls for non-return valves . . .
  - bearings, bushings . . .
  - PTFE/woven-glass composites . . .
  - heavy-wall tubing . . .

  - assemblies for piping systems, sprinklers, mixers . . .
  - plain, coloured, striped and multilumen tubing fabrications for instrumentation; automotive push-pull cables; industrial and process hydraulics and other fluids . . .
  - piping liners for glass-lined reactors, stainless-steel reactors, glass equipment and mixers . . .
- Electricity & electronics
  - coaxial cable connectors, terminal and high-voltage insulators; transformer, relay, antenna, power amplifier components . . .
  - laminates for critical microwave components, antennas and subassemblies, RF/microwave materials, hybrid RF multilayers, digital/microwave hybrid multilayer PCB assemblies, cellular base station antennas . . .
  - dual-band high-power passive circuits . . .
  - millimetre-wave components . . .
  - PTFE/woven-glass composites . . .
  - lowest loss applications . . .
  - telecommunications . . .
  - wireless communications . . .
- Films, sheets, pressure-sensitive tapes and other bonding films . . .
- Expanded, microporous PTFE
  - medical applications such as synthetic blood vessels and patches for soft tissue regeneration; surgical sutures for use in vascular, cardiac, general surgery and orthopaedic procedures . . .
  - knitted, woven, braided or sewn fibres: compression packing, sewing thread, architectural fabric and dental floss . . .
  - gaskets and sealants . . .
  - membranes, filter media, filter bags, cartridges, microfiltration membranes, vents and adsorbent products . . .

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at:

- PTFE: up to 260°C
- PFA: from 240°C up to 260°C
- FEP: up to 205°C.

The UL temperature indices of specific grades can be lower, 180°C for example.

Service temperatures are noticeably lower under loading because of low moduli, modulus decay, strain, creep, relaxation . . . For example:

- the percentage retention of tensile strength at 250°C compared to the tensile strength at ambient temperature is claimed at roughly 25–30% for given PTFE and PFA grades
- the percentage retention of moduli at 250°C compared to the moduli at ambient temperature is claimed at roughly 9–20% for given PTFE and PFA grades
- HDTs under 0.46 MPa range from 70°C up to 120°C
- HDTs under 1.8 MPa can be as low as 45°C.

These results relate to some grades only and cannot be generalized.

Figure 4.88 displays two examples of tensile stress and modulus retention (relative to/linked to the properties at 20°C) versus temperature for a given PTFE grade.

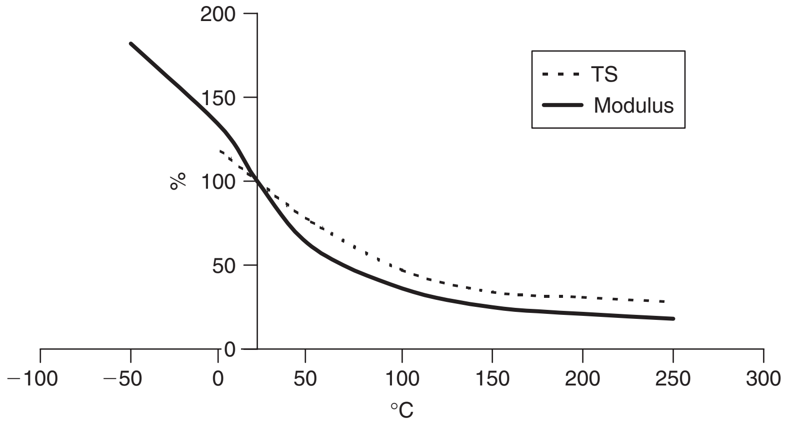


Figure 4.88. PTFE examples of tensile stress and modulus retentions (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered. Impact strength and elongation at break are especially heat-sensitive characteristics.

Temperatures for lifetimes of 20 000 h based on a 50% retention of elongation at break are, for example:

- 260°C for PTFE
- 260°C for PFA
- 205°C for FEP.

At low temperatures, the behaviour can be reasonably good down to −200°C, according to the grades and the mechanical constraints imposed.

At −40°C, for two given PTFE and FEP grades, notched Izod impact strengths are, respectively, 107 J/m and 155 J/m.

At −55°C, for another given PTFE grade, notched Izod impact strength is roughly 100 J/m.

At −200°C, for a given PFA grade, notched Izod impact strength is roughly 60 J/m.

The glass transition temperature of PTFE is about 19°C.

These results relate to some grades only and cannot be generalized.

Optical properties

General-purpose grades of PTFE are whitish and translucent with a transmittance of 82% for a thickness of 0.1 mm and 40% for a 1-mm thickness. Refractive indices are roughly:

- 1.35 for PTFE
- 1.34 for PFA
- 1.34 for FEP.

A specific PTFE grade is transparent with a light transmission of the order of 90% for a sheet 2.8 mm thick.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties at room temperature are generally rather weak with a low modulus. When the temperature rises, the mechanical performances do not decrease as quickly as for many other thermoplastics, and at high temperature mechanical performances are among the best. As for other polymers, mechanical characteristics can be improved by fibre reinforcement.

The abrasion resistance, generally fair, depends on the roughness, type and morphology of the opposing sliding surface. PTFE are often used for tribological applications.

Friction

A broad choice of lubricating, thermally conducting and reinforcing additives leads to coefficients of friction in a good range, from 0.1 up to 0.3, and wear ranging from fair up to good, on condition that the pressure is in proportion with the low compression strength and modulus. PTFE remains efficient when the temperature rises.

For example, under a pressure of 0.2 MPa, and a velocity of 0.5–1 m/s, dynamic coefficients of friction are:

- 0.26 for a neat PTFE
- 0.21 for a bronze-filled PTFE
- 0.15 for a glass fibre reinforced PTFE
- 0.14 for a carbon fibre reinforced PTFE.

Dimensional stability

Alterations by moisture exposure are very weak but shrinkage and coefficients of thermal expansion are high, as for other crystalline polymers. Moreover, the glass transition temperature is at room temperature. Creep resistance is low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular orientation. For given samples, Poisson's ratios are evaluated at 0.46–0.48. This is an example only and cannot be generalized.

Creep

PTFE has low moduli that involve high strains for low loading. Consequently, creep moduli are also low at room temperature, as we can see in Figure 4.89(a). Despite the low level of loading, creep moduli are less than 0.5 GPa.

Reinforcement with carbon and glass fibres moderately improves moduli, as shown in Figure 4.89(b). Note that the load is 14 MPa for reinforced grades and 7 MPa for the neat grade.

When the temperature rises the creep modulus decreases, significantly at first and then more slowly, as we can see from Figure 4.89(c).

These results relate to a few grades only and cannot be generalized.

Dynamic fatigue

The dynamic fatigue can be good to excellent for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the low modulus. For example, PTFE is used to manufacture bellows with excellent dynamic endurance.

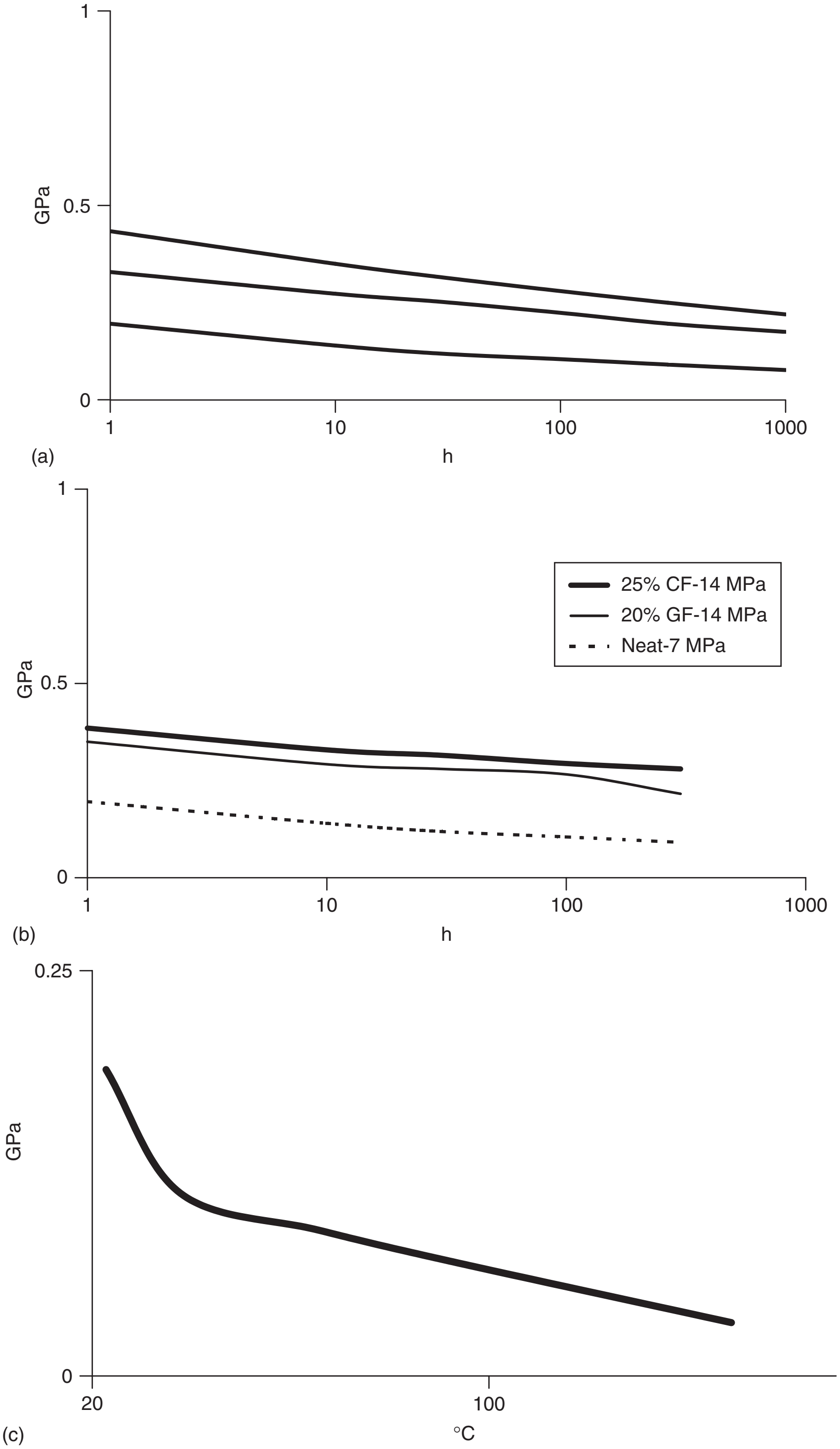


Figure 4.89. (a) Neat PTFE creep: examples of creep modulus (GPa) versus time (h) for loading from 3.5 up to 7 MPa; (b) Neat and reinforced PTFE: examples of creep modulus (GPa) versus time (h) for loading from 7 up to 14 MPa; (c) Neat PTFE: examples of creep modulus after 100 h (GPa) versus temperature (°C) under 7 MPa

For example:

- 30 mm and 50 mm long bellows withstand 10 million extensions of 20 mm
- strips of PTFE withstand folding more than a million times.

Weathering

PTFE and other perfluorinated thermoplastics are not sensitive to moisture or UV. Stabilization is not needed.

After one-year outdoor exposures of 3 mm thick samples, retentions of tensile strengths and elongation at break are 100%.

After 15-year outdoor exposures of 0.1–0.15 mm thick films, the retentions of tensile strengths and elongations at break range from 91% up to 125% without visible change.

These results are examples only and cannot be generalized.

High-energy radiation

PTFE, FEP and PFA are sensitive to high-energy radiation. Exposure to 1 Mrad can lead to a measurable degradation.

Chemicals

Chemical inertness is excellent.

PTFE, FEP and PFA are attacked only by alkaline metals and their organic derivatives; elemental fluorine and chlorine trifluoride; alkali and alkaline earth metals with their oxides and carbonates above 350°C. The other halogens, aqua regia, nitrosulfuric acid mixtures, oleum (fuming sulfuric acid) and solvents are without significant effects.

Styrene monomer leads to a phenomenon known as 'popcorning', resulting from polymerization of the styrene within the PTFE microvoids.

Table 4.63 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the perfluorinated thermoplastics. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.63 Perfluorinated thermoplastics: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour			Chemical	Concentration (%)	Estimated behaviour		
		PTFE	PFA	FEP			PTFE	PFA	FEP
Acetic acid	⩾10	S	S	S	Amyl acetate	100	S	S	S
Acetic aldehyde	100	S	S	S	Amyl alcohol	100	S	S	S
Acetic anhydride	100	S	S	S	Aniline	100	S	S	S
Acetone	100	S	S	S	Antimony chloride	10	S	S	S
Acetonitrile	100	S	S	S	Aqua regia	Unknown	S	S	S
Acetophenone	100	S	S	S	Arsenic acid	Unknown	S	S	S
Acetyl chloride	100	S	S	S	ASTM1 oil	100	S	S	S
Acrylic acid	100	S	S	S	ASTM2 oil	100	S	S	S
Aluminium chloride	Solution	S	S	S	ASTM3 oil	100	S	S	S
Aluminium sulfate	Unknown	S	S	S	Barium chloride	Saturated	S	S	S
Ammonium hydroxide	30	S	S	S	Benzaldehyde	100	S	S	S
Ammonium sulfate	50	S	S	S	Benzene	100	S	S	S

(*Continued*)

Table 4.63 (Continued)

Chemical	Concentration (%)	Estimated behaviour		
		PTFE	PFA	FEP
Benzylchloride	100	S	S	S
Benzyl alcohol	100	S	S	S
Boric acid	Unknown	S	S	S
Bromine (liquid)	100	l	S	S
Butanol	100	S	S	S
Butyl acetate	100	S	S	S
Butylamine	Unknown	S	S	S
Butylchloride	100	S	S	S
Butyric acid	Unknown	S	S	S
Calcium chloride	Unknown	S	S	S
Carbon sulfide	100	S	S	S
Carbon tetrachloride	100	S	S	S
Castor oil	100	S	S	S
Cellosolve	100	S	S	S
Cellosolve acetate	100	S	S	S
Chlorine (dry gas)	100	S	S	S
Chlorine dioxide	Unknown	S	S	S
Chlorine water	Unknown	S	S	S
Chloroacetic acid	Unknown	S	S	S
Chlorobenzene	100	S	S	S
Chloroform	100	S	S	S
Chlorosulfonic acid	Unknown	S	S	S
Chromic acid	Unknown	S	S	S
Citric acid	10	S	S	S
Colza oil	100	S	S	S
Copper sulfate	Unknown	S	S	S
Cresol	100	S	S	S
Cyclohexane	100	S	S	S
Cyclohexanol	100	S	S	S
Cyclohexanone	100	S	S	S
Decaline	100	S	S	S
Dichloroethylene	100	S	S	S
Diethylamine	100	S	S	S
Diethyleneglycol	100	S	S	S
Diethylether	100	S	S	S
Dimethylamine	100	S	S	S
Dimethylformamide	100	S	S	S
Dimethylhydrazine	100	S	S	S
Dioctylphthalate	100	S	S	S
Dioxan	100	S	S	S
Ethanol	Unknown	S	S	S
Ethylacetate	100	S	S	S
Ethylamine	100	S	S	S
Ethylchloride	100	S	S	S
Ethylene glycol	Unknown	S	S	S
Ethylenebromide	100	S	S	S
Fluorine	100	S	S	S
Fluosilicic acid	Unknown	S	S	S
Formic acid	40–85	S	S	S
Freon 11	100	n	n	n
Freon 113	100	l	l	l
Freon 115	100	S	S	S
Freon 12	100	n	n	n
Freon 13b1	100	S	S	S
Freon 21	100	S	S	S
Freon 22	100	l to n	l	l
Freon 32	100	S	S	S
Furfural	100	S	S	S
Glycerol	100	S	S	S
Hexane	100	S	S	S
Hydrazine	100	S	S	S
Hydrobromic acid	48	S	S	S
Hydrochloric acid	10–37	S	S	S
Hydrofluoric acid	40	S	S	S
Hydrogen peroxide	30–90	S	S	S
Hydrogen sulfide gas	Unknown	S	S	S
Iron(III) chloride	Unknown	S	S	S
Isooctane (Fuel A)	100	S	S	S
Isopropanol	100	S	S	S
Lactic acid	90	S	S	S
Lead acetate	10	S	S	S
Linseed oil	100	S	S	S
Liquid paraffin	100	S	S	S
Magnesium chloride	Unknown	S	S	S
Magnesium sulfate	Unknown	S	S	S
Mercury chloride	Unknown	S	S	S
Methanol	100	S	S	S
Methylbromide	100	S	S	S
Methylene chloride	100	S	S	S
Methylethylketone	100	S	S	S
Mineral oil	100	S	S	S
Molasses	Unknown	S	S	S
Monoethanolamine	Unknown	S	S	S
Nickel chloride	Unknown	S	S	S
Nitric acid	⩾10	S	S	S
Nitrobenzene	100	S	S	S
Nitromethane	100	S	S	S
Nitropropane	100	S	S	S
Oleic acid	Unknown	S	S	S
Olive oil	100	S	S	S
Oxalic acid	Unknown	S	S	S
Ozone	Unknown	S	S	S
Perchloroethylene	100	S	S	S
Petroleum	100	S	S	S
Phenol	Unknown	S	S	S
Phosphoric acid	85	S	S	S
Picric acid	Solution	S	S	S
Potassium cyanide	Unknown	S	S	S
Potassium fluoride	Unknown	S	S	S
Potassium hydroxide	45	S	S	S
Potassium permanganate	20	S	S	S
Potassium sulfate	Unknown	S	S	S
Propanol	100	S	S	S
Propionic acid	100	S	S	S
Propylene oxide	100	S	S	S

Table 4.63 (Continued)

Chemical	Concentration (%)	Estimated behaviour			Chemical	Concentration (%)	Estimated behaviour		
		PTFE	PFA	FEP			PTFE	PFA	FEP
Pyridine	Unknown	S	S	S	Tin chloride	Unknown	S	S	S
Sea water	100	S	S	S	Titanium tetrachloride	Unknown	S	S	S
Silicone oil	100	S	S	S	Toluene	100	S	S	S
Silver nitrate	Unknown	S	S	S	Transformer oil	100	S	S	S
Sodium borate	Unknown	S	S	S	Trichloroacetic acid	10	S	S	S
Sodium carbonate	10	S	S	S	Trichloroethane	100	S	S	S
Sodium chloride	25	S	S	S	Trichloroethylene	100	S	S	S
Sodium cyanide	Unknown	S	S	S	Tricresylphosphate	Unknown	S	S	S
Sodium hydroxide	10–55	S	S	S	Triethanolamine	Unknown	S	S	S
Sodium hypochlorite	20	S	S	S	Triethylamine	Unknown	S	S	S
Sodium nitrate	Solution	S	S	S	Turpentine oil	100	S	S	S
Styrene	100	S	S	S	Vegetable oil	100	S	S	S
Sulfamic acid	Solution	S	S	S	Vinyl chloride	Unknown	S	S	S
Sulfuric acid	⩾10	S	S	S	Vinyl acetate	100	S	S	S
Sulfurous anhydride(gas)	Unknown	S	S	S	Water	100	S	S	S
					White spirit	100	S	S	S
Tetrachloroethane	100	S	S	S	Wine	Unknown	S	S	S
Tetrahydrofuran	100	S	S	S	Xylene	100	S	S	S
Thionyl chloride	100	S	S	S	Zinc chloride	Unknown	S	S	S

S: satisfactory; l: limited; n: not satisfactory

Among the above chemicals, less than ten are harmful for the three perfluorinated thermoplastics.

Permeability

Perfluorinated thermoplastics are generally rather permeable, especially PTFE because of the processing methods used.

Fire resistance

Fire resistance is naturally excellent but perfluorinated thermoplastics release corrosive and toxic fumes. Oxygen indices are at least 95 and UL94 rating is V0.

Electrical properties

Perfluorinated thermoplastics are excellent insulators even in wet environments, with high resistivities and dielectric strengths, and very low loss factors.

Electrical properties are not so temperature dependant as for many other thermoplastics. For example:

- at 150°C, the resistivity is 10^{18} for a given grade
- dielectric strength slowly decreases when the temperature rises to 50°C and then stabilizes.

Joining, decoration

Welding is very difficult for PTFE and definitely alters mechanical properties.

Gluing is very difficult for PTFE, FEP and PFA, needing surface treatment by alkaline metal derivatives. The assembly can be tough but chemical and thermal resistances are weakened.

The choice of adhesive can be made only after thorough research and preliminary tests. The parts should not be subjected to high stresses.

All precautions must be taken concerning safety and hygiene according to local laws and regulations.

Specific ISO standards concerning perfluorothermoplastics

ISO 7258:1984 Polytetrafluoroethylene (PTFE) tubing for aerospace applications – Methods for the determination of the density and relative density

ISO 7313:1984 Aircraft – High temperature convoluted hose assemblies in polytetrafluoroethylene (PTFE)

ISO 8829:1990 Aerospace – Polytetrafluoroethylene (PTFE) hose assemblies – Test methods

ISO 8913:1994 Aerospace – Lightweight polytetrafluoroethylene (PTFE) hose assemblies, classification 204 degrees C/21 000 kPa – Procurement specification

ISO 9528:1994 Aerospace – Standard-weight polytetrafluoroethylene (PTFE) hose assemblies, classification 204 degrees C/21 000 kPa – Procurement specification

ISO 9938:1994 Aerospace – Polytetrafluoroethylene (PTFE) hose assemblies, classification 204 degrees C/28 000 kPa – Procurement specification

ISO 10502:1992 Aerospace – Hose assemblies in polytetrafluoroethylene (PTFE) for use up to 232 degrees C and 10 500 kPa – Procurement specification

ISO 13000-1:1997 Plastics – Polytetrafluoroethylene (PTFE) semi-finished products – Part 1: Requirements and designation

ISO 13000-2:1997 Plastics – Polytetrafluoroethylene (PTFE) semi-finished products – Part 2: Preparation of test specimens and determination of properties

Trade name examples

Algoflon, Dyneon, Fluon, Halon, Hiflon, Hostaflon, Neoflon, Polyflon, Soreflon, Teflon, Teflon FEP, Teflon PFA.

Property tables

Table 4.64 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

4.19.2 Tetrafluoroethylene and ethylene copolymer (ETFE)

The TFE/ethylene ratio of tetrafluoroethylene-ethylene copolymers is greater than 75% leading to fluorine contents of about 60% or more.

The main purpose of ETFE is to provide properties near to those of PTFE with easier and more economical processing.

Advantages

ETFE is appreciated for: easy processability, good chemical resistance, good resistance to heat and low temperature; good electrical insulating properties even in hot and wet environments,

Table 4.64 Perfluorinated thermoplastics: examples of properties

	FEP		PFA		PTFE	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	2.1	2.2	2.1	2.2	2.1	2.2
Shrinkage (%)	3	6	3	5	3	6
Absorption of water (%)	0.01	0.01	0.01	0.03	0.01	0.01
Mechanical properties						
Shore hardness, D	55	65	60	65	50	65
Rockwell hardness, R	30	55	35	55	<30	55
Rockwell hardness, M	<20	<20	<20	<20	<20	<20
Tensile strength (MPa)	19	21	27	30	15	35
Elongation at break (%)	250	300	300	300	200	400
Tensile modulus (GPa)	0.3	0.7	0.6	0.8	0.4	0.8
Flexural modulus (GPa)	0.3	0.7	0.7	0.8	0.4	0.8
Notched impact strength ASTM D256 (J/m)	NB	NB	NB	NB	160	200
Thermal properties						
HDT B (0.46 MPa) (°C)	70	70	70	75	70	120
HDT A (1.8 MPa) (°C)					45	50
Continuous use temperature (°C)	205	205	240	260	260	260
Melting temperature (°C)	275	275	305	305	327	342
Brittle point (°C)	−150	−150	−150	−150	−200	−200
Thermal conductivity (W/m.K)	0.25	0.25	0.2	0.25	0.24	0.24
Specific heat (cal/g/°C)	0.28	0.28	0.28	0.28	0.25	0.25
Coefficient of thermal expansion (10^{-5}/°C)	8	10	8	12	7	20
Electrical properties						
Volume resistivity (ohm.cm)	10^{17}	10^{18}	10^{16}	10^{18}	10^{17}	10^{18}
Dielectric constant	2.1	2.1	2.1	2.1	2.1	2.1
Loss factor (10^{-4})	7	7	2	5	2	2
Dielectric strength (kV/mm)					17	24
Dielectric strength of films (kV/mm)	70	70	80	185	157	165
Arc resistance (s)	165	180	300	>300	200	300
Fire behaviour						
Oxygen index (%)	95	95	95	95	95	95
UL94 fire rating	V0	V0	V0	V0	V0	V0

Perfluorinated thermoplastics	PTFE					FEP
	PTFE Glass fibre		PTFE Carbon fibre		PTFE Bronze	FEP Glass fibre
	Min.	Max.	Min.	Max.	Average	Average
Miscellaneous properties						
Density (g/cm^3)	2.2	2.3	2.1	2.1	3.5	2.2
Absorption of water (%)	0.01	0.15				
Mechanical properties						
Shore hardness, D	60	72	63	65	65	68
Rockwell hardness, R	35	75	45	55	55	65
Rockwell hardness, M	<20	<20	<20	<20	<20	<20
Tensile strength (MPa)	7	20	15	15	15	40
Elongation at break (%)	250	260	80	180	100	3
Tensile modulus (GPa)	1	1.7				
Flexural modulus (GPa)	1	1.7				5
Notched impact strength ASTM D256 (J/m)	120	144				200

(*Continued*)

Table 4.64 (Continued)

Perfluorinated thermoplastics	PTFE					FEP
	PTFE Glass fibre		PTFE Carbon fibre		PTFE Bronze	FEP Glass fibre
	Min.	Max.	Min.	Max.	Average	Average
Thermal properties						
HDT B (0.46 MPa) (°C)	125	125				260
HDT A (1.8 MPa) (°C)	110	110				160
Continuous use temperature (°C)	180	260				150
Thermal conductivity (W/m.K)	0.33	0.42	0.64	0.68	0.7	
Coefficient of thermal expansion (10^{-5}/°C)	7	12	9	10	10	5
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{3}	10^{3}		10^{14}
Dielectric constant	2.2	2.8				2.5
Loss factor (10^{-4})	30	30				5
Dielectric strength (kV/mm)	13	40				13
Arc resistance (s)	165	180				
Fire behaviour						
Oxygen index (%)	95	95				95
UL94 fire rating	V0	V0			V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Excellent resistance
Weak acids	Good behaviour
Strong acids	Good behaviour
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Excellent resistance, attacked only by alkaline metals and their organic derivatives; elemental fluorine and chlorine trifluoride, alkali and alkaline earth metals with their oxides and carbonates above 350°C
Food contact	Possible for special grades

good resistance to light, UV and weathering; flexibility, good fatigue resistance under low stresses, fire resistance (but beware of toxic fumes); attractive performance/cost ratios, food grades, very low water absorption, passable high-energy radiation resistance.

Drawbacks

ETFE is handicapped by sensitivity to creep and abrasion, the price (justified by the performance), density, corrosive and toxic fumes in the event of fire, the limited number of sources and grades.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, compression, coating, powder for rotational moulding, thin or thick parts, various flow rates . . .

- high-temperature, flexible, reinforced, reduced flammability, food contact, improved stress cracking resistance, low warpage, antistatic, improved adhesion to polyamides . . .
- for E&E, food industry, anticorrosion, lining . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide an idea. They are generally of the order of a few tens of Euros per kilogram, roughly twice as much as PTFE.

Processing

ETFE can be processed by conventional molten-state methods such as extrusion, injection, compression, transfer, rotational and blow moulding.

Applications

(See Chapter 2 for further information.)

The global consumption should be, perhaps, between those of FEP and PFA.

ETFEs are only used for relatively high-performance applications related to heat, low temperature, chemical inertness and electrical insulation.

- E&E
  - electrical sleeving, wire and cable insulation and jacketing, appliance wires, motor lead wires, compact wire and cables, airframe wiring, extruded coatings . . .
  - battery components . . .
  - coil forms . . .
  - electrical components: sockets, connectors, switches, insulators, cable clamps . . .
- Industry
  - linings, linings of components used in chemical processing, sleeves . . .
  - pump housings, compressor linings and components . . .
  - extruded tubing, pipes, hoses, fittings, fluid handling, profiles . . .
  - injection- and blow-moulded articles . . .
  - containers, vessels, process vessels, tank construction and linings, columns, elbows, tees . . .
  - fasteners . . .
  - instrument components . . .
  - cryogenic applications, super-cold refrigeration components . . .
  - valves, seats, seals, gaskets, diaphragms, liquid gauge seals . . .
  - bearings, thrusts . . .
- Films
  - food packaging, pharmaceutical packaging, industry . . .
  - heat-shrinkable films, oriented films . . .
  - optical recording . . .
  - electroluminescent display panels . . .

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 135°C up to 150°C.

Service temperatures are noticeably lower under loading because of low moduli, modulus decay, strain, creep, relaxation . . . For example:

- the percentage retention of tensile strength at 140°C compared to the tensile strength at ambient temperature is roughly 25–30%
- the percentage retention of modulus and tensile strength at 150°C compared to the same properties at ambient temperature are roughly 10% and 25%
- HDT under 0.46 MPa is 105°C for a given grade
- HDTs under 1.8 MPa can be as low as 70°C.

These results relate to some grades only and cannot be generalized.

Figure 4.90 displays two examples of the retention of tensile stress and elongation at break (relative to the properties at 20°C) versus temperature for an ETFE.

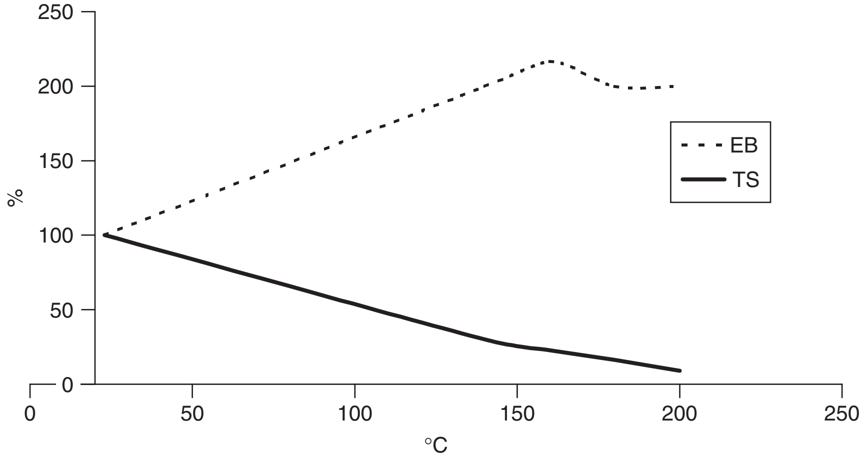


Figure 4.90. ETFE examples of tensile stress (TS) & elongation at break (EB) retentions (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered. Impact strength and elongation at break are especially heat-sensitive characteristics.

After 150 days of exposure in air at 210°C, retentions are roughly, for example:

- 60% for tensile strength
- More than 50% for elongation at break
- More than 25% for dielectric strength.

After 7 days of exposure in air at 230°C, retentions of tensile strength, elongation at break and dielectric strength are more than 90%.

At low temperatures, the behaviour can be reasonably good down to −100°C according to the grades and the mechanical constraints undergone.

At −54°C, for two given ETFE grades, notched Izod impact strengths are more than 1000 J/m.

These results relate to some grades only and cannot be generalized.

Optical properties

General-purpose grades of ETFE are whitish and translucent. However, for certain grades in thin widths, for example a film of 0.025 mm, transmittance is about 95%. Refractive indices are roughly 1.407.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties at room temperature are generally fair with a low modulus and an excellent impact strength, but performances decrease when the temperature rises.

Friction

Neat and glass fibre reinforced grades can be used for tribological applications with rather high coefficients of friction in a range from 0.3 up to 0.5.

For example, against steel and under a pressure of 0.2 MPa, velocity can vary from 0.025 m/s to 0.09 m/s.

Dimensional stability

Alteration by moisture exposure is very weak but shrinkage and coefficients of thermal expansion are high; creep resistance is low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular orientation.

Creep

ETFE has low moduli that involve high strains for low loading. Consequently, creep moduli are also low at room temperature.

Reinforcement with glass fibres improves moduli and creep moduli, leading to fair creep behaviour, as we can see in Figure 4.91, which shows creep moduli at room temperature and 100°C under an unknown loading.

These results relate to a few grades only and cannot be generalized.

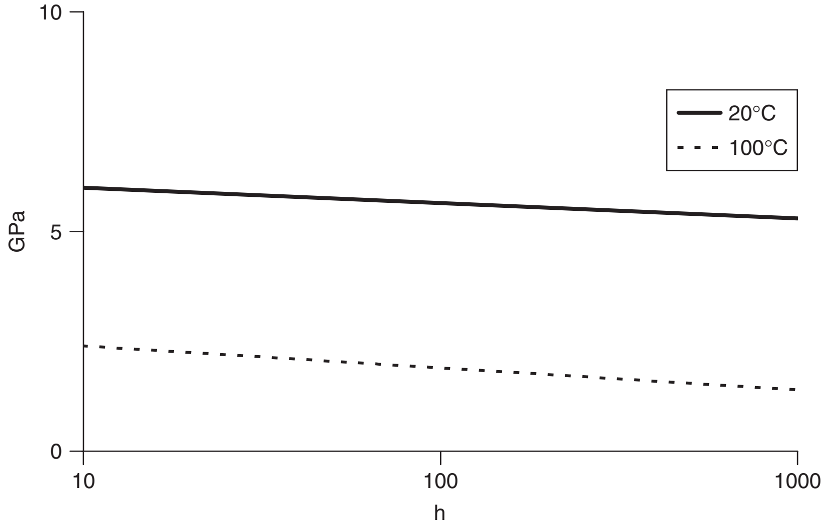


Figure 4.91. Glass fibre reinforced ETFE creep: examples of creep modulus (GPa) versus time (h) at 20°C and 100°C

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the low modulus.

For example it is possible to exceed 10 million cycles in traction/compression if stresses are limited to:

- 12 MPa for a neat grade
- 21 MPa for a glass fibre reinforced grade.

These results relate to a few grades only and cannot be generalized.

Weathering

ETFEs are inherently insensitive to moisture and UV. Stabilization is not needed.

However, glass fibre reinforced grades can be altered by long outdoor exposures.

High-energy radiation

ETFE is less sensitive than PTFE to high-energy radiation.

Chemicals

Chemical inertness is excellent but not as good as for PTFE, especially when the temperature rises.

ETFE are not sensitive to strong mineral acids, halogens, metal salt solutions and inorganic bases.

Carboxylic acids, anhydrides, aromatic and aliphatic hydrocarbons, alcohols, aldehydes, ketones, esters, and chlorinated solvents have only a slight effect.

When the temperature rises, or near the boiling point of the considered chemicals, very strong oxidizing acids such as nitric acid, organic bases such as amines, and sulfonic acids at high concentrations can alter ETFE to a greater or lesser degree.

Table 4.65 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the ETFE. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: ETFE has a rather low permeability, evaluated at 0.4 for a full range of 0.05 up to 400 for all tested plastics.
- Gases: ETFE has a rather high permeability, evaluated at:
  - carbon dioxide: 2400 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 300 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 1000 versus a full range of <1 up to 11 000 for all tested plastics.

Table 4.65 ETFE: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10–96	S
Acetic aldehyde	100	S
Acetic anhydride	100	S
Acetone	100	S
Acetophenone	100	S
Acetyl chloride	100	S
Acrylic acid	100	S
Alcohols	100	S
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonium chloride	Unknown	S
Ammonium hydroxide	30	S
Ammonium sulfate	50	S
Amyl acetate	100	S
Amyl alcohol	100	S
Antimony chloride	10	S
Aqua regia	Unknown	l
Arsenic acid	Unknown	S
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Benzaldehyde	100	S
Benzene	100	S
Benzoic acid	Solution	S
Benzylchloride	100	S
Benzyl alcohol	100	S
Boric acid	Unknown	S
Bromine (liquid)	100	S
Butanol	100	S
Butyl acetate	100	S
Butylamine	Unknown	S
Butylchloride	100	S
Butyric acid	Unknown	S
Calcium chloride	Unknown	S
Carbon sulfide	100	S
Carbon tetrachloride	100	S
Castor oil	100	S
Cellosolve	100	S
Cellosolve acetate	100	S
Chlorine (dry gas)	100	S
Chlorine dioxide	Unknown	S
Chlorine water	Unknown	S
Chloroacetic acid	Unknown	S
Chlorobenzene	100	S
Chloroform	100	S
Chlorosulfonic acid	Unknown	S
Chromic acid	30	S
Citric acid	10	S
Colza oil	100	S
Concentrated acids	Concentrated	S
Copper sulfate	Unknown	S
Cresol	100	S
Cyclohexane	100	S
Cyclohexanol	100	S
Cyclohexanone	100	S
Decaline	100	S
Diacetone alcohol	100	S
Dichloroethane	100	S
Dichloroethylene	100	S
Diethylamine	100	S
Diethyleneglycol	100	S
Diethylether	100	S
Diisopropylbenzene	100	S
Diluted acids	Dilute	S
Dimethylamine	100	S
Dimethylformamide	100	S
Dimethylhydrazine	100	S
Dioctylphthalate	100	S
Dioxan	100	S
Ethanol	96	S
Ethylacetate	100	S
Ethylamine	100	S
Ethylchloride	100	S
Ethylene glycol	100	S
Ethylenebromide	100	S
Ethylhexanol	100	S
Fluorine	100	S
Fluosilicic acid	Unknown	S
Formaldehyde	37	S
Formic acid	85	S
Freon 11	100	S
Freon 113	100	S
Freon 115	100	S
Freon 12	100	S
Freon 13b1	100	S
Freon 21	100	S
Freon 22	100	S
Freon 32	100	S
Furfural	100	S
Glycerol	100	S
Glycol esters	100	S
Hexane	100	S
Hydrazine	100	S
Hydrobromic acid	48	S
Hydrochloric acid	10–37	S
Hydrofluoric acid	40	S
Hydrogen peroxide	3–90	S
Hydrogen sulfide	Saturated	S
Hydrogen sulfide gas	Unknown	S
Iron(III) chloride	Unknown	S
Isobutanol	100	S
Isooctane (Fuel A)	100	S
Isopropanol	100	S
Kerosene	100	S
Lactic acid	90	S
Lead acetate	10	S
Linseed oil	100	S

(*Continued*)

Table 4.65 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Liquid paraffin	100	S	Silicone oil	100	S
Magnesium chloride	Unknown	S	Silver nitrate	Unknown	S
Manganese sulfate	Unknown	S	Sodium borate	Unknown	S
Mercury	100	S	Sodium carbonate	10	S
Mercury chloride	Unknown	S	Sodium chloride	25	S
Methanol	100	S	Sodium cyanide	Unknown	S
Methylbromide	100	S	Sodium hydroxide	10–55	S
Methylene chloride	100	S	Sodium hypochlorite	20	S
Methylethylketone	100	S	Sodium nitrate	Solution	S
Methylglycol	Unknown	S	Strong bases	Unknown	S
Methylisobutylketone	Unknown	S	Styrene	100	S
Mineral oil	100	S	Sulfamic acid	Solution	S
Molasses	Unknown	S	Sulfur dioxide (gas)	Unknown	S
Monochlorobenzene	100	S	Sulfuric acid	⩾10	S
Monoethanolamine	Unknown	S	Sulfurous anhydride (gas)	Unknown	S
Monoethyleneglycol	Unknown	S	Tetrachloroethane	100	S
Naphtha	Unknown	S	Tetrachloroethylene	100	S
Nickel chloride	Unknown	S	Tetrahydrofuran	100	S
Nitric acid	5–65	S	Thionyl chloride	100	S
Nitrobenzene	100	S	Tin chloride	Unknown	S
Nitromethane	100	S	Titanium tetrachloride	Unknown	S
Nitropropane	100	S	Toluene	100	S
Nonanol	100	S	Transformer oil	100	S
Oleic acid	Unknown	S	Trichloroacetic acid	Unknown	S
Olive oil	100	S	Trichloroethane	100	S
Oxalic acid	Unknown	S	Trichloroethylene	100	S
Ozone	Unknown	S	Tricresylphosphate	Unknown	S
Perchloroethylene	100	S	Triethanolamine	Unknown	S
Petroleum	100	S	Triethylamine	Unknown	S
Phenol	Unknown	S	Trimethylbenzene	100	S
Phosphoric acid	85	S	Turpentine oil	100	S
Picric acid	Solution	S	Urea	Solution	S
Potassium cyanide	Unknown	S	Vegetable oil	100	S
Potassium fluoride	Unknown	S	Vinyl chloride	Unknown	S
Potassium hydroxide	45	S	Vinyl acetate	100	S
Potassium permanganate	20	S	Water	100	S
Potassium sulfate	Unknown	S	Weak acids	Unknown	S
Propanol	100	S	White spirit	100	S
Propionic acid	100	S	Wine	Unknown	S
Propylene oxide	100	S	Xylene	100	S
Pyridine	Unknown	S	Zinc chloride	Unknown	S
Sea water	100	S			

S: satisfactory; l: limited; n: not satisfactory

Fire resistance

Fire resistance is naturally good but ETFE releases corrosive and toxic fumes. Oxygen indices are about 30–32 and UL94 rating is V0. Grades with reduced flammability are marketed.

Electrical properties

ETFE are good insulators even in wet environments, with high resistivities and low loss factors.

Joining, decoration

Welding is possible for certain grades by thermal and friction processes but not by using high frequencies.

Gluing is also possible. Preliminary tests are essential.

All precautions must be taken concerning health and safety according to local laws and regulations.

Trade name examples

Hostaflon ET, Neoflon, Tefzel.

Property tables

Table 4.66 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.66 ETFE: examples of properties

	ETFE		25% Glass fibre		Static dissipative	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.7	1.7	1.8	1.9	1.7	1.7
Shrinkage (%)	2	4				
Absorption of water (%)	0.03	0.07				
Mechanical properties						
Shore hardness, D	63	80	70	80		
Rockwell hardness, R	50	90	74	74		
Rockwell hardness, M	<20	30	<20	30		
Tensile strength (MPa)	40	50	82	83	35	35
Elongation at break (%)	200	460	8	8	200	200
Tensile modulus (GPa)	0.8	1.4	8	9		
Flexural modulus (GPa)	1.2	1.4	6	7		
Notched impact strength ASTM D256 (J/m)	NB	NB	480	485		
Thermal properties						
HDT B (0.46 MPa) (°C)	104	105	265	265		
HDT A (1.8 MPa) (°C)	70	100	210	210		
Continuous use temperature (°C)	135	150	150	200	150	150
Melting temperature (°C)	255	280	270	280	255	280
Brittle point (°C)	−100	−100				
Thermal conductivity (W/m.K)	0.24	0.24	0.24	0.25		
Specific heat (cal/g/°C)	0.4	0.5				
Coefficient of thermal expansion (10^{-5}/°C)	5	14	2	3		
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{17}	10^{15}	10^{17}	7	7
Dielectric constant	2.3	2.6	3	3.4		
Loss factor (10^{-4})	6	100	20	120		
Dielectric strength of films (kV/mm)	216	220				
Arc resistance (s)	75	122	110	110		
Fire behaviour						
Oxygen index (%)	30	32				
UL94 fire rating	V0	V0	V0	V0		

(*Continued*)

Table 4.66 (Continued)

	Uniaxially oriented films		
Thickness (μm)	23	64	127
Area factor (m^2/kg)	26	9	5
Miscellaneous properties			
Specific gravity (g/cm^3)		1.7	
Moisture absorption (%)		0.03	
Mechanical properties			
	Machine direction		Transverse direction
Tensile strength (MPa)	234		48
Elongation at break (%)	45		650
Tensile modulus (GPa)	73		0.9
Tensile creep (35 MPa, 1000 h) (%)	0.8		8
Thermal properties			
Melting temperature (°C)		270	
Continuous use temperature (°C)		150	
Oxygen index (%)		30	
Optical properties			
Light transmission (%)		95	
Refractive index		1.407	

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Excellent
Weak acids	Good behaviour
Strong acids	Good behaviour
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Possible slight effects from carboxylic acids, anhydrides, aromatic and aliphatic hydrocarbons, alcohols, aldehydes, ketones, esters, chlorinated solvents When the temperature rises, or near the boiling point of the considered chemicals, very strong oxidizing acids such as nitric acid, organic bases such as amines, sulfonic acids at high concentrations can alter ETFE to a greater or lesser degree
Food contact	Possible for special grades

4.19.3 Polychlorotrifluoroethylene (PCTFE)

Monochlorotrifluoroethylene results from the replacement of one fluorine atom in tetrafluoroethylene by a chlorine. It contains 49% fluorine but also 30% chlorine, that is, a halogen total of 79%. The crystallinity of this semicrystalline polymer can be controlled between 30% and 70% by selection of the molecular weight and adjustment of the thermal history resulting from processing and possible heat treatments. High crystallinity leads to high mechanical strength and low elongation, while amorphous PCTFE is optically clear and less stiff.

More easily processable than PTFE, it also has better or poorer performances according to the properties considered.

Advantages

PCTFE is appreciated for: good chemical resistance; exceptional low-temperature behaviour down to −240/250°C; gas barrier properties; excellent resistance to light, UV and weathering; good resistance to heat; good electrical insulating properties even in hot and wet environments; non-flammability (but toxic and corrosive fumes); optical transparency of amorphous films; processability; very low water absorption; food and pharmaceutical grades; low outgassing.

Drawbacks

PCTFE is handicapped by its high cost (justified by the performances), density, corrosive and toxic fumes in the event of fire, the limited number of sources and grades.

Special grades

They can be classified according to the type of processing, specific properties or targeted applications:

- extrusion, injection, compression . . .
- food and drug contact . . .
- for E&E, food industry, pharmaceutical films . . .

Costs

The cost is high and, as for all plastics, fluctuates highly with the crude oil price. It can be, for example, of the order of a few tens of Euros, more expensive than PTFE.

Processing

PCTFE can be processed by conventional molten-state methods such as extrusion, injection, compression, transfer. Films can be laminated and metallized.

Applications

(See Chapter 2 for further information.)

PCTFEs are only used for high-performance applications requiring gas barrier effects, low temperatures, chemical inertness, electrical insulation.

- Industry
  - cryogenic applications, super-cold refrigeration components . . .
  - valves, seats, seals, gaskets, diaphragms . . .
  - bearings, thrusts . . .
  - pipes . . .
- Films
  - food, pharmaceutical, healthcare, medical, industrial and chemical packaging . . .
  - moisture-proof film packaging, protection of sonar buoys . . .
  - optical recording . . .
  - electroluminescent display panels . . .

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated in a range from 120°C up to 150°C.

Service temperatures are distinctly lower under loading because of low moduli, modulus decay, strain, creep, relaxation . . . For example:

- the percentage of stress at yield retained at 120°C compared to the stress at yield at ambient temperature is roughly 10%
- the percentage of tensile strength retained at 120°C compared to tensile strength at ambient temperature is roughly 30–40%
- the percentage of flexural modulus retained at 100°C compared to flexural modulus at ambient temperature is roughly 11%
- HDT under 0.46 MPa is 120–125°C for a given grade.

These results relate to some grades only and cannot be generalized.

Figure 4.92 displays an example of flexural modulus retention (relative to the properties at 20°C) versus temperatures for a PCTFE.

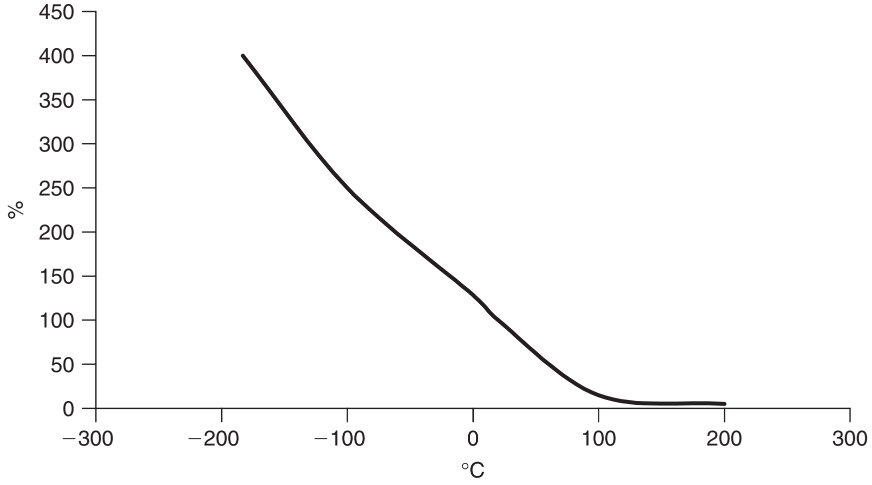


Figure 4.92. PCTFE examples of flexural modulus retention (%) versus temperature (°C)

Optical properties

When amorphous, PCTFE can be clear. For example, for a given film of 0.025 mm thickness, transmittance is about 95%. Refractive indices are roughly 1.43.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties at room temperature are generally fair with a rather low modulus and a fair impact strength, but performances decrease when the temperature rises.

Dimensional stability

Alterations by moisture exposure are very weak but shrinkage and coefficients of thermal expansion are rather high; creep moduli are low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular orientation. For a certain grade it is estimated at 0.33. This figure relates to one grade only and cannot be generalized.

Creep

PCTFE has low moduli that involve high strains for low loading. Consequently, creep moduli are also low at room temperature.

After 24 h under 7 MPa, creep moduli are, for example:

- 0.7 GPa for creep at 23°C
- 0.3 GPa for creep at 70°C
- 0.06 GPa for creep at 125°C.

These results relate to a few grades only and cannot be generalized.

Weathering

PCTFEs are insensitive to moisture and UV. Stabilization is not needed.

High-energy radiation

PCTFE is less sensitive than PTFE to high-energy radiation. For example, after a 50 Mrad irradiation, the tensile strength decay is 50%.

Chemicals

Chemical inertness is excellent but not as good as for PTFE especially when the temperature rises.

PCTFE is not sensitive to strong mineral acids and other mineral chemicals as well as most organic reactants.

However, it should be noted that, above 300°C, PCTFE tends to depolymerize and the lower molecular weight products are less inert and can react with moisture to release acid products.

Table 4.67 displays some results concerning the swelling of PCTFE when immersed for a number of days in various chemicals. Note the short immersion times and the limited area of these tests, which relate to only one property. A low swelling is not a sufficient indication of suitability and other performances should be tested. These results are not necessarily representative of all the PCTFEs and should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Permeability

PCTFE is an excellent gas barrier.

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: PCTFE has the lowest permeability, evaluated at 0.05 up to 0.1 for a full range of 0.05 up to 400 for all tested plastics.

Table 4.67 PCTFE: examples of swelling for short immersion times

Chemical	Concentration (%)	Temperature (°C)	Days	Swelling (%)
Acetic acid	100	25	7	0
Acetic acid	100	50	7	0
Acetic acid	100	70	7	0.2
Acetic acid	100	135	14	1.9
Acetic acid	100	175	7	2.5
Acetic acid	50	25	7	0
Acetic acid	50	175	7	0.1
Acetic anhydride	Unknown	25	7	0
Acetic anhydride	Unknown	70	7	0.1
Acetic anhydride	Unknown	139	1	3.6
Acetone	Unknown	25	7	0
Acetone	Unknown	50	7	0.9
Acetonitrile	Unknown	25	40	0
Acetonitrile	Unknown	100	11	0.9
Acetophenone	Unknown	25	7	0
Acetyl chloride	Unknown	25	7	0.1
Allylchloride	Unknown	25	7	0.2
Amyl acetate	Unknown	25	7	0
Amyl acetate	Unknown	70	7	0.9
Aniline	Unknown	25	7	0
Aniline	Unknown	70	7	0.01
Aniline	Unknown	100	7	0.4
Aqua regia	Unknown	25	7	0
Aqua regia	Unknown	100	7	0.3
Benzaldehyde	Unknown	25	7	0
Benzene chloride	Unknown	100	7	3.8
Benzoic acid	Unknown	90	7	0.1
Benzonitrile	Unknown	25	7	0
Benzoyl chloride	Unknown	25	7	0
Benzyl chloride	Unknown	25	7	0
Benzyl chloride	Unknown	50	7	0.25
Benzyl alcohol	Unknown	25	7	0
Bromobenzene	Unknown	25	7	0
Bromobenzene	Unknown	70	7	1.9
Bromoform	Unknown	25	7	0
Bromoform	Unknown	50	7	0
Bromoform	Unknown	100	7	2
Butanol n	Unknown	25	7	0
Butanol n	Unknown	70	7	0.01
Butyl oxide	Unknown	25	7	0
Butylacetate	Unknown	25	7	0.8
Butylacetate	Unknown	50	7	2.5
Butylacetate	Unknown	90	7	5.8
Butylacetate	Unknown	135	7	6.5
Butylsebacate	Unknown	25	7	0
Carbon sulfide	Unknown	25	7	0.1
Carbon tetrachloride	Unknown	25	7	0.4
Carbon tetrachloride	Unknown	50	7	9.7
Carbon tetrachloride	Unknown	100	7	18
Carbon tetrachloride	Unknown	135	7	600
Chlorhydrine sulfur	Unknown	25	40	0
Chlorobenzene	Unknown	25	7	0.7
Chlorobenzene	Unknown	50	7	2.8
Chlorobenzene	Unknown	100	7	6.8
Chloroform	Unknown	25	7	1.6

Table 4.67 (Continued)

Chemical	Concentration (%)	Temperature (°C)	Days	Swelling (%)
Chloronitropropane	Unknown	25	7	0
Chloropropane	Unknown	25	7	0.3
Chlorotoluene	Unknown	25	7	0
Chromic acid	Unknown	25	7	0
Cresol	Unknown	25	7	0
Cyclohexanone	Unknown	25	7	0
Dibutylphthalate	Unknown	25	7	0
Dibutylsebacate	Unknown	25	7	0
Dibutylsebacate	Unknown	100	7	0
Dichlorobenzene	Unknown	100	7	7.5
Dichlorobutane	Unknown	25	7	0
Dichloroethane	Unknown	25	4	0.02
Dichloroethane	Unknown	90	1/2	2.4
Dichloroethylether	Unknown	25	7	0
Dichlorohexafluoro cyclobutane	Unknown	25	7	0.1
Dichlorotoluene	Unknown	25	7	0
Dichlorotrifluoromethylbenzene	Unknown	25	7	1
Dichlorotrifluoromethylbenzene	Unknown	50	7	4.2
Dichlorotrifluoromethylbenzene	Unknown	100	7	19.5
Diethylamine	Unknown	25	7	1.9
Diethylene triamine	Unknown	25	7	0
Diisobutylketone	Unknown	90	7	1.2
Dimethylacetamide	Unknown	125	8	4.8
Dimethylformamide	Unknown	125	8	2.8
Dimethylhydrazine	Unknown	25	30	0
Dimethylsulfoxide	Unknown	125	8	0.3
Dioxane	Unknown	25	7	0
Dioxane	Unknown	50	7	0.5
Dioxane	Unknown	100	7	5.7
Ethanol	Unknown	25	7	0
Ethanol	Unknown	78	7	0
Ethanol	Unknown	135	7	0.38
Ethylacetate	Unknown	25	7	1.5
Ethylacetate	Unknown	70	7	6.5
Ethylacrylate	Unknown	25	7	0.5
Ethylacrylate	Unknown	50	7	1.6
Ethylbutyrate	Unknown	25	7	0.5
Ethylene chloride	Unknown	25	7	0
Ethylene chloride	Unknown	70	7	12
Ethylene diamine	Unknown	25	30	0
Ethylene diamine	Unknown	100	7	0.3
Ethylene glycol	Unknown	25	7	0
Ethylene glycol	Unknown	175	7	0.1
Ethylformate	Unknown	25	7	0.2
Ethylglycol acetate	Unknown	25	7	0
Ethyllaurate	Unknown	25	7	0
Ethyllaurate	Unknown	100	7	0.7
Ethylmyristate	Unknown	25	7	0
Ethylmyristate	Unknown	100	7	0
Ethyloleate	Unknown	25	7	0
Ethyloleate	Unknown	100	7	0
Ethyloxide	Unknown	25	7	5.7
Ethyloxide	Unknown	35	7	6.5
Ethylpropionate	Unknown	25	7	1

(*Continued*)

Table 4.67 (Continued)

Chemical	Concentration (%)	Temperature (°C)	Days	Swelling (%)
Ethylricinoleate	Unknown	25	7	0
Ethylricinoleate	Unknown	100	7	0
Fluosilicic acid	Unknown	25	7	0
Fluosilicic acid	Unknown	50	7	0
Forane 11 (refrigerant)	Unknown	25	7	6.4
Forane 113	Unknown	25	7	2.2
Forane 113	Unknown	50	7	14
Forane 113	Unknown	90	7	22
Forane 12	Unknown	25	7	3
Forane 122	Unknown	25	7	1.8
Forane 122	Unknown	50	7	17
Forane 122	Unknown	100	7	18
Forane 22	Unknown	25	7	2.2
Formic acid	100	25	7	0
Formic acid	100	100	7	0.5
Formic acid	37	90	7	0.02
Formic acid	37	135	7	2.9
Formol	30	25	7	0.3
Formol	Unknown	100	7	0.3
Formol, anhydrous	Unknown	25	7	1.3
Furane	Unknown	25	7	2.4
Furfuryl alcohol	Unknown	25	30	0
Gallic acid	Saturated	175	7	0.2
Glycerol	Unknown	25	7	0
Glycerol	Unknown	175	7	0.8
Glycerol oleate	Unknown	25	7	0
Glycerol oleate	Unknown	100	7	0
Hydrobromic acid	48	135	7	0.2
Hydrochloric acid	30	25	7	0
Hydrochloric acid	37	175	7	0.3
Hydrofluoric acid	50	25	7	0
Hydrofluoric acid, anhydrous	Unknown	25	7	0
Hydrogen sulphide, solution	Saturated	175	7	0.07
Isoamyl alcohol	Unknown	135	7	1.4
Isopropanol	Unknown	25	7	0.3
Isopropanol	Unknown	100	7	0.5
Isopropyl myristate	Unknown	25	7	0
Isopropyl myristate	Unknown	100	7	0
Isopropyl nitrate	Unknown	25	30	0
Isopropyl oleate	Unknown	25	7	0
Isopropyl oleate	Unknown	100	7	0
Isopropyl oxide	Unknown	25	7	0.5
Isopropyl oxide	Unknown	67	7	3.1
Isopropyl palmitate	Unknown	25	7	0
Isopropyl palmitate	Unknown	100	7	0
Lauroylchloride	Unknown	25	2	0
Lauroylchloride	Unknown	80	2	0.1
Methanol	Unknown	25	7	0
Methanol	Unknown	65	7	0
Methyloxide	Unknown	25	7	6.4
Methylpyrrolidone	Unknown	25	7	0
Methylpyrrolidone	Unknown	100	7	2
Methylacetate	Unknown	25	7	1
Methylchloroform	Unknown	25	7	0.5
Methylene chloride	Unknown	41	7	3

Table 4.67 (Continued)

Chemical	Concentration (%)	Temperature (°C)	Days	Swelling (%)
Methylethylketone	Unknown	25	7	0.3
Methylethylketone	Unknown	80	7	4.6
Methylformate	Unknown	25	7	0.1
Methylisobutylketone	Unknown	25	7	0
Methylisobutylketone	Unknown	50	7	0.5
Methylisobutylketone	Unknown	100	7	4.8
Methylpropionate	Unknown	25	7	1.4
Naphtha solvent	Unknown	25	7	0
Nitric acid	25	175	5	0.01
Nitric acid	53	25	7	0
Nitric acid	53	70	7	0.01
Nitric acid	96	25	7	0
Nitric acid	96	50	7	0.01
Nitric acid	96	100	7	0.3
Nitric acid	Fuming	25	7	0
Nitric acid	Fuming	50	90	0.3
Nitric acid	Fuming	90	7	0.3
Nitrobenzene	Unknown	25	7	0
Nitromethane	Unknown	25	7	0
Oleic acid	Unknown	25	7	0
Oleum 20% SO_3	20% SO_3	25	7	0
Oleum 65% SO_3	65% SO_3	25	7	0
Oleum 65% SO_3	65% SO_3	50	7	0.01
Oxalic acid	10	25	30	0
Oxalic acid	10	100	11	0
Pentachloroethane	Unknown	25	7	0
Perfluorotriethylamine	Unknown	25	7	0
Petrol (60–95)	Unknown	100	7	0
Phenol	Unknown	25	7	0
Phenol	Unknown	70	7	0
Phenol	5	100	7	0.3
Phenol	5	175	7	0.3
Phosphoric acid	30	175	7	0
Phosphoric acid	100	25	7	0
Phosphoric acid	100	50	90	0
Phosphoric acid	85	100	7	0
Phosphoric acid	85	135	7	0
Phosphoric acid	85	175	7	0
Piperazine	Unknown	50	40	0.5
Piperidine	Unknown	25	7	0
Propylacetate	Unknown	25	7	0.6
Propylformate	Unknown	25	7	0.1
Propyloxide	Unknown	25	7	0.3
Propylpropionate	Unknown	25	7	0.4
Propylene chloride	Unknown	25	7	0
Pyridine	Unknown	50	40	0.5
Pyridine	Unknown	115	1	7.4
Pyrogallic acid	Saturated	175	7	0.05
Salicylic acid	Saturated	175	7	0.2
Silicone fluid DC 200	Unknown	50	7	0.1
Skydrol 500	Unknown	120	14	0.5
Skydrol 500	Unknown	175	7	0.1
Sulfurylchloride	Unknown	25	30	13
Sulfurylchloride	Unknown	70	7	20

(*Continued*)

Table 4.67 (Continued)

Chemical	Concentration (%)	Temperature (°C)	Days	Swelling (%)
Sulfuric acid	96	25	7	0
Sulfuric acid	96	70	7	0
Sulfuric acid	96	175	7	0
Sulfuric acid	50	135	30	0
Sulfuric acid	30	175	7	0
Sulfurous anhydride	100	25	7	0.1
Tetrabromoethane	Unknown	25	30	0
Tetrabromoethane	Unknown	50	11	0.25
Tetrachloroethane	Unknown	25	30	0
Tetrachloroethane	Unknown	50	11	0.25
Tetrachloroethane	Unknown	100	11	7.8
Tetrachloroethylene	Unknown	25	7	0.8
Tetrachloroethylene	Unknown	50	11	11
Tetrachloroethylene	Unknown	100	7	15
Tetrachloroethylene	Unknown	121	7	18
Tetrahydrofuran	Unknown	40	40	7
Thionyl chloride	Unknown	90	7	8.5
Trichloroacetic acid	Unknown	25	7	0
Trichloroacetic acid	Unknown	70	7	0.03
Trichloroacetic acid	Unknown	100	7	2.8
Trichloroacetyl chloride	Unknown	25	7	0.6
Trichloroacetyl chloride	Unknown	50	7	5
Trichloroacetyl chloride	Unknown	100	7	19.5
Trichloroethane	Unknown	25	7	0
Trichloroethylene	Unknown	25	7	9.6
Trichloroethylene	Unknown	90	7	9.8
Trichloroethylene	Unknown	100	7	13
Trichloropropane	Unknown	25	7	0
Tricresylphosphate	Unknown	25	7	0
Tricresylphosphate	Unknown	135	7	0
Triethanolamine	Unknown	25	7	0.3
Triethylamine	Unknown	25	7	0.2
Trimethylamine	25	25	11	0
Vinyl acetate	Unknown	25	7	0.5
Vinyl acetate	Unknown	50	7	1.5
Vinyl acetate	Unknown	100	7	4
Voltalef 1S oil	Unknown	25	7	0
Voltalef 1S oil	Unknown	50	7	3.1
Voltalef 1S oil	Unknown	100	7	25
Voltalef 3S oil	Unknown	25	7	0
Voltalef 3S oil	Unknown	50	7	0
Voltalef 3S oil	Unknown	100	7	10
Voltalef 10S oil	Unknown	25	7	0
Voltalef 10s oil	Unknown	50	7	0
Voltalef 10S oil	Unknown	100	7	3
Water	100	25	7	0
Xylidine	Unknown	25	7	0

- Gases: PCTFE has very low permeability, evaluated at:
  - carbon dioxide: 30 up to 130 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 5–8 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 15 up to 50 versus a full range of <1 up to 11 000 for all tested plastics

- ○ hydrogen: 400 up to 1100 versus a full range of 400 up to 20 000 for all tested plastics
- ○ air: 15 versus a full range of 3 up to 2750 for all tested plastics.

Fire resistance

Fire resistance is naturally good but PCTFE releases corrosive and toxic fumes in the event of fire. Oxygen indices are 95 or more and UL94 rating is V0.

Electrical properties

PCTFEs are good insulators even in wet environments, with high resistivities.

Joining, decoration

Welding is difficult but possible for certain grades using thermal processes.

All precautions must be taken concerning health and safety according to the local laws and regulations.

Trade name examples

Aclar, Kel-F, Neoflon PCTFE, Voltalef.

Property tables

Table 4.68 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

4.19.4 Ethylene chlorotrifluoroethylene copolymer (ECTFE)

ECTFE, being a copolymer of monochlorotrifluoroethylene and ethylene, has a lower halogen content than PCTFE, and the outstanding performances are of a somewhat lower level. On the other hand, it offers easier processing and the mechanical characteristics are better.

Crystallinity is generally about 50%.

Advantages

ECTFE is appreciated for: relative easy processability, good chemical resistance, good resistance to heat and low temperature; good electrical insulating properties even in hot and wet environments, good resistance to light, UV and weathering; very low water absorption, fire resistance (but beware of toxic fumes); performance/cost ratio; food grades; fair high-energy radiation resistance.

Drawbacks

ECTFE is handicapped by sensitivity to creep, the price (justified by the performances), density, corrosive and toxic fumes in the event of fire, the limited number of sources and grades.

Table 4.68 PCTFE: examples of properties

	Min.	Max.
Miscellaneous properties		
Density (g/cm^3)	2.1	2.2
Shrinkage (%)	0.5	4
Absorption of water (%)	0.01	0.05
Mechanical properties		
Shore hardness, D	75	85
Rockwell hardness, R	85	110
Rockwell hardness, M	<20	40
Tensile strength (MPa)	31	41
Elongation at break (%)	80	250
Tensile modulus (GPa)	1	2.1
Flexural modulus (GPa)	1.2	1.5
Notched impact strength ASTM D256 (J/m)	130	250
Thermal properties		
HDT B (0.46 MPa) (°C)	120	125
Continuous use temperature (°C)	120	150
Melting temperature (°C)	200	212
Brittle point (°C)	−250	−240
Thermal conductivity (W/m.K)	0.2	0.24
Specific heat (cal/g/°C)	0.22	0.22
Coefficient of thermal expansion (10^{-5}/°C)	4	7
Electrical properties		
Volume resistivity (ohm.cm)	10^{14}	10^{16}
Dielectric constant	2	3
Loss factor (10^{-4})	100	250
Dielectric strength (kV/mm)	16	24
Dielectric strength of films (kV/mm)	138	138
Arc resistance (s)	350	400
Fire behaviour		
Oxygen index (%)	95	95
UL94 fire rating	V0	V0

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, compression, coating, powder for rotational moulding, foam, various viscosities, crosslinkable by irradiation, electrostatic powdering . . .
- reinforced, heat-resistant, low coefficient of friction . . .
- for E&E, anticorrosion, lining, medical and pharmaceutical applications . . .

Processing

ECTFE can be processed by conventional molten-state methods such as extrusion, injection, compression, transfer, rotational and blow-moulding processes.

Applications

(See Chapter 2 for further information.)

ECTFEs are only used for relatively high-performance applications related to heat, low temperature, chemical inertness, electrical insulation.

- E&E
  - electrical wire and cable insulation and jacketing, wire wraps, motor lead wires, compact wire and cables, airframe wiring, extruded coatings . . .
  - coil forms . . .
  - electrical components: sockets, connectors, switches, insulators, cable clamps . . .
- Industrial
  - linings, linings of components used in chemical processing, sleeves . . .
  - pump housings, compressor linings and components . . .
  - extruded tubing, pipes, hoses, fittings, fluid handling, profiles . . .
  - injection- and blow-moulded articles . . .
  - containers, vessels, process vessels, tank construction and linings, columns . . .
  - cryogenic applications, super-cold refrigeration components . . .
  - valves, seats, seals, gaskets, diaphragms . . .
  - bearings, thrusts . . .
- Medical applications
  - syringes, sterilizable packaging; membranes, tubes . . .
  - oxygen tents . . .
  - prosthesis . . .
- Technical packaging
  - pharmaceutical and industrial packaging . . .
  - pouches for gas sampling . . .

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 150°C up to 170°C.

Service temperatures are noticeably lower under loading because of low moduli, modulus decay, strain, creep, relaxation . . . For example:

- the percentages of tensile strength and stress at yield retained at 140°C compared to the same properties at ambient temperature are roughly 15%
- the percentage retention of modulus at 100°C compared to the same property at ambient temperature is roughly 20%
- HDT under 0.46 MPa is 90–115°C for a given grade
- HDTs under 1.8 MPa can be as low as 63°C.

These results relate to some grades only and cannot be generalized.

Figure 4.93 displays two examples of tensile stress (TS) and modulus retention (relative to the properties at 20°C) versus temperature for an ECTFE.

For long-term heat ageing, property retention depends on the property and grades considered. Impact strength and elongation at break are especially heat-sensitive characteristics.

Lifetimes based on a 50% decay of elongation at break are evaluated at:

- 10 years at 165°C
- 5 years at 169°C
- 2 years at 175°C
- 1 year at 181°C.

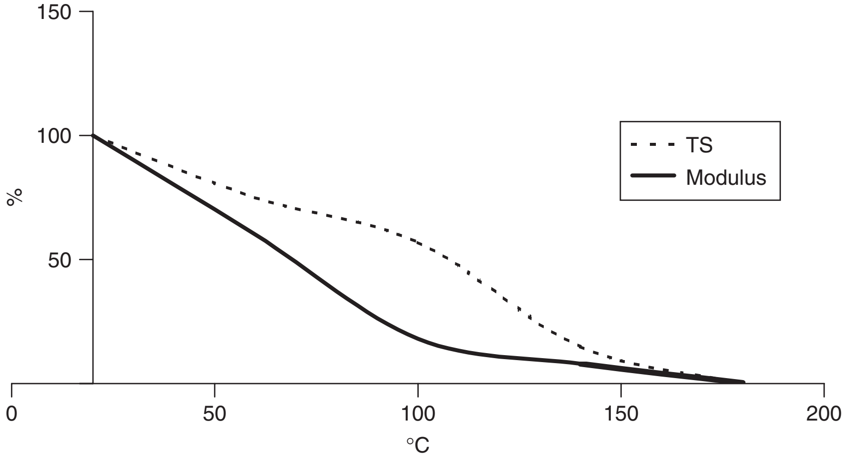


Figure 4.93. ECTFE examples of tensile stress (TS) & modulus retentions (%) versus temperature (°C)

At low temperatures, the behaviour can be reasonably good down to −76°C and even −200°C, depending on the grade and the mechanical constraints undergone.

At −40°C, for a given ECTFE grade, notched Izod impact strength is about 160 J/m.

These results relate to some grades only and cannot be generalized.

Optical properties

The refractive index is roughly 1.447. This relates to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties at room temperature are generally fair with a rather low modulus and an excellent impact strength, but performances decrease as the temperature rises.

Dimensional stability

Alterations by moisture exposure are very weak but shrinkage and coefficients of thermal expansion are high; creep resistance is low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular orientation.

Creep

ECTFE has rather low moduli that involve high strains for low loading. Consequently, creep moduli are also low at room temperature. For a certain grade, the creep modulus after 100 h is:

- about 1 GPa under a load of 14 MPa at room temperature
- about 0.04 GPa under a load of 2 MPa at 120°C.

These results relate to one grade only and cannot be generalized.

Weathering

ECTFEs are inherently insensitive to moisture and UV. Stabilization is not needed.

High-energy radiation

ECTFE is less sensitive than PTFE to high-energy radiation. Its radiation resistance is estimated at 200 Mrad by certain sources.

Chemicals

Chemical inertness is excellent but not as good as for PTFE, especially when the temperature rises.

ECTFEs are not sensitive to strong mineral and oxidizing acids, metal salt solutions, or inorganic bases.

Bromine, chlorinated solvents, amines, propylene oxide and tetrahydrofuran (THF) can have more or less severe effects at room temperature. Alterations increase when the temperature rises.

Table 4.69 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the ECTFEs. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.69 ECTFE: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10 to >96	S
Acetic aldehyde	100	S
Acetic anhydride	100	S
Acetone	100	S
Acetyl chloride	100	S
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonia	30	S
Ammonia gas	100	S
Ammonium hydroxide	10–30	S
Ammonium sulfate	50	S
Amyl acetate	100	S
Amyl alcohol	100	S
Aniline	100	S
Antimony chloride	10	S
Aqua regia	Unknown	S
Arsenic acid	Unknown	S
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Benzaldehyde	100	S
Benzene	100	S
Benzylchloride	100	S
Benzyl alcohol	100	S
Boric acid	Unknown	S
Bromine	Unknown	l
Bromine (dry gas)	100	l
Bromine (liquid)	100	S
Bromobenzene	100	S
Butanol	100	S
Butyl acetate	100	S
Butylamine	Unknown	S
Butylchloride	100	S
Butyric acid	Unknown	S
Calcium chloride	Unknown	S
Carbon tetrachloride	100	S
Castor oil	100	S
Cellosolve	100	S
Cellosolve acetate	100	S
Chlorine (dry gas)	100	S
Chlorine water	Unknown	S
Chloroacetic acid	Unknown	S
Chlorobenzene	100	S
Chloroform	100	S
Chlorosulfonic acid	Unknown	S
Chromic acid	50	S
Citric acid	10	S
Colza oil	100	S
Copper sulfate	Unknown	S
Cyclohexane	100	S
Cyclohexanol	100	S
Cyclohexanone	100	S

(*Continued*)

Table 4.69 (Continued)

Chemical	Concentration (%)	Estimated behaviour
Decaline	100	S
Dichloroethylene	100	S
Diethyleneglycol	100	S
Diethylether	100	S
Dimethylamine	100	n
Dimethylformamide	100	S
Dioctylphthalate	100	S
Dioxan	100	S
Ethanol	Unknown	S
Ethylacetate	100	S
Ethylamine	100	S
Ethylchloride	100	S
Ethylene diamine	Unknown	S
Ethylene glycol	100	S
Ethylenebromide	100	S
Fluorine	100	S
Fluosilicic acid	Unknown	S
Formaldehyde	37	S
Formic acid	85	S
Freon 11	100	S
Freon 113	100	S
Freon 12	100	S
Freon 22	100	S
Glycerol	100	S
Hexane	100	S
Household bleach	Unknown	S
Hydrobromic acid	48	S
Hydrochloric acid	>10	S
Hydrofluoric acid	4–48	S
Hydrogen peroxide	30	S
Hydrogen sulfide gas	Unknown	S
Iron(III) chloride	Unknown	S
Isooctane (Fuel A)	100	S
Isopropanol	100	S
Kerosene	100	S
Lactic acid	90	S
Lead acetate	10	S
Linseed oil	100	S
Liquid paraffin	100	S
Magnesium chloride	Unknown	S
Manganese sulfate	Unknown	S
Mercury chloride	Unknown	S
Methane	100	S
Methanol	100	S
Methylbromide	100	S
Methylene chloride	100	l
Methylethylketone	100	S
Mineral oil	100	S
Molasses	Unknown	S
Monoethanolamine	Unknown	S
Nickel chloride	Unknown	S
Nitric acid	>5	S
Nitrobenzene	100	S
Nitromethane	100	S
Oleic acid	Unknown	S
Oleum	Unknown	S
Olive oil	100	S
Oxalic acid	Unknown	S
Ozone	Unknown	S
Perchloric acid	70	S
Perchloroethylene	100	S
Petroleum	100	S
Phenol	Unknown	S
Phosphoric acid	85	S
Picric acid	Solution	S
Potassium cyanide	Unknown	S
Potassium fluoride	Unknown	S
Potassium hydroxide	45	S
Potassium permanganate	20	S
Potassium sulfate	Unknown	S
Propanol	100	S
Propionic acid	100	S
Propylene oxide	100	n
Sea water	100	S
Silver nitrate	Unknown	S
Sodium borate	Unknown	S
Sodium carbonate	10	S
Sodium chloride	25	S
Sodium cyanide	Unknown	S
Sodium hydroxide	10–55	S
Sodium hypochlorite	20	S
Sodium nitrate	Solution	S
Styrene	100	S
Sulfamic acid	Solution	S
Sulfur dioxide (gas)	Unknown	S
Sulfuric acid	⩾10	S
Sulfurous anhydride (gas)	Unknown	S
Tetrahydrofuran	100	n
Tin chloride	Unknown	S
Toluene	100	S
Transformer oil	100	S
Trichloroacetic acid	Unknown	S
Trichloroethane	100	l
Trichloroethylene	100	S
Turpentine oil	100	S
Vegetable oil	100	S
Vinyl acetate	100	S
Water	100	S
White spirit	100	S
Wine	Unknown	S
Xylene	100	S
Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Permeability

Permeability is higher than that of PCTFE.

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: ECTFE has a medium permeability, evaluated at 6 for a full range of 0.05 up to 400 for all tested plastics.
- Gases: ECTFE has a medium permeability, evaluated at:
  - carbon dioxide: 1100 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 95 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 24 versus a full range of <1 up to 11 000 for all tested plastics.

Fire resistance

Fire resistance is naturally good but ECTFE releases corrosive and toxic fumes in the event of fire. Oxygen indices are about 56–60 and UL94 rating is V0.

Electrical properties

ECTFE are good insulators, even in wet environments, with high resistivities.

Joining, decoration

Welding is possible for certain grades by thermal processes.

All precautions must be taken concerning health and safety according to local laws and regulations.

Trade name examples

Halar.

Property tables

Table 4.70 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

4.19.5 Polyvinylidene fluoride (PVDF)

PVDF is a difluoro derivative, leading to the following formula $-(-CH_2-CF_2-)_n-$ and a fluorine content of 59%. PVDF is semicrystalline with three possible crystal forms, one of which has interesting pyro- and piezoelectric properties. Copolymers are marketed for applications needing flexibility.

Advantages

PVDF is appreciated for: easier processability; good chemical resistance; good resistance to heat and low temperature; good electrical insulating properties even in hot and wet environments;

Table 4.70 ECTFE: examples of properties

	Min.	Max.
Miscellaneous properties		
Density (g/cm^3)	1.6	1.7
Absorption of water (%)	0.01	0.01
Mechanical properties		
Shore hardness, D	75	85
Rockwell hardness, R	90	100
Rockwell hardness, M	<20	50
Stress at yield (MPa)	30	32
Strain at yield (%)	5	5
Tensile strength (MPa)	41	49
Elongation at break (%)	200	300
Tensile modulus (GPa)	1.4	1.8
Flexural modulus (GPa)	1.6	1.8
Notched impact strength ASTM D256 (J/m)	NB	NB
Thermal properties		
HDT B (0.46 MPa) (°C)	90	116
HDT A (1.8 MPa) (°C)	63	77
Continuous use temperature (°C)	150	170
Melting temperature (°C)	240	245
Brittle point (°C)	−76	−76
Thermal conductivity (W/m.K)	0.23	0.23
Specific heat (cal/g/°C)	0.23	0.23
Coefficient of thermal expansion (10^{-5}/°C)	8	10
Electrical properties		
Volume resistivity (ohm.cm)	10^{16}	10^{18}
Dielectric constant	2.5	2.6
Loss factor (10^{-4})	6	150
Dielectric strength (kV/mm)	19	20
Dielectric strength of films (kV/mm)	78	79
Fire behaviour		
Oxygen index (%)	56	60
UL94 fire rating	V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Excellent
Weak acids	Good behaviour
Strong acids	Good behaviour
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Bromine, chlorinated solvents, amines, propylene oxide, THF can be more or less harmful, the more so as the temperature rises

excellent resistance to light, UV and weathering; a certain flexibility for specific copolymers; fire resistance (but beware of toxic fumes); interesting performance/cost ratio; food and high-purity grades; low water absorption, passable high-energy radiation resistance; the possibility of favouring a crystal form with pyro- and piezoelectric properties.

Drawbacks

PVDF is handicapped by the price (justified by the performances), density, corrosive and toxic fumes in the event of fire, the small number of sources and grades.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, transfer, centrifugal moulding, compression, coating, powder for rotational moulding, thin or thick parts, various flow rates, dispersions for coating and spreading . . .
- high temperature, flexible or high rigidity, reinforced, reduced flammability, food contact, high purity, low warpage, antistatic, lubricated . . .
- for E&E, wire coating, semiconductors, piezoelectric films, food industry, corrosion proofing, lining, dispersion coating . . .

Costs

The costs, as for all plastics, fluctuate highly with the crude oil price, and are only given to provide a general idea. They are generally of the order of a few tens of Euros per kilogram, roughly 25–40% more than PTFE.

Processing

PVDF can be processed by all the conventional molten-state methods, such as extrusion, injection, compression, transfer, rotational and blow moulding, thermoforming and centrifugal processes. It can be also processed by powdering and dispersion applications.

Applications

(See Chapter 2 for further information.)

The global consumption is likely to be between 25 000 and 35 000 t/year.

PVDF is only used for relatively high-performance applications related to chemical inertness, electrical insulation, weathering. The main outlet is in industrial applications.

- Industrial
  - linings, linings of components used in chemical processing . . .
  - pump housings, compressor linings and components . . .
  - extruded tubing, pipes, hoses, fittings, fluid handling, profiles . . .
  - injection and blow-moulded articles . . .
  - containers, vessels, process vessels, tank construction and linings, columns, elbows, tees . . .
  - fasteners . . .
  - instrument components . . .
  - valves, seats, seals, gaskets, diaphragms, liquid gauge seals . . .
  - cocks . . .
  - bearings, thrusts . . .
- E&E
  - wire and cable insulation and jacketing, telecommunication wires and cables, optical fibre coating, extruded coatings . . .
  - semiconductors
  - electrical components: sockets, connectors, switches, insulators, cable clamps . . .
- Films
  - cast or extruded films . . .
  - oriented films . . .
  - piezoelectric films . . .

- Construction and building
  - liquid surface coating systems for architectural fabrics . . .
- Miscellaneous
  - fibres, screens . . .
  - weathering protection for other thermoplastics and metals . . .

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at up to 150°C.

Service temperatures are distinctly lower under loading because of medium moduli, modulus decay, strain, creep, relaxation . . . For example:

- the percentage retention of stress at yield at 150°C compared to the stress at yield at ambient temperature is roughly 10–16%. Retention of moduli is slightly inferior
- HDTs under 1.8 MPa are generally more than 100°C for homopolymers but can be as low as 40°C for some copolymers.

These results relate to some grades only and cannot be generalized.

Figure 4.94 displays two examples of retention of stress at yield and elongation at break (relative to the properties at 20°C) versus temperature for a PVDF. Note the very rapid increase of elongation at break when the temperature rises above 50°C.

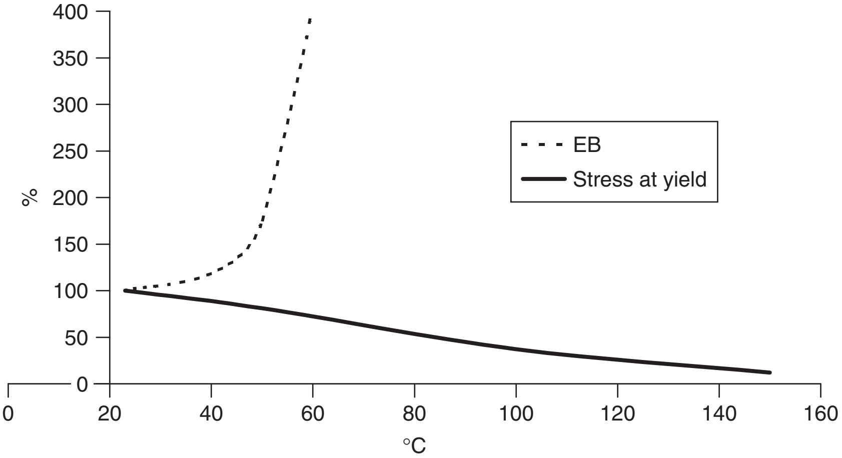


Figure 4.94. PVDF examples of stress at yield & elongation at break (EB) retentions (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered. Impact strength and elongation at break are especially heat-sensitive characteristics.

After 1000 days of exposure in air at 165°C, retentions are roughly, for example:

- 85% or more for stress at yield
- slightly more than 100% for tensile strength.

At low temperatures, the behaviour can be reasonably good down to −40°C, depending on the grade and the mechanical constraints undergone.

These results relate to some grades only and cannot be generalized.

Optical properties

General-purpose grades of PVDF are translucent. However, for certain grades in thin widths, for example a film of 0.025 mm, transmittance is about 90–95% with haze of about 3% up to 10%. Refractive indices are roughly 1.42.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties at room temperature are generally fair, with a medium modulus for the homopolymers and a low modulus for copolymers. The performances decrease as the temperature rises.

Friction

General-purpose grades have a high coefficient of friction, 0.35–0.45 for example, but special grades are marketed for tribological applications with coefficients of friction ranging from 0.15 up to 0.2.

Dimensional stability

Alterations by moisture exposure are very weak but shrinkage and coefficients of thermal expansion are high.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular orientation. For a certain grade, it is estimated at 0.34. This result relates to one grade only and cannot be generalized.

Creep

PVDF has medium or rather low moduli that involve high strains for low loading. Consequently, creep moduli are also low at room temperature.

Reinforcement with carbon fibres improves moduli and creep moduli, leading to fair creep behaviour.

Figure 4.95 shows creep moduli at 60°C and 90°C under 10 MPa.

These results relate to a few grades only and cannot be generalized.

Weathering

PVDF is inherently insensitive to moisture and UV. Stabilization is not needed.

High-energy radiation

PVDF is less sensitive than PTFE to high-energy radiation. Above 10 Mrad there is significant crosslinking and, according to the grade, the end use and the ambient conditions, resistance to radiation can reach 40 Mrad.

Chemicals

Chemical inertness is good but not as good as for PTFE, especially when the temperature rises.

PVDFs are not sensitive to most strong mineral and organic acids, oxidizing agents, aromatic and aliphatic hydrocarbons, some halogenated solvents, alcohols, bromine, metal salt solutions, or weak bases.

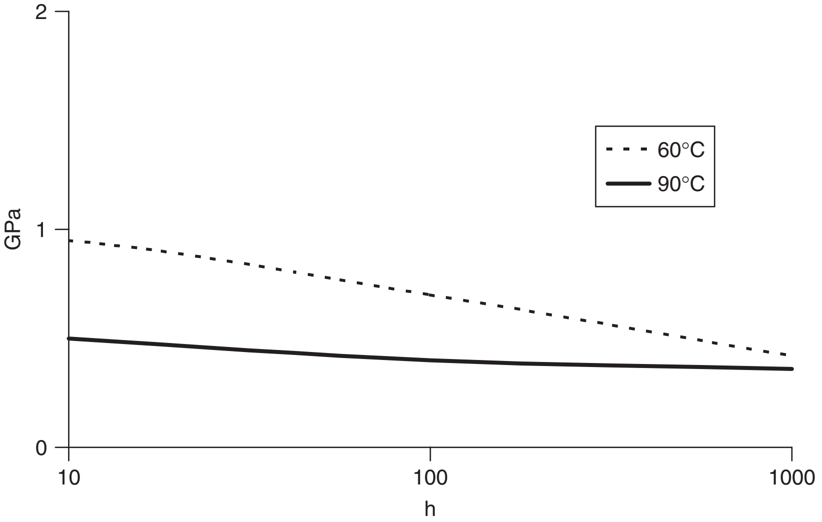


Figure 4.95. Neat PVDF creep: examples of creep modulus (GPa) versus time (h) at 60°C and 90°C under 10 MPa

They are attacked by fuming sulfuric acid, some amines, strong bases, ketones, esters, dimethylformamide, dimethylsulfoxide.

Table 4.71 displays general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all PVDFs. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.71 PVDF: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	>10	S	ASTM3 oil	100	S
Acetic aldehyde	100	S	Barium chloride	Saturated	S
Acetic anhydride	100	l	Benzaldehyde	100	S
Acetone	100	l	Benzene	100	S
Acetonitrile	100	l	Benzoic acid	Solution	S
Acetophenone	100	S	Benzylchloride	100	S
Acetyl chloride	100	S	Benzyl alcohol	100	S
Alcohols	100	S	Boric acid	Unknown	S
Aliphatic hydrocarbons	100	S	Bromine (liquid)	100	S
Aluminium chloride	Solution	S	Butanol	100	S
Aluminium sulfate	Unknown	S	Butyl acetate	100	S
Ammonium chloride	Unknown	S	Butylamine	Unknown	l
Ammonium hydroxide	30	l	Butyric acid	Unknown	S
Ammonium sulfate	50	S	Calcium chloride	Unknown	S
Amyl acetate	100	S	Calcium hypochlorite	15	S
Amyl alcohol	100	S	Carbon sulfide	100	S
Antimony chloride	10	S	Carbon tetrachloride	100	S
Aqua regia	Unknown	l	Castor oil	100	S
Aromatic hydrocarbons	100	S	Cellosolve	100	S
Arsenic acid	Unknown	S	Cellosolve acetate	100	S
ASTM1 oil	100	S	Chlorinated hydrocarbons	100	S
ASTM2 oil	100	S	Chlorinated solvents	100	S

Table 4.71 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Chlorine (dry gas)	100	S	Hydrogen sulfide gas	Unknown	S
Chlorine dioxide	Unknown	S	Iron(III) chloride	Unknown	S
Chlorine water	Unknown	S	Isobutanol	100	S
Chloroacetic acid	Unknown	S	Isooctane (Fuel A)	100	S
Chlorobenzene	100	S	Isopropanol	100	S
Chloroform	100	S	Kerosene	100	S
Chlorosulfonic acid	Unknown	l	Ketones	100	n
Chromic acid	20–30	S	Lactic acid	90	S
Citric acid	10	S	Lead acetate	10	S
Colza oil	100	S	Linseed oil	100	S
Copper sulfate	Unknown	S	Liquid paraffin	100	S
Cresol	100	S	Magnesium chloride	Unknown	S
Cyclohexane	100	S	Magnesium hydroxide	Unknown	S
Cyclohexanol	100	S	Manganese sulfate	Unknown	S
Cyclohexanone	100	l	Mercury	100	S
Decaline	100	S	Mercury chloride	Unknown	S
Diacetone alcohol	100	S	Methanol	100	S
Dibutylphthalate	100	l	Methylbromide	100	S
Dichloroethane	100	S	Methylene chloride	100	S to l
Dichloroethylene	100	S	Methylethylketone	100	l
Diethylamine	100	l	Methylisobutylketone	Unknown	S
Diethyleneglycol	100	S	Mineral oil	100	S
Diethylether	100	S	Molasses	Unknown	S
Diluted acids	Dilute	S	Monochlorobenzene	100	S
Dimethylamine	100	l	Monoethanolamine	Unknown	n
Dimethylformamide	100	n	Monoethyleneglycol	Unknown	S
Dioctylphthalate	100	S	Naphtha	Unknown	S
Dioxan	100	l	Nickel chloride	Unknown	S
Esters	100	n	Nitric acid	10–65	S
Ethanol	96	S	Nitrobenzene	100	S
Ethylacetate	100	l	Nitromethane	100	S
Ethylchloride	100	S	Oleic acid	Unknown	S
Ethylene glycol	100	S	Oleum	Unknown	n
Ethylenebromide	100	S	Olive oil	100	S
Fluorine	100	n	Oxalic acid	Unknown	S
Fluosilicic acid	Unknown	S	Ozone	Unknown	S
Formaldehyde	37	S	Perchloroethylene	100	S
Formic acid	85	S	Petroleum	100	S
Freon 11	100	S	Petroleum ether	100	S
Freon 113	100	S	Phenol	Unknown	S
Freon 115	100	S	Phosphoric acid	85	S
Freon 12	100	l	Picric acid	Solution	S
Freon 21	100	S	Potassium cyanide	Unknown	S
Freon 22	100	S	Potassium dichromate	Saturated	S
Freon 32	100	S	Potassium ferrocyanide	Saturated	S
Glycerol	100	S	Potassium hydroxide	Solution	S to l
Hexane	100	S	Potassium hydroxide	45	l
Household bleach	Unknown	l	Potassium permanganate	20	S
Hydrobromic acid	48	S	Potassium sulfate	Unknown	S
Hydrochloric acid	10–36	S	Propanol	100	S
Hydrofluoric acid	40	S	Propylene oxide	100	l
Hydrogen peroxide	3–90	S	Sea water	100	S
Hydrogen sulfide	Saturated	l	Silver nitrate	Unknown	S

(*Continued*)

Table 4.71 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Sodium borate	Unknown	S	Toluene	100	S
Sodium carbonate	10	S	Transformer oil	100	S
Sodium chloride	25	S	Trichloroacetic acid	Unknown	S
Sodium cyanide	Unknown	S	Trichloroethylene	100	S
Sodium hydroxide	10–55	l	Triethanolamine	Unknown	S
Sodium hypochlorite	20	S	Triethylamine	Unknown	l
Sodium nitrate	Solution	S	Turpentine oil	100	S
Strong bases	Unknown	S	Urea	Solution	S
Styrene	100	S	Vegetable oil	100	S
Sulfamic acid	Solution	S	Vinyl chloride	Unknown	S
Sulfur dioxide (gas)	Unknown	S	Vinyl acetate	100	S
Sulfuric acid	Fuming	l	Water	100	S
Sulfuric acid	10–96	S	Weak acids	Unknown	S
Sulfurous anhydride (gas)	Unknown	S	Weak bases	Unknown	S
Tetrachloroethane	100	S	White spirit	100	S
Tetrachloroethylene	100	S	Wine	Unknown	S
Tetrahydrofuran	100	S	Xylene	100	S
Thionyl chloride	100	S	Zinc chloride	Unknown	S
Tin chloride	Unknown	S			

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: PVDF has a medium permeability, evaluated at 17 for a full range of 0.05 up to 400 for all tested plastics.
- Gases: PVDF has a rather low permeability, evaluated at:
  - carbon dioxide: 210 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 55 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 12 up to 50 versus a full range of <1 up to 11 000 for all tested plastics.

Fire resistance

Fire resistance is naturally good but PVDF releases corrosive and toxic fumes. Oxygen indices are about 44 and the UL94 rating is V0. Grades with reduced flammability are marketed.

Electrical properties

PVDFs are good insulators even in wet environments, with high resistivities, dielectric constants and loss factors. Films with suitable crystallinity have pyro- and piezoelectric properties.

Joining, decoration

Welding is possible by all the processes: thermal, friction, ultrasound and high frequencies.

Gluing is also possible with solvents. Preliminary tests are essential.

All precautions must be taken concerning health and safety according to local laws and regulations.

Specific ISO standards concerning PVDF

ISO 4433-4:1997 Thermoplastics pipes – Resistance to liquid chemicals – Classification – Part 4: Poly(vinylidene fluoride) (PVDF) pipes

ISO 9393-2:1997 Thermoplastics valves – Pressure test methods and requirements – Part 2: Test conditions and basic requirements for PE, PP, PVC-U and PVDF valves

ISO 10931-1:1997 Plastics piping systems for industrial applications – Poly(vinylidene fluoride) (PVDF) – Part 1: General

ISO 10931-2:1997 Plastics piping systems for industrial applications – Poly(vinylidene fluoride) (PVDF) – Part 2: Pipes

ISO 10931-3:1996 Plastics piping systems for industrial applications – Poly(vinylidene fluoride) (PVDF) – Part 3: Fittings

ISO 10931-4:1997 Plastics piping systems for industrial applications – Poly(vinylidene fluoride) (PVDF) – Part 4: Valves

ISO 10931-5:1998 Plastics piping systems for industrial applications – Poly(vinylidene fluoride) (PVDF) – Part 5: Fitness for purpose of the system.

Trade name examples

Kynar, Neoflon PVDF, Solef.

Property tables

Table 4.72 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.72 PVDF: examples of properties

	Homopolymer		Copolymer		Antistatic	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.7	1.8	1.7	1.8	1.73	1.73
Shrinkage (%)	2	4	2	4	2	2
Absorption of water (%)	0.03	0.06	0.03	0.06	0.07	0.07
Mechanical properties						
Shore hardness, D	75	82	65	70	82	82
Rockwell hardness, R	80	110	55	75	105	115
Rockwell hardness, M	<20	35	<20	<20	30	40
Stress at yield (MPa)	49	56	20	46	50	50
Strain at yield (%)	8	10	8	12		
Tensile strength (MPa)	35	45	24	42	43	43
Elongation at break (%)	12	100	200	450	9	9
Tensile modulus (GPa)	2	2.6	0.5	1.5	3.8	3.8
Flexural modulus (GPa)	2.1	2.5	0.6	1.5	4.5	4.5
Notched impact strength ASTM D256 (J/m)	130	400	130	400		
Thermal properties						
HDT A (1.8 MPa) (°C)	104	113	40	50	129	129
Continuous use temperature (°C)	150	150	150	150	150	150
Melting temperature (°C)	169	172	140	160	177	177

(*Continued*)

Table 4.72 (Continued)

	Homopolymer		Copolymer		Antistatic	
	Min.	Max.	Min.	Max.	Min.	Max.
Glass transition temperature (°C)	−40	−22	−38	−36	−35	−35
Thermal conductivity (W/m.K)	0.17	0.19	0.16	0.19	0.23	0.23
Specific heat (cal/g/°C)	0.23	0.29	0.23	0.33		
Coefficient of thermal expansion (10^{-5}/°C)	8	15	8	16	3	4
Electrical properties						
Volume resistivity (ohm.cm)	10^{12}	2×10^{14}	10^{12}	2×10^{14}	10^{3}	10^{4}
Dielectric constant	5	10	6	9		
Loss factor (10^{-4})	200	2900	100	>100		
Dielectric strength (kV/mm)	10	60				
Dielectric strength of films (kV/mm)	150	160	150	160		
Arc resistance (s)	50	70	50	70		
Fire behaviour						
Oxygen index (%)	44	44	44	44		
UL94 fire rating	V0	V0	V0	V0		
	Self-lubricating		Carbon fibre reinforced		Mica-filled	
Miscellaneous properties						
Density (g/cm^3)	1.7	1.8	1.7	1.8	1.8	1.9
Shrinkage (%)	2	3	1	1	1	1
Absorption of water (%)	0.04	0.04	0.05	0.05	0.04	0.04
Mechanical properties						
Shore hardness, D	78	78	82	82	81	81
Rockwell hardness, R	95	100	105	115	105	110
Rockwell hardness, M	20	25	30	40	30	40
Stress at yield (MPa)	53	53	93	93	49	49
Tensile strength (MPa)	46	46	93	93	47	47
Elongation at break (%)	70	70	1	1	6	6
Tensile modulus (GPa)	2.3	2.3	6	6	4.2	4.2
Flexural modulus (GPa)	2.2	2.2	6	6	4.7	4.7
Thermal properties						
HDT A (1.8 MPa) (°C)	117	117	134	134		
Continuous use temperature (°C)	150	150	150	150	150	150
Melting temperature (°C)	174	174	176	176	177	177
Glass transition temperature (°C)	−40	−40	−35	−35		
Thermal conductivity (W/m.K)	0.19	0.19	0.22	0.22		
Coefficient of thermal expansion (10^{-5}/°C)	10	11	3	4		
Electrical properties						
Volume resistivity (ohm.cm)	10^{14}	10^{14}	10^{13}	10^{13}	10^{14}	2×10^{14}
Fire behaviour						
UL94 fire rating	V0	V0	V0	V0	V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Excellent
Weak acids	Good behaviour
Strong acids	Good except with fuming sulfuric acid and oleum
Weak bases	Good behaviour
Strong bases	Good to limited behaviour except when the temperature rises
Solvents	Good behaviour with most strong mineral and organic acids, aromatic and aliphatic hydrocarbons, halogenated solvents, alcohols, bromine, metal salt solutions, and weak bases Attacked by fuming sulfuric acid, some amines, hot strong bases, ketones, esters, dimethylformamide, dimethylsulfoxide
Food contact	Possible for special grades

4.19.6 Polyvinyl fluoride (PVF)

PVF is a monofluoro derivative leading to the following formula $-(-CH_2-CHF-)_n-$ and a fluorine content of 41%. It is semicrystalline.

The main purpose of PVF is to manufacture films for surface proofing of various materials.

Advantages

PVF films are appreciated for: weatherability, good chemical and staining resistance; good non-stick properties, easy-to-clean properties; low permeability; good behaviour at low temperature; good electrical insulating properties even in hot and wet environments; fire resistance (but beware of toxic fumes).

Drawbacks

PVF is handicapped by its sensitivity to heat, preventing injection moulding and limiting the upper service temperature; high price; density; corrosive and toxic fumes in the event of fire; the small number of sources and grades.

Special grades

They are limited to transparent films and low gloss or satin white films.

Costs

The costs are generally high and fluctuate greatly with the crude oil price, as for all plastics.

Applications

(See Chapter 2 for further information.)

PVFs are only used for relatively high-performance applications related to weathering, chemical inertness, fire resistance:

- weather-resistant film for glazing panels, glazing for solar panels
- surface covering for PVC film
- film covering in aircraft interiors to reduce flammability
- UV-screening films
- gas sampling bags
- printed circuit lamination, release film in the manufacture of printed circuit boards
- sign industry: surface protection
- label materials for harsh environments
- electrical and wire marking applications.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at 100°C up to 110°C.

Service temperatures are noticeably lower under loading because of medium moduli, modulus decay, strain, creep, relaxation . . . For example:

- the percentage of tensile strength retained at 100°C compared to the tensile strength at ambient temperature is roughly 30–35%
- HDT under 0.46 MPa is about 120°C for a given grade.

These results relate to some grades only and cannot be generalized.

Figure 4.96 displays two examples of tensile stress and elongation at break retention (relative to the properties at 20°C) versus temperature for a PVF grade. For elongation at break, very different data can be found for other grades.

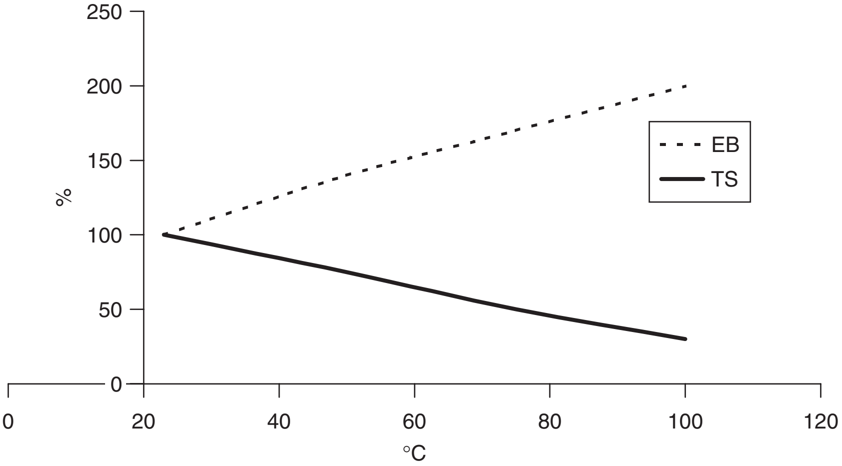


Figure 4.96. PVF examples of tensile stress (TS) & elongation at break (EB) retentions (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered. Impact strength and elongation at break are especially heat-sensitive characteristics.

After 40 days of exposure in air at 150°C, retentions are roughly, for example:

- 50% for tensile strength
- 25% or less for elongation at break
- 10% or less for impact strength.

At low temperatures, the behaviour can be reasonably good down to −70°C, depending on the grades and the mechanical constraints experienced.

These results relate to some grades only and cannot be generalized.

Optical properties

Clear films in thin widths, for example 0.025 mm, are transparent in the visible light, near-UV and near-infrared spectrum with a transmittance of about 90% and haze of a few percent.

Refractive indices are roughly 1.46.

Some other films can be UV screening.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties at room temperature are generally fair with a medium modulus and a fair wear resistance. The performances decrease as the temperature rises.

Friction

Coefficients of friction range from 0.18 up to 0.21 and the wear resistance is good.

Dimensional stability

Alterations by moisture exposure are weak but shrinkage and coefficients of thermal expansion are high.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular orientation.

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For example, the original flex life ranges from 10000 up to 100000 cycles but decreases after ageing, to 1000 cycles after 500 h at 150°C.

These results relate to a few grades only and cannot be generalized.

Weathering

PVFs are inherently resistant to weathering.

After 6 years of outdoor exposure in a sunny climate, retentions of properties are about:

- 80% for tensile strength
- 55% for elongation at break.

These results relate to a few grades only and cannot be generalized.

Chemicals

Chemical inertness is good but not as good as for PTFE, especially when the temperature rises.

PVFs are not sensitive to strong acids and bases, aromatic and aliphatic hydrocarbons, chlorinated solvents, greases and oils.

PVFs are attacked by ketones and esters.

Table 4.73 displays some assessments of satisfactory behaviour for given grades after prolonged immersions in a range of chemicals at room and elevated temperatures. The results are not necessarily representative of all PVFs. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: PVF has a medium permeability, evaluated at 31 for a full range of 0.05 up to 400 for all tested plastics.

Table 4.73 PVF: examples of chemical behaviour after immersion

Chemical	Concentration (%)	Temperature (°C)	Days	Estimated behaviour
Acetic acid	Glacial	20	365	S
Acetic acid	Glacial	75	31	S
Acetone	100	20	365	S
Ammonium hydroxide	12	20	365	S
Ammonium hydroxide	39	20	365	S
Ammonium hydroxide	10	75	31	S
Benzene	100	20	365	S
Benzyl alcohol	100	75	31	S
Dioxane	100	75	31	S
Ethyl acetate	100	75	31	S
Ethyl alcohol	Unknown	75	31	S
Heptane	100	20	365	S
Hydrochloric acid	10	75	31	S
Hydrochloric acid	30	75	31	S
Hydrochloric acid	10	20	365	S
Kerosene	100	20	365	S
Methylethylketone	100	75	31	S
Nitric acid	20	20	365	S
Nitric acid	10	75	31	S
Nitric acid	40	75	31	S
Phenol	Unknown	20	365	S
Phenol	5	75	31	S
Phosphoric acid	20	20	365	S
Sodium chloride	10	20	365	S
Sodium hydroxide	10	20	365	S
Sodium hydroxide	10	75	31	S
Sodium hydroxide	54	75	31	S
Sodium sulfide	9	75	31	S
Sulfuric acid	20	20	365	S
Sulfuric acid	30	75	31	S
Toluene	100	75	31	S
Trichloroethylene	100	75	31	S
Tricresylphosphate	Unknown	75	31	S

- Gases: PVF has a low permeability, evaluated at:
  - carbon dioxide: 110 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 2.4 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 3 versus a full range of <1 up to 11 000 for all tested plastics.

Fire resistance

Fire resistance is naturally good but PVF releases corrosive and toxic fumes in the event of fire. Oxygen indices are about 35 and the UL94 rating is V0.

Electrical properties

PVFs are good insulators even in wet environments, with good resistivities.

Joining, decoration

Films are supplied with one or both sides pre-treated to enable the use of adhesives such as acrylics, polyesters, epoxies, rubbers and pressure-sensitive mastics.

Preliminary tests are essential.

All precautions must be taken concerning health and safety according to local laws and regulations.

Trade name examples

Norton PVF, Tedlar.

Property tables

Table 4.74 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.74 PVF: examples of properties

	Transparent		White	
	Min.	Max.	Min.	Max.
Miscellaneous properties				
Density (g/cm^3)	1.37	1.4	1.46	1.71
Shrinkage (%)	2.5	6	2.5	5
Absorption of water (%)	0.05	0.05	0.05	0.05
Mechanical properties				
Shore hardness, D	80	80	80	80
Rockwell hardness, R	105	110	105	110
Rockwell hardness, M	30	30	30	30
Stress at yield (MPa)	35	40	35	40
Strain at yield (%)	30	30	30	30
Tensile strength (MPa)	40	110	40	110
Elongation at break (%)	90	100	90	110
Tensile modulus (GPa)	2	2.1	2.1	2.7
Notched impact strength ASTM D256 (J/m)	180	180	180	180
Thermal properties				
HDT B (0.46 MPa) (°C)	120	120	120	120
HDT A (1.8 MPa) (°C)	80	80	80	80
Continuous use temperature (°C)	105	110	105	110
Brittle point (°C)	−70	−70	−70	−70
Specific heat (cal/g/°C)	0.2	0.4	0.2	0.3
Coefficient of thermal expansion (10^{-5}/°C)	8	9	7	10
Electrical properties				
Volume resistivity (ohm.cm)	10^{13}	10^{14}	10^{13}	10^{14}
Dielectric constant	7	11		
Loss factor (10^{-4})	140	400		
Dielectric strength of films (kV/mm)	120	140		
Arc resistance (s)	50	50		
Fire behaviour				
Oxygen index (%)	35	35	35	35
UL94 fire rating	V0	V0	V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Excellent resistance
Strong acids	Good behaviour
Strong bases	Good behaviour
Solvents	PVFs are not sensitive to strong acids and bases, aromatic and aliphatic hydrocarbons, chlorinated solvents, greases and oils. PVFs are attacked by ketones and esters
Food contact	Possible for special grades

4.20 Cellulosics (CA, CAB, CP)

Cellulosics are esters of natural cellulose derived from wood. The most common are:

- cellulose acetate: CA
- cellulose acetobutyrate: CAB
- cellulose propionate: CP.

The properties can be modified via the broad possibilities offered by plasticization. Relatively hard, rigid and strong original polymers can be plasticized to produce tough, more-flexible but weaker materials.

Cellulose acetate is chosen for its transparency but is sensitive to water and weathering.

CAB is less sensitive to weathering, water and chemicals but has a stronger smell.

CP has better mechanical properties, is odourless and sterilizable.

Advantages

Cellulosics are appreciated for their: easy processability; aesthetics; transparency; high gloss; pleasant feel; aptitude for colouring and decoration; low electrostatic build up; balance of fair mechanical properties and chemical resistance to oils, greases and aliphatic hydrocarbons; possibilities of plasticization allowing very low moduli to be obtained; fair electrical insulating properties; fair performance/cost ratios; food contact possibilities.

Drawbacks

Cellulosics are handicapped by their sensitivity to heat, several common chemicals, and water; the price (justified by the performances); density; the small number of sources and grades.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, compression, film, various flow rates . . .
- transparent natural, clear, amber or smoke; translucent black; flexible, rigid, tough, better dimensional stability, reduced flammability, food contact . . .
- for aesthetic products, packaging, food industry . . .

Costs

The costs, as for all plastics, fluctuate with the cost of energy, and are only given to provide a general idea. They are typically of the order of a few Euros per kilogram.

Processing

Cellulosics are easy to process by conventional molten-state methods such as extrusion, injection, compression, transfer, rotomoulding, thermoforming; They can also be processed in the solvent phase, and by welding and machining.

Applications

(See Chapter 2 for further information.)

Global consumption is not listed in official statistics.

Cellulosics are only used for aesthetic applications related to colour, gloss and feel.

- Automotive
  - furniture trims . . .
  - sun visors . . .
  - face shields . . .
- Packaging
  - films, transparent wrappers . . .
  - containers, bottles, boxes and tubing . . .
  - blister packaging . . .
- Healthcare, cosmetics, perfumery and personal care supplies
  - packaging . . .
  - containers . . .
  - furniture trims . . .
  - combs . . .
- Medical
  - ophthalmic, optical safety frames . . .
  - spectacles, sunglasses . . .
- Lighting, signs
  - diffusers, lighting devices and accessories . . .
  - displays and profiles . . .
- Films, extruded sheets and plates, thin-gauge extruded tubes . . .
- Household, appliances items
  - toothbrushes . . .
  - door handles, curtain rings . . .
  - hairdressing items . . .
  - stoppers on scent vials . . .
  - knitting needle cases, dice . . .
  - knife handles . . .
- Industry
  - hand tools, screwdriver handles, buttons, handles, hammer heads . . .
  - metallized parts, vacuum metallized parts, reflectors . . .
- Pen/stationary supplies
  - pen barrels . . .
  - writing instruments . . .
  - squares . . .
- Miscellaneous
  - recreational parts . . .
  - costume jewellery . . .
  - toys and sporting goods . . .

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated to range from 45°C up to 105°C.

Service temperatures are significantly lower under loading because of low moduli for certain grades, modulus decay, strain, creep, relaxation . . . For example:

- HDTs under 0.46 MPa range from 50°C up to 120°C for given grades
- HDTs under 1.8 MPa can be as low as 44°C.

These results relate to some grades only and cannot be generalized.

For long-term heat ageing, property retention depends on the property and grades considered. Impact strength and elongation at break are especially heat-sensitive characteristics.

At low temperatures, the behaviour depends on the chemical nature, the plasticization and the mechanical constraints undergone.

At −40°C, notched Izod impact strengths are, for example:

- 59 J/m for a given CA grade
- 96 J/m for a given CAB grade
- 107 J/m for a given CP grade.

These results relate to some grades only and cannot be generalized.

Optical properties

General-purpose grades of cellulosics are transparent or translucent. Certain grades in thick films or sheets, 1.5 mm thick for example, have transmittances superior to 90% with a haze inferior to 8%. Refractive indices are roughly 1.47–1.48.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties at room temperature depend on the chemical nature and the plasticization. They are generally fair with a low to medium modulus and a low to excellent impact strength, but performances decrease when the temperature rises.

Dimensional stability

Cellulosics are moisture sensitive, have fair shrinkage and high coefficients of thermal expansion.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular orientation.

Weathering

Cellulosics are inherently moisture- and UV-sensitive, requiring efficient stabilization. Cellulose acetate is particularly sensitive to water and weathering.

Chemicals

Cellulosics are sensitive to many chemicals especially as the degree of plasticization and the temperature rise.

They are generally resistant to oils, greases and aliphatic hydrocarbons.

Aromatic or chlorinated hydrocarbons, detergents, dilute acids and bases have a limited effect.

Cellulosics are attacked or dissolved by esters, ketones, phenols, concentrated acids and bases, and alcohols.

Table 4.75 displays some general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the cellulosics. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.75 Cellulosics: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	⩾10	n
Acetic aldehyde	100	n
Acetic anhydride	100	n
Acetone	100	n
Acetonitrile	100	n
Acetophenone	100	n
Acetyl chloride	100	n
Alcohols	100	n
Aliphatic hydrocarbons	100	S
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonium hydroxide	30	n
Ammonium sulfate	50	S
Amyl acetate	100	n
Amyl alcohol	100	n
Aniline	100	n
Aqua regia	Unknown	n
Aromatic hydrocarbons	100	l
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Battery acid	Unknown	n
Benzaldehyde	100	n
Benzene	100	S
Benzyl chloride	100	n
Benzyl alcohol	100	n
Boric acid	Unknown	l
Bromine (liquid)	100	n
Butanol	100	n
Butyl acetate	100	n
Butylamine	Unknown	n
Butylchloride	100	n
Butyric acid	Unknown	n
Calcium chloride	Unknown	S
Carbon sulfide	100	n
Carbon tetrachloride	100	n
Castor oil	100	l
Cellosolve	100	n
Cellosolve acetate	100	n
Chlorinated hydrocarbons	100	l
Chlorinated solvents	100	l
Chlorine (dry gas)	100	n
Chlorine dioxide	Unknown	n
Chloroacetic acid	Unknown	n
Chlorobenzene	100	n
Chloroform	100	n
Chlorosulfonic acid	Unknown	n
Chromic acid	Unknown	n
Citric acid	10	l
Colza oil	100	S
Concentrated acids	Concentrated	n
Copper sulfate	Unknown	S
Cresol	100	n
Cyclohexane	100	S
Cyclohexanol	100	l
Cyclohexanone	100	n
Detergent	Unknown	l
Dichloroethane	100	n
Dichloroethylene	100	n
Diethylether	100	S
Dilute acids	Dilute	l
Dimethylamine	100	n
Dioctylphthalate	100	S
Esters	100	n
Ethanol	Unknown	l to n
Ethanol	96	n
Ethylacetate	100	n
Ethylchloride	100	n
Ethylene glycol	100	l
Fluorine	100	n
Fluosilicic acid	Unknown	n
Formaldehyde	37	n
Formic acid	85	n
Freon 11	100	n
Freon 113	100	S
Freon 12	100	n
Freon 13b1	100	S
Freon 21	100	n
Freon 32	100	l
Furfural	100	n
Glycerol	100	l
Grease	Unknown	S
Hexane	100	S
Hydrobromic acid	48	n
Hydrochloric acid	10	l
Hydrochloric acid	36	n
Hydrofluoric acid	40	n

(*Continued*)

Table 4.75 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Hydrogen peroxide	30–90	n	Propanol	100	n
Hydrogen sulfide gas	Unknown	S	Pyridine	Unknown	n
Iron(III) chloride	Unknown	S	Sea water	100	S
Isooctane (Fuel A)	100	S	Silicone oil	100	S
Isopropanol	100	n	Silver nitrate	Unknown	S
Ketones	100	n	Sodium carbonate	10	S
Lactic acid	90	n	Sodium chloride	25	S
Linseed oil	100	S	Sodium hydroxide	⩾10	n
Liquid paraffin	100	S	Sodium hypochlorite	20	n
Magnesium chloride	Unknown	n	Sodium nitrate	Solution	S
Mercury chloride	Unknown	n	Strong acids	Unknown	n
Methanol	100	n	Sulfur dioxide (gas)	Unknown	n
Methylene chloride	100	n	Sulfuric acid	⩾10	n
Methylethylketone	100	n	Sulfurous anhydride (gas)	Unknown	n
Mineral oil	100	S	Tetrachloroethane	100	n
Nitric acid	⩾10	n	Thionyl chloride	100	n
Nitrobenzene	100	n	Toluene	100	n
Oils & greases	100	S	Transformer oil	100	n
Oleic acid	Unknown	S	Trichloroacetic acid	Unknown	n
Oxalic acid	Unknown	n	Trichloroethylene	100	n
Pentylacetate	100	n	Tricresylphosphate	Unknown	S
Perchloroethylene	100	S	Triethanolamine	Unknown	S
Petrol	100	S	Turpentine oil	100	S
Petroleum	100	S	Water	100	S
Phenol	Unknown	n	Weak acids	Unknown	l
Phosphoric acid	85	n	White spirit	100	S
Potassium cyanide	Unknown	n	Wine	Unknown	S
Potassium hydroxide	45	n	Xylene	100	S
Potassium permanganate	20	n	Zinc chloride	Unknown	n
Potassium sulfate	Unknown	S			

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

CA and CAB have high permeabilities to water vapour, respectively evaluated at 95 up to 400, and 300 up to 400, for a full range of 0.05 up to 400 for all tested plastics.

Cellulosics have high permeabilities to gases, evaluated at:

- carbon dioxide:
  - CA: 8000–9000 versus a full range of 30 up to 59 000 for all tested plastics
  - CAB: 59 000 versus a full range of 30 up to 59 000 for all tested plastics
- nitrogen:
  - CA: 300–400 versus a full range of 1 up to 3500 for all tested plastics
  - CAB: 2400 versus a full range of 1 up to 3500 for all tested plastics

- oxygen:
  - CA: 1100–1500 versus a full range of <1 up to 11 000 for all tested plastics
  - CAB: 9400 versus a full range of <1 up to 11 000 for all tested plastics.

Fire resistance

Fire resistance is naturally weak with oxygen indices of 17 and a poor HB UL94 rating. Grades with reduced flammability are marketed.

Electrical properties

Cellulosics are fair insulators in a dry environment. For a polymer, electrostatic build-up is low, leading to moderate dusting.

Joining, decoration

Welding is easy by all the processes.

Cellulosics are easily coloured, suitable for dyeing by immersion in dye baths, and can be solvent polished, cut, cemented, drilled and decorated. Varnishing and serigraphy are easily used.

Gluing is also possible by solvents with or without addition of resin. They can be easily joined to wood, copper, elastomers . . .

Preliminary tests are essential.

All precautions must be taken concerning health and safety according to the local laws and regulations.

Specific ISO standards concerning cellulosics

ISO 585:1990 Plastics – Unplasticized cellulose acetate – Determination of moisture content

ISO 1061:1990 Plastics – Unplasticized cellulose acetate – Determination of free acidity

ISO 1598:1990 Plastics – Cellulose acetate – Determination of insoluble particles

ISO 1599:1990 Plastics – Cellulose acetate – Determination of viscosity loss on moulding

ISO 1600:1990 Plastics – Cellulose acetate – Determination of light absorption on moulded specimens produced using different periods of heating

ISO 1875:1982 Plastics – Plasticized cellulose acetate – Determination of matter extractable by diethyl ether

ISO 3451-3:1984 Plastics – Determination of ash – Part 3: Unplasticized cellulose acetate

ISO 14446:1999 Binders for paints and varnishes – Determination of the viscosity of industrial cellulose nitrate solutions and classification of such solutions

ISO/ASTM 51650:2002 Practice for use of cellulose acetate dosimetry system.

Trade name examples

Cellidor, Setilithe, Tenite.

Property tables

Table 4.76 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.76 Cellulosics: examples of properties

	CA		CAB		CP	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.22	1.34	1.15	1.22	1.17	1.24
Shrinkage (%)	0.3	1.0	0.2	0.9	0.1	0.9
Absorption of water (%)	1.9	7.0	0.9	2.2	1.2	3.0
Mechanical properties						
Shore hardness, D	>50	<95	60	90	>40	90
Rockwell hardness, R	<125	<125	<125	<125	<125	<125
Rockwell hardness, M	<80	<90	<70	<70	<75	75
Stress at yield (MPa)	23	23	34	34	32	32
Tensile strength (MPa)	13	67	18	48	14	50
Elongation at break (%)	6	70	40	90	30	100
Tensile modulus (GPa)	0.6	2.8	0.4	1.7	0.45	1.4
Flexural modulus (GPa)	0.6	2.8	0.6	2.1	0.45	1.4
Notched impact strength ASTM D256 (J/m)	50	400	50	500	25	NB
Thermal properties						
HDT B (0.46 MPa) (°C)	50	100	54	108	60	120
HDT A (1.8 MPa) (°C)	44	90	45	94	44	110
Continuous use temperature (°C)	45	95	60	105	60	105
Glass transition temperature (°C)	100	130	80	120	80	120
Brittle point (°C)	−30	−30				
Specific heat (cal/g/°C)	0.30	0.40	0.30	0.40	0.40	0.40
Coefficient of thermal expansion (10^{-5}/°C)	8	18	10	17	10	17
Electrical properties						
Volume resistivity (ohm.cm)	10^{13}	2×10^{13}	10^{11}	2×10^{15}	2×10^{15}	3×10^{15}
Dielectric constant	3	8	3	7	3	4
Loss factor (10^{-4})	100	1000	100	400	60	300
Dielectric strength (kV/mm)	8	15	10	17	12	18
Arc resistance (s)	50	300			175	190
Fire behaviour						
Oxygen index (%)	17	17	17	17	17	17
UL94 fire rating	HB	HB	HB	HB	HB	HB

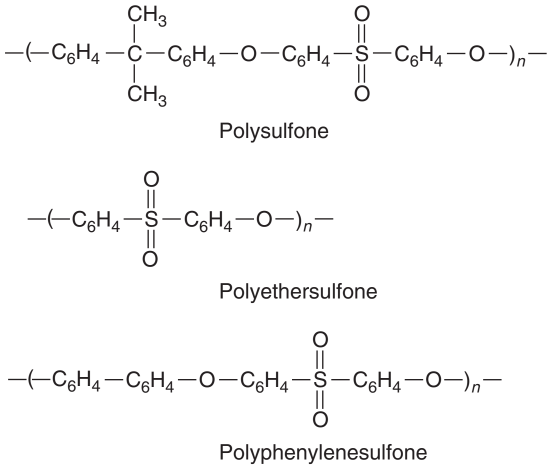
General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilization is needed
Weak acids	Limited behaviour
Strong acids	Unsatisfactory
Weak bases	Limited behaviour
Strong bases	Unsatisfactory
Solvents	Cellulosics generally resist oils, greases and aliphatic hydrocarbons Aromatic or chlorinated hydrocarbons, detergents have a limited effect They are attacked or dissolved by esters, ketones, phenols, concentrated acids and bases, alcohols
Food contact	Possible for special grades

4.21 Polysulfone, polyarylsulfone, polyethersulfone, polyphenylenesulfone, (PSU, PAS, PESU, PPSU)

The polyarylsulfone family comprises three chemical entities:

- polysulfone: PSU
- polyethersulfone: PES also referred to as PESU
- polyphenylenesulfone: PPSU.



$$—(—C_6H_4—\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}—C_6H_4—O—C_6H_4—\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}—C_6H_4—O—)_n—$$

Polysulfone

$$—(—C_6H_4—\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}—C_6H_4—O—)_n—$$

Polyethersulfone

$$—(—C_6H_4—C_6H_4—O—C_6H_4—\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}—C_6H_4—O—)_n—$$

Polyphenylenesulfone

Figure 4.97. Polysulfone formulae

In addition, some polysulfones are modified to produce materials with specific properties. Figure 4.97 shows examples of formulae.

The main difference between these entities is the thermal behaviour, which increases in the following order:

- polysulfones and modified polysulfones
- polyethersulfones
- polyphenylenesulfones.

All polysulfones are amorphous.

4.21.1 General properties

Advantages

Polysulfones are appreciated for their: good mechanical and electrical properties, rigidity, good creep behaviour, fatigue endurance, fair shrinkage and moisture uptake, broad range of service temperatures (−100 up to +150/200°C), optical and microwave transparency, fire resistance, suitability for food contact and sterilization.

Drawbacks

Polysulfones are handicapped by: light and UV sensitivity requiring an efficient protection for outdoor exposure; sensitivity to environmental stress cracking and attacks by chemicals such as aromatic hydrocarbons, chlorinated solvents and ketones; the cost (justified by the performances); sometimes an insufficient fire resistance, but special grades are marketed.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection, blow moulding, thermoforming, structural foam, blown film, foam, for thin or thick parts; low, medium or high fluidity, solvent processing . . .

- high transparency, impact modified, heat and/or hydrolysis stabilized; better resistance to stress cracking, high rigidity, food contact, low warpage, reinforced, antistatic; FDA, NSF, 3A-Dairy and USP Class VI compliant . . .
- for electrical applications, printed circuits, bearings, food industry, films . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide a general idea. They are typically of the order of several Euros to a few tens of Euros per kilogram.

Processing

All the molten-state methods are usable: extrusion, injection, blowing, compression, thermoforming, co-injection, machining, welding. Specific grades can be used for foam, structural foam and solvent processing.

Consumption

The consumption of polysulfones varies according to the country and the source. Global consumption can be estimated between 30 000 and 40 000 tonnes/year, and can be approximately divided into four main sectors:

- 30% for E&E
- 30% for consumer goods
- 20% for automotive & transport
- 20% for industry.

This is an example and other data can be found elsewhere depending on the source and country.

Applications

(See Chapter 2 for further information.)

Polysulfones are engineering plastics used only for specialized and technical applications.

The main applications for polysulfones are:

- Automobile & transportation
  - under-the-hood parts, fasteners . . .
  - connectors, fuses . . .
  - plane interior parts . . .
  - visor of astronaut helmets . . .
- Electricity, electronics, office automation
  - frames of integrated circuits . . .
  - connectors, switches, insulators, sockets . . .
  - reels . . .
  - plates on terminals . . .
  - TV components . . .
  - films for capacitors . . .
  - parts of alkaline batteries . . .
  - cartridges of printers . . .

- Medical, laboratory equipment
  - sterilizable containers, steam-cleaning equipment components . . .
  - haemodialysis equipment parts, membranes for artificial kidneys, blood purification . . .
  - endoscopic probe positioning ferrules . . .
  - surgical instrument handles . . .
  - orthopaedic implant trails . . .
- Household appliances, leisure
  - parts for coffee machines, drinks dispensers, tubes, water tanks . . .
  - components for humidifiers, cookers . . .
  - reusable crockery . . .
  - portholes . . .
  - components for cameras, projectors . . .
- Industrial
  - fluid handling, coupling and fitting applications . . .
  - manifolds, distributor valves . . .
  - lighting fixtures, portholes . . .
  - chemical process equipment, semiconductor process equipment components . . .
  - plumbing fixtures, faucet components . . .
  - ESD trays . . .
- Food service components
  - potable water fittings
  - porous filaments or membranes for micro- and ultra-filtration and reverse osmosis . . .
  - membranes for wastewater recovery, food and beverage processing, municipal drinking water . . .
- Films
- Foams for cores of sandwich composites.

4.21.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 150°C for polysulfones up to 180°C for polyethersulfone and higher for polyphenylenesulfone and special heat-resistant grades.

The UL temperature indices of specific polysulfone grades can range from 140°C up to 160°C for the electrical and mechanical properties including impact.

Service temperatures are significantly lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- for a given grade of polyethersulfone, compared to the value at ambient temperature, the retention percentage of tensile strength is roughly:
  - 82% at 100°C
  - 65% at 150°C
- for a special heat-resistant grade, compared to the value at ambient temperature, the retention percentage of modulus is roughly:
  - 73% at 180°C
  - 37% at 230°C
- HDTs under 1.8 MPa range from:
  - 174°C up to 205°C for neat PSU

- ○ 195°C up to 205°C for a neat PES
- ○ 200°C up to 208°C for a neat PPSU.

Figure 4.98 displays an example of tensile strength retention versus temperature for a neat polyethersulfone. Note the slow decay considering the high temperatures and the significant value of 35% for the retention at 200°C, that is, 30 MPa.

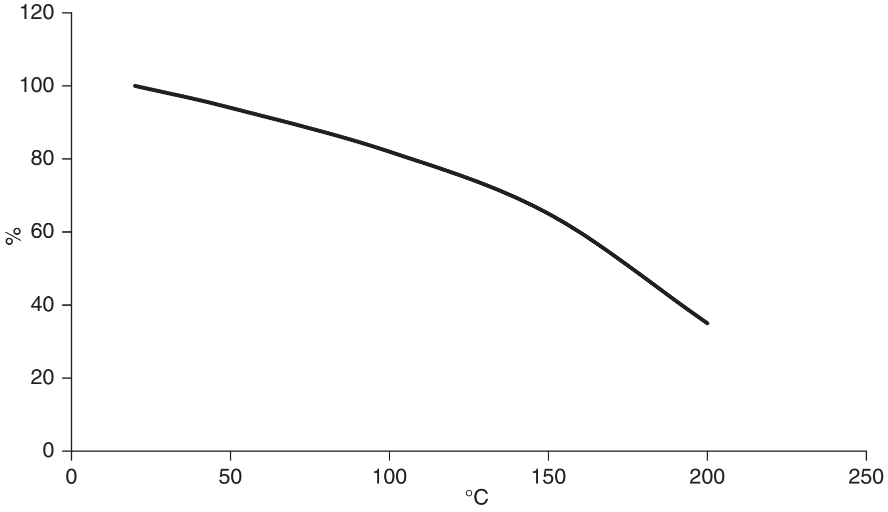


Figure 4.98. PES examples of tensile strength retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially heat-sensitive characteristics.

Half-lives of specific PES grades based on tensile strength are:

- 11–18 years at 180°C
- up to 5 years at 200°C
- 1–2 years at 220°C.

At low temperatures, the behaviour can be reasonably good down to −100°C, depending on the grades and the mechanical constraints experienced.

Generally, notched Izod impact strengths slowly decrease between room temperature and −40°C retaining, for example, 90% of the original value.

Glass transition temperatures are high, roughly 185°C up to 200°C, and even 260°C for a special heat-resistant grade.

These results relate to some grades only and cannot be generalized.

4.21.3 Optical properties

Amorphous polysulfones are transparent with:

- light transmittance in a range from 70% (PSU and PPSU) up to 80% (PES)
- haze inferior to 3%
- refractive indices of about 1.633 for PSU and PESU and 1.672 for PPSU.

These results relate to some grades only and cannot be generalized.

4.21.4 Mechanical properties

The mechanical properties are generally good with medium to low elongations at break and more limited strains at yield. Moduli and hardnesses are in a medium range but notched impact strengths are limited, which must be considered when designing. The abrasion resistance of polysulfones depends on the roughness, type and morphology of the opposing sliding surface. The wear resistance and coefficient of friction of special grades are suitable for tribological applications.

Friction

Some self-lubricating grades of polysulfone containing specific additives, and possibly reinforced with glass or carbon fibres, are marketed. The coefficients of friction are good, for example 0.1 or less, and remain unchanged at high temperature.

These results relate to a few grades only and cannot be generalized.

Dimensional stability

Alterations by moisture exposure are fair; shrinkage and coefficient of thermal expansion are those of amorphous thermoplastics, namely rather low; creep resistance is good, the more so the higher the glass fibre content.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular or reinforcement orientation. For given samples of neat grades, it is evaluated at:

- 0.40 for a given PES
- 0.37 for a given PSU.

These examples cannot be generalized.

Creep

Creep behaviour is good even when the temperature rises. Neat polysulfones have medium moduli that involve medium strains for moderate loading. Consequently, creep moduli are also in a medium range at room temperature but they decrease more slowly than the majority of other thermoplastics when the temperature rises. Reinforcement with fibres leads to high moduli and consequently high creep moduli.

Figure 4.99(a) shows the creep modulus decrease when the load increases from 10 MPa up to 50 MPa at room temperature.

Figure 4.99(b) shows:

- the slow decrease of the creep modulus at room temperature
- the small difference between creep at 22°C and 60°C
- the wide difference in creep between 60°C and 100°C but the fair level of creep modulus at 100°C and even at 150°C.

These results relate to a few grades only and cannot be generalized.

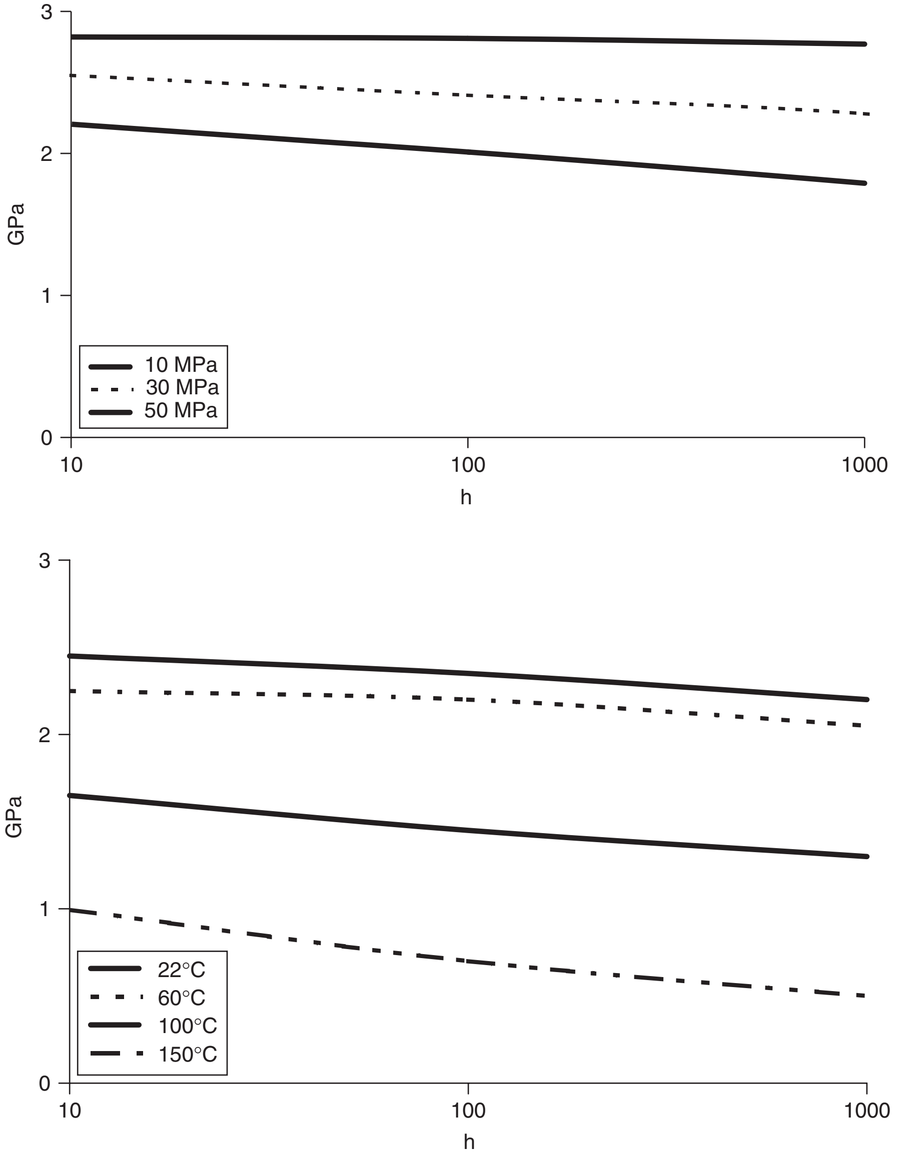


Figure 4.99. (a) PES examples of creep modulus (GPa) versus time (h) under 10 to 50 MPa at room temperature; (b) PSU examples of creep modulus (GPa) versus time (h) under 21 MPa at various temperatures

4.21.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For a given grade of neat PES, Figure 4.100 displays an example of an SN or Wöhler's curve with a stress of $\pm\sigma$.

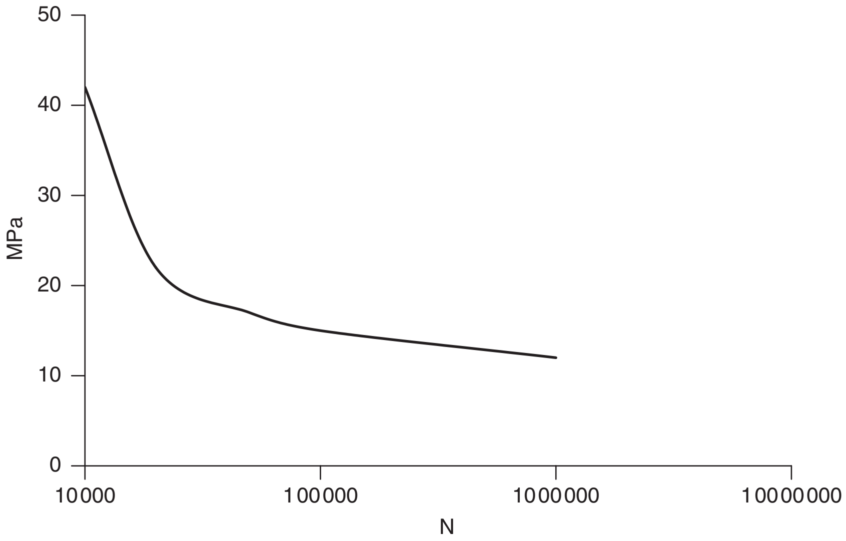


Figure 4.100. SN curve of neat PES, examples of maximum stress (MPa) versus number of cycles at rupture (N)

These results are examples only and they cannot be generalized.

Weathering

Polysulfones are inherently UV sensitive and must be protected by addition of anti-UV and other protective agents. Black compounds are generally more resistant.

High-energy radiation

After exposure to gamma radiation at doses of:

- 50 Mrad, property retentions are about 100% for tensile strength and 86% for elongation at break
- 250 Mrad, property retentions are about 92% for tensile strength and 13% for elongation at break.

Chemicals

Polysulfones are sensitive to stress cracking.

The resistance to moisture and hot water is good, with no hydrolysis, and the polysulfones can withstand multiple steam sterilizations. However, a certain absorption of water does occur involving a plasticization with improvement of the impact resistance.

Suitably formulated compounds are usable in contact with food.

Polysulfones resist acids at medium concentrations, alcohols, aliphatic hydrocarbons, greases, oils, gasoline, bases, chlorine water.

They are attacked by aromatic hydrocarbons, chlorinated solvents, ketones, esters, phenols, aldehydes, amines.

Table 4.77 displays some general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the polysulfones. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.77 Polysulfones: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10 to >96	S
Acetic aldehyde	100	n
Acetic anhydride	100	n
Acetone	100	n
Acetonitrile	100	n
Acetophenone	100	n
Acetyl chloride	100	n
Alcohols	100	S
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonium chloride	Unknown	S
Ammonium hydroxide	10–30	S
Ammonium sulfate	50	S
Amyl acetate	100	l
Amyl alcohol	100	n
Aniline	100	n
Antimony chloride	10	S
Aqua regia	Unknown	n
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Benzaldehyde	100	n
Benzene	100	l
Benzenesulfonic acid	Unknown	S
Benzoic acid	Solution	S
Benzylchloride	100	n
Benzyl alcohol	100	l
Boric acid	Unknown	S
Bromine (liquid)	100	n
Bromine water	Unknown	n
Butane	100	S
Butanol	100	S
Butyl acetate	100	l
Butylamine	Unknown	n
Butylchloride	100	n
Calcium chloride	Unknown	S
Calcium hypochlorite	15	S
Carbon sulfide	100	l
Carbon tetrachloride	100	S
Castor oil	100	S
Cellosolve	100	S
Chlorine (dry gas)	100	n
Chlorine dioxide	Unknown	n
Chlorine water	Unknown	l
Chloroacetic acid	Unknown	S
Chlorobenzene	100	n
Chloroform	100	n
Chlorosulfonic acid	Unknown	n
Chromic acid	Unknown	S to n
Chromic acid	20–30	n
Citric acid	10 to saturated	S
Copper sulfate	Unknown	S
Creosote	Unknown	S
Cresol	100	n
Cyclohexane	100	S
Cyclohexanol	100	S
Cyclohexanone	100	n
Detergent	Unknown	S
Diacetone alcohol	100	n
Dibutylphthalate	100	S
Dichlorobenzene	100	n
Dichloroethane	100	n
Dichloroethylene	100	l
Diethylamine	100	l
Diethyleneglycol	100	S
Diethylether	100	S
Diisopropylbenzene	100	n
Dimethylformamide	100	n
Dioctylphthalate	100	S
Dioxan	100	l
Ethanol	96	S
Ethylacetate	100	n
Ethylchloride	100	n
Ethylene glycol	100	S
Ethylhexanol	100	S
Fluorine	100	n
Formaldehyde	Unknown	S to n
Formaldehyde	37	l
Formic acid	85	S
Freon 11	100	l
Freon 113	100	l

Table 4.77 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Freon 115	100	l	Oleum	Unknown	n
Freon 12	100	l	Oxalic acid	Unknown	S
Freon 13b1	100	l	Paraffin	Unknown	l
Freon 21	100	l	Pentylacetate	100	l
Freon 22	100	l	Perchloroethylene	100	n
Freon 32	100	l	Petrol	100	l
Furfural	100	n	Petroleum	100	l
Glycerol	100	S	Petroleum ether	100	S
Glycol esters	100	n	Phenol	Unknown	n
Heptane	100	S	Potassium cyanide	Unknown	S
Hexane	100	S	Potassium fluoride	Unknown	S
Household bleach	Unknown	S	Potassium hydroxide	10–45	S
Hydrazine	100	l	Potassium permanganate	20	S
Hydrobromic acid	48	n	Potassium sulfate	Unknown	S
Hydrochloric acid	10	S	Propane	100	S
Hydrochloric acid	36	l	Pyridine	Unknown	n
Hydrofluoric acid	40	l	Sea water	100	S
Hydrogen peroxide	3–30	S	Silicone oil	100	S
Hydrogen sulfide	Saturated	S	Silver nitrate	Unknown	S
Hydrogen sulfide gas	Unknown	S	Sodium borate	Unknown	S
Iron(III) chloride	Unknown	S	Sodium carbonate	10	S
Isobutanol	100	S	Sodium chloride	25	S
Isooctane (Fuel A)	100	S	Sodium cyanide	Unknown	S
Isopropanol	100	S	Sodium hydroxide	10	l
Kerosene	100	S	Sodium hydroxide	20–55	S
Ketones	100	n	Sodium hypochlorite	20	S
Lactic acid	Unknown	S to l	Sodium nitrate	Solution	S
Lactic acid	90	l	Strong bases	Unknown	S
Lead acetate	10	S	Styrene	100	n
Linseed oil	100	S	Sulfamic acid	Solution	S
Liquid paraffin	100	l	Sulfur dioxide (gas)	Unknown	n
Magnesium chloride	Unknown	S	Sulfuric acid	10–70	S
Manganese sulfate	Unknown	S	Sulfuric acid	⩾96	n
Mercury	100	S	Sulfurous anhydride (gas)	Unknown	n
Mercury chloride	Unknown	S	Tetrachloroethylene	100	n
Methanol	100	S	Tetrahydrofuran	100	n
Methylene chloride	100	n	Tin chloride	Unknown	S
Methylethylketone	100	n	Toluene	100	l
Methylglycol	Unknown	S	Transformer oil	100	l
Methylisobutylketone	Unknown	n	Trichloroethane	100	n
Milk	100	S	Trichloroethylene	100	n
Mineral oil	100	S	Trimethylbenzene	100	n
Monochlorobenzene	100	n	Turpentine oil	100	S
Monoethyleneglycol	Unknown	S	Vegetable oil	100	S
Naphtha	Unknown	l	Water	100	S
Nickel chloride	Unknown	S	Weak acids	Unknown	S
Nitric acid	5–10	S	Weak bases	Unknown	S
Nitric acid	⩾65	n	White spirit	100	S
Nitrobenzene	100	n	Wine	Unknown	S
Nonanol	100	S	Xylene	100	n
Oleic acid	Unknown	S	Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Permeability

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: polysulfone has a medium permeability, evaluated at 4 for a full range of 0.05 up to 400 for all tested plastics.
- Gases: polysulfone has a rather high permeability, evaluated at:
  - carbon dioxide: 9400 versus a full range of 30 up to 59 000 for all tested plastics
  - nitrogen: 400 versus a full range of 1 up to 3500 for all tested plastics
  - oxygen: 2250 versus a full range of <1 up to 11 000 for all tested plastics
  - hydrogen: 17 500 versus a full range of 400 up to 20 000 for all tested plastics.

Fire resistance

Polysulfones are naturally somewhat fire resistant with oxygen indices ranging from 30 up to 34. Compounding can improve these performances and numerous grades reach a UL94 rating of V0 with oxygen indices of 38–41. Smoke emission in the event of fire is low for PES.

4.21.6 Electrical properties

Polysulfones are good insulators even in hot environments, with high dielectric resistivities and low or moderate loss factors. Special grades are marketed for electrical applications.

4.21.7 Joining, decoration

Welding is easy by the thermal processes and by ultrasound but is not possible by high-frequency current.

Gluing is possible with solvents, dimethylformamide for example. Preliminary tests are essential.

All precautions must be taken concerning health and safety according to local laws and regulations.

Polysulfones can generally be decorated by painting, metallization (vacuum deposition and sputtering), printing, varnishing with suitable materials and processing.

4.21.8 Foam

The polyethersulfone foams are specific low-density foams, named 'Airex R80.90', specially developed by Airex to obtain a good balance of:

- fire resistance
- high thermal behaviour
- transparency to radar frequencies.

Table 4.78 shows examples of PES foam properties (specific properties are the ratio of the property divided by the density). Data cannot be used for designing.

The major applications of this foam are sandwich structures for:

- Aeronautics
- Aerospace technology
- Transmissions and telecommunications (transparency to radar frequencies).

Table 4.78 Examples of PES foam properties

Density (kg/m^3)	90
Density (g/cm^3)	0.09
Compression strength (MPa)	0.790
Compression modulus (GPa)	0.025
Flexural strength (MPa)	1.500
Specific flexural strength (MPa)	17
Flexural modulus (GPa)	0.045
Specific flexural modulus (GPa)	0.5
Thermal conductivity (W/m.K)	0.039

4.21.9 Trade name examples

Airex, Mindel, Radel, Stabar, Udel, Ultrason . . .

4.21.10 Property tables

Table 4.79 relates to examples only and cannot be generalized. Data cannot be used for design purposes.

Table 4.79 Polysulfones: examples of properties

	PSU		PES		PPSU	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.24	1.29	1.37	1.4	1.29	1.3
Shrinkage (%)	0.6	0.7	0.6	0.7	0.7	0.7
Absorption of water (%)	0.2	1.1	0.1	1.1	0.37	0.4
Mechanical properties						
Shore hardness, D	90	90	95	95	85	90
Rockwell hardness, R	>120	>120	127	127	110	122
Rockwell hardness, M	69	70	85	90	50	75
Stress at yield (MPa)	72	83	85	90		
Strain at yield (%)					7	8
Tensile strength (MPa)	63	80	70	95	70	80
Elongation at break (%)	40	100	6	80	60	120
Tensile modulus (GPa)	2.1	2.7	2.3	2.8	2.3	2.4
Flexural modulus (GPa)	2.3	2.9	2.4	2.9	2.4	2.5
Notched impact strength, ASTM D256 (J/m)	53	70	53	NB	365	700
Modulus retention at 180°C (%)	66	66	88	88		
Thermal properties						
HDT B (0.46 MPa) (°C)	181	181	210	210		
HDT A (1.8 MPa) (°C)	174	205	195	204	200	208
Continuous use temperature (°C)	150	150	160	180		
Steam sterilization (cycles)					>1000	>1000
Glass transition temperature (°C)	187	190	210	230	220	220
Brittle point (°C)	−100	−100	−100	−100		
Thermal conductivity (W/m.K)	0.26	0.26	0.18	0.18		
Specific heat (cal/g/°C)	0.27	0.27	0.27	0.27		
Coefficient of thermal expansion (10^{-5}/°C)	3	6	2.7	6	1.7	6
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{17}	10^{15}	10^{18}	10^{15}	10^{16}
Dielectric constant	3.1	3.2	3.5	3.5	3.4	3.5

(*Continued*)

Table 4.79 (Continued)

	PSU		PES		PPSU	
	Min.	Max.	Min.	Max.	Min.	Max.
Loss factor (10^{-4})	11	50	10	35		
Dielectric strength (kV/mm)	20	30	16	16	14	18
Arc resistance (s)	60	60	20	120		
Fire behaviour						
Oxygen index (%)	30	38	34	38		
UL94 fire rating	V1	V0	V1	V0	V1	V0

	PSU 30% Glass fibre		PSU Mineral		PESU 10–30% GF	
Miscellaneous properties						
Density (g/cm^3)	1.4	1.5	1.5	1.6	1.5	1.6
Shrinkage (%)	0.1	0.6	0.4	0.5	0.2	0.3
Absorption of water (%)	0.3	0.4	0.3	0.3	0.2	0.9
Mechanical properties						
Shore hardness, D	95	>95	90	90	95	95
Rockwell hardness, M	87	100	70	74	90	100
Stress at yield (MPa)	100	125	65	70	75	140
Strain at yield (%)	2	3	2	5	2	6
Tensile strength (MPa)	100	125	65	70	75	140
Elongation at break (%)	2	3	2	5	2	6
Tensile modulus (GPa)	9	10	3.8	4.5	3.5	8.5
Flexural modulus (GPa)	7	8.5	4	5	3.8	8.4
Notched impact strength ASTM D256 (J/m)	55	80	35	55	55	90
Thermal properties						
HDT B (0.46 MPa) (°C)	180	190	180	185	215	221
HDT A (1.8 MPa) (°C)	175	185	175	180	210	216
Continuous use temperature (°C)	150	150	150	170	180	180
Glass transition temperature (°C)	187	190	187	190	210	230
Coefficient of thermal expansion (10^{-5}/°C)	2	3	3	4	2	3
Electrical properties						
Volume resistivity (ohm.cm)					10^{16}	10^{17}
Fire behaviour						
UL94 fire rating	V1	V0	V1	V0	V1	V0

	Specific modified grades for engineering and electrical applications					
Electrical grades	Modified		Glass modified		Modified 30% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.23	1.23	1.47	1.47	1.52	1.52
Shrinkage (%)	0.7	0.7	0.3	0.5	0.25	0.25
Absorption of water (%)	0.2	0.2	0.1	0.2	0.1	0.1
Mechanical properties						
Shore hardness, D			90	95		
Rockwell hardness, R			>100	>120		
Rockwell hardness, M			75	85		
Stress at yield (MPa)	65	65				
Strain at yield (%)	5	6				
Tensile strength (MPa)	57	57	103	103	121	121
Elongation at break (%)	100	100	2	3	2	3
Tensile modulus (GPa)	2.4	2.4				
Flexural modulus (GPa)	2.6	2.7	6	7	9	10
Notched impact strength ASTM D256 (J/m)	85	85	53	54	96	96

Table 4.79 (Continued)

	Specific modified grades for engineering and electrical applications					
Electrical grades	Modified		Glass modified		Modified 30% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Thermal properties						
HDT A (1.8 MPa) (°C)	149	149	160	160	166	166
Continuous use temperature (°C)			160	160	150	150
Number of autoclave cycles					>1000	>1000
Thermal conductivity (W/m.K)			0.22	0.22		
Coefficient of thermal expansion (10^{-5}/°C)	10	11	2	3		
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{17}			10^{16}	10^{17}
Dielectric constant	3.1	3.2	3	4		
Loss factor (10^{-4})	30	30	30	30		
Dielectric strength (kV/mm)	20	30	20	30		
Arc resistance (s)			125	125		
Fire behaviour						
Oxygen index (%)			35	35		
UL94 fire rating	V0	V0	V0	V0	V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilization is needed
Weak acids	Good behaviour
Strong acids	Unsatisfactory versus concentrated acids
Weak bases	Good behaviour
Strong bases	Good to limited behaviour
Solvents	Polysulfones resist acids at medium concentrations, alcohols, aliphatic hydrocarbons, greases, oils, gasoline, chlorine water They are attacked by aromatic hydrocarbons, chlorinated solvents, ketones, esters, phenols, aldehydes, amines
Food contact	Possible for special grades

4.22 Polyphenylene sulfide or polyphenylene sulphide (PPS)

Polyphenylene sulfide is a semicrystalline and opaque polymer with the following formula:

$$-(C_6H_4-S-)_n-$$

Crystallinity can be controlled by processing and post-annealing.

This polymer is nearly always used in a fibre-reinforced or mineral-filled form, or a mix of both.

4.22.1 General properties

Advantages

Polyphenylene sulfides are appreciated for their: good mechanical and electrical properties, rigidity, good creep behaviour, fatigue endurance, low shrinkage and moisture uptake, broad range of service temperatures (−196°C up to +200/240°C), weathering resistance, good chemical resistance, fire resistance, suitability for food contact.

Drawbacks

Polyphenylene sulfides are handicapped by their sensitivity to notched impact, requiring special care when designing; the cost, which is justified by the performances.

Special grades

They can be classified according to the type of processing, specific properties and targeted applications:

- extrusion, injection; for thin or thick parts; low, medium or high fluidity . . .
- high molecular weight, glass-reinforced grades, glass fibre/mineral-filled grades, cost-effective compounds, improved hot-water resistance, high tracking resistance, high temperature ratings, carbon-fibre-reinforced grades, high tensile strength, low coefficient of friction, lubricated fibre-filled grades with added PTFE and silicone, high rigidity, food contact, low warpage, antistatic, conductive, less sensitive to internal crazing, better resistance of welded joints . . .
- for electrical applications, reflectors, printed circuits, bearings, food industry, films . . .

Costs

The costs, as for all plastics, fluctuate greatly with the crude oil price, and are only given to provide an idea. They are generally of the order of several Euros to a few tens of Euros per kilogram.

Processing

Injection and extrusion are the main processes used. Thermoforming, machining and welding are used for secondary transformations.

Consumption

The consumption of PPS varies according to the country and the source. Global consumption can be estimated between 60 000 and 90 000 tonnes/year, and can be approximately divided into three main sectors:

- 50% for automotive & transport
- 30% for E&E
- 15% for industrial.

This is an example and other data can be found elsewhere depending on the source and country.

Applications

(See Chapter 2 for further information.)

Polyphenylene sulfides are engineering plastics used only for specialized and technical applications.

- Automotive & transportation
  - ○ exhaust gas return valves . . .
  - ○ carburettor parts, fuel lines . . .
  - ○ ignition plates . . .
  - ○ pump rotors . . .

  - flow control valves for heating systems, heat exchange elements . . .
  - parts under the hood, cases . . .
  - reflectors . . .
- Electrical & electronics (E&E)
  - connectors, terminal blocks, relay components, switch components . . .
  - coil formers, bobbins . . .
  - moulded bulb sockets for electrical power stations, thermostat parts, halogen lamp housings . . .
  - control panels, plates on terminals . . .
  - brush holders . . .
  - motor housings . . .
  - electrical appliance and PC brackets, components for floppy disk drives . . .
  - parts for heaters, grids of hair dryers, parts of domestic irons, coffee machines, microwave ovens, cooking appliances . . .
- Industrial
  - thrusters of pumps, hot-water pumps . . .
  - bearings (PTFE lubricated) . . .
  - precision parts for mechanical and regulation components . . .
  - sterilizable medical, dental and laboratory equipment
  - hair dryer grilles and components, cutting heads for electric shaves . . .
  - air outlet grilles for microscopes . . .

4.22.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 200°C up to 240°C, or slightly more, 250°C for example.

The UL temperature indices of specific grades can range from 200°C up to 240°C for the electrical and mechanical properties excluding impact and up to 220°C for mechanical properties including impact.

Service temperatures are lower under loading because of moderate modulus decay, strain, creep, relaxation . . . For example:

- for given grades of polyphenylene sulfide, compared to the value at ambient temperature, the retention percentages of tensile strength are roughly 24% up to 35% at 200°C
- for a special heat-resistant grade, compared to the value at ambient temperature, the retention percentage of the modulus is roughly 35% up to 60% at 200°C, according to the crystallinity
- HDTs under 1.8 MPa range from 170°C up to 270°C.

Figure 4.101 displays an example of tensile strength versus temperature for a polyphenylene sulfide. Note the slow decay and the significant value of 40%, or 45 MPa, for the retention at 200°C.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially heat-sensitive characteristics.

After 1 year in air at 200°C, the retention of properties relative to the corresponding values at 20°C is roughly:

- 57% for tensile strength
- 50% for elongation at break.

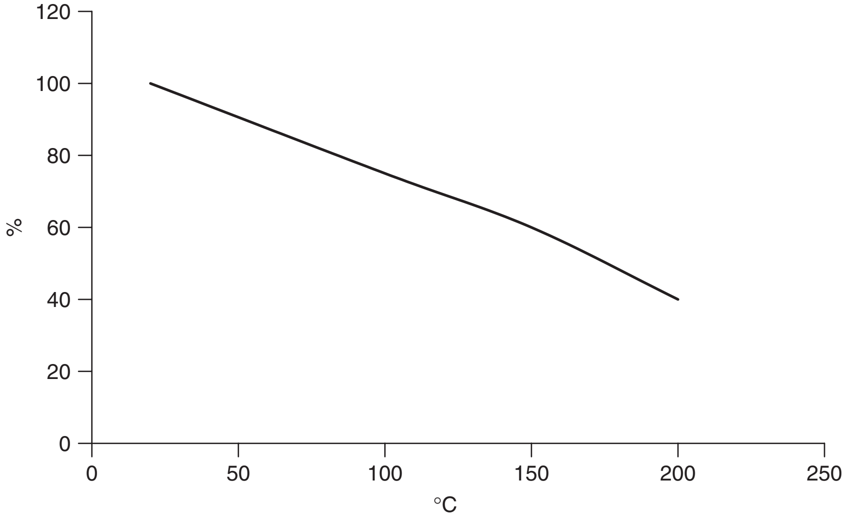


Figure 4.101. PPS examples of tensile strength retention (%) versus temperature (°C)

At low temperatures, polyphenylene sulfide is used for cryogenic applications at −269°C.

Generally, notched Izod impact strength does not significantly decrease between room temperature and −40°C.

Glass transition temperatures are high, roughly 88–93°C.

These results relate to some grades only and cannot be generalized.

4.22.3 Optical properties

Semicrystalline polyphenylene sulfide is opaque.

4.22.4 Mechanical properties

The mechanical properties depend on the actual crystallinity but are always good, with high moduli and hardnesses but limited notched impact strengths and low elongations at break. The abrasion resistance of polyphenylene sulfide depends on the roughness, type and morphology of the opposing sliding surface. Wear resistance and coefficient of friction of special grades are suitable for tribological applications.

Friction

Some self-lubricating grades of polyphenylene sulphide, containing specific additives and reinforced with glass or carbon fibres, are marketed. The coefficients of friction are good, for example 0.2 for a carbon fibre reinforced compound.

These results relate to a few grades only and cannot be generalized.

Dimensional stability

Alterations by moisture exposure are weak; shrinkage and coefficient of thermal expansion are low; creep resistance is good, the more so the higher the glass fibre content.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular or reinforcement orientation. For a given grade, a value of 0.38 is quoted.

Creep

Polyphenylene sulfides have high moduli that involve low strains for moderate loading. Consequently, creep moduli are also in a high range.

Figure 4.102 shows:

- the high creep moduli of two examples of polyphenylene sulfide with, however, a significant difference between them
- the slow decrease of creep modulus with time
- the high level of the creep modulus at 120°C.

These results relate to a few grades only and cannot be generalized.

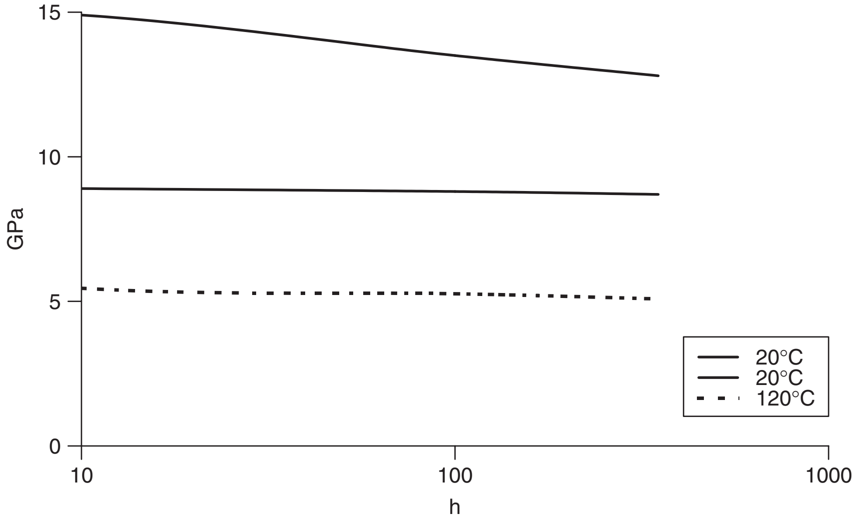


Figure 4.102. PPS examples of creep modulus (GPa) versus time (h) under 30 MPa at room temperature and 120°C

4.22.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For two given grades of PPS, one glass-fibre-reinforced and the other glass fibre/mineral-filled, Figure 4.103 displays examples of SN or Wöhler's curves.

These results are examples only and they cannot be generalized.

Weathering

Polyphenylene sulfides are inherently resistant to UV, weathering and hydrolysis. Black compounds are the most UV-resistant.

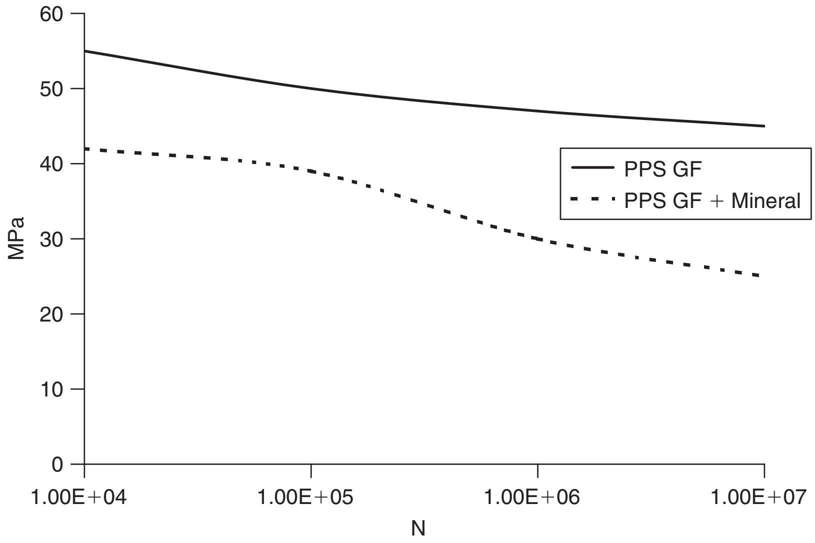


Figure 4.103. SN curves of PPS, examples of maximum stress (MPa) versus number of cycles at rupture (N)

The mechanical characteristics of a PPS grade remain fair after an exposure of 10 000 h in a Weather-Ometer.

High-energy radiation

After exposure to gamma radiation at doses of 300 Mrad at 50°C, property retentions are about:

- 95–100% for the tensile strength
- 95–132% for the elongation at break
- 96% for the notched Izod impact strength.

Chemicals

The resistance to moisture and hot water is good without hydrolysis but the resistances of glass fibre reinforced compounds can decrease significantly because of polymer/fibre interface alterations. For example, after 1 year in water at 120°C, tensile strength retention is 50% for a given compound. However, special grades with improved hot-water resistance are marketed and are successfully used in hot-water pumps.

Suitably formulated compounds are usable in contact with food.

At room temperature, polyphenylene sulfide generally resists most alcohols, aliphatic and aromatic hydrocarbons, greases, oils, gasoline, ketones, esters, ethers, glycols.

Behaviour with halogenated solvents, bases, oxidizing acids, amines and aromatic oxygenated solvents can be limited.

When the temperature rises, polyphenylene sulfide can be attacked by hot strong acids and bases, chlorinated solvents, oxidizing agents, halogens, amines. For example, a given grade is unusable after a few months in 10% nitric acid at 90°C. After 1 year at 90°C in 37% hydrochloric acid, the retention of tensile strength is 29%.

Table 4.80 displays some general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily

Table 4.80 Polyphenylene sulfide: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	⩾10	S
Acetic aldehyde	100	S
Acetic anhydride	100	S
Acetone	100	S
Acetonitrile	100	S
Acetophenone	100	S
Acetyl chloride	100	S
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonium hydroxide	30	S
Ammonium sulfate	50	S
Amyl acetate	100	S
Amyl alcohol	100	S
Aqua regia	Unknown	n
Aromatic hydrocarbons	100	S
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Benzaldehyde	100	l
Benzene	100	S
Benzylchloride	100	S
Benzyl alcohol	100	l
Boric acid	Unknown	S
Bromine (liquid)	100	n
Butanol	100	S
Butyl acetate	100	S
Butylamine	Unknown	l
Butylchloride	100	S
Calcium chloride	Unknown	S
Carbon sulfide	100	S
Carbon tetrachloride	100	n
Castor oil	100	S
Cellosolve	100	S
Cellosolve acetate	100	S
Chlorinated hydrocarbons	100	S
Chlorinated solvents	100	S
Chlorine (dry gas)	100	S
Chlorine dioxide	Unknown	n
Chlorine water	Unknown	S
Chloroacetic acid	Unknown	S
Chlorobenzene	100	S
Chloroform	100	S
Chlorosulfonic acid	Unknown	n
Chromic acid	Unknown	n
Citric acid	10	S
Colza oil	100	S
Concentrated bases	Unknown	l
Copper sulfate	Unknown	S
Cresol	100	S
Cyclohexane	100	S
Cyclohexanol	100	S
Cyclohexanone	100	S
Diacetone alcohol	100	S
Dibutylphthalate	100	S
Dichloroethane	100	S
Dichloroethylene	100	S
Diethylamine	100	n
Diethyleneglycol	100	S
Diethylether	100	S
Diisopropylbenzene	100	S
Dilute bases	Unknown	l
Dimethylamine	100	n
Dimethylformamide	100	S
Dioctylphthalate	100	S
Dioxan	100	S
Ethanol	96	S
Ethylacetate	100	S
Ethylamine	100	n
Ethylchloride	100	S
Ethylene glycol	100	S
Ethylhexanol	100	S
Fluorine	100	n
Formaldehyde	37	S
Formic acid	85	S
Freon 11	100	S
Freon 113	100	S
Freon 115	100	S
Freon 12	100	S
Freon 13b1	100	S
Freon 21	100	S
Freon 22	100	S
Freon 32	100	S
Furfural	100	S
Glycerol	100	S
Hexane	100	S
Hydrobromic acid	48	S
Hydrochloric acid	⩾10	S
Hydrofluoric acid	40	S
Hydrogen peroxide	30	S
Hydrogen sulfide	Saturated	S
Hydrogen sulfide gas	Unknown	n
Iron(III) chloride	Unknown	S
Isobutanol	100	S
Isooctane (Fuel A)	100	l
Isopropanol	100	S
Kerosene	100	S
Lactic acid	90	S
Linseed oil	100	S
Liquid paraffin	100	S
Magnesium chloride	Unknown	S
Magnesium hydroxide	Unknown	S
Mercury chloride	Unknown	S
Methanol	100	S
Methylethylketone	100	S
Methylglycol	Unknown	S

(*Continued*)

Table 4.80 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Methylisobutylketone	Unknown	S	Sea water	100	S
Mineral oil	100	S	Silver nitrate	Unknown	S
Monochlorobenzene	100	S	Sodium borate	Unknown	S
Monoethyleneglycol	Unknown	S	Sodium carbonate	10	S
Naphtha	Unknown	S	Sodium chloride	25	S
Nickel chloride	Unknown	S	Sodium cyanide	Unknown	S
Nitric acid	5–10	S	Sodium hydroxide	10–55	S
Nitric acid	65	l	Sodium hypochlorite	20	S
Nitric acid	75	n	Sodium nitrate	Solution	S
Nitrobenzene	100	S	Strong bases	Unknown	l
Nonanol	100	S	Sulfur dioxide (gas)	Unknown	S
Oleic acid	Unknown	S	Sulfuric acid	10–96	S
Olive oil	100	S	Sulfurous anhydride (gas)	Unknown	S
Oxalic acid	Unknown	S	Tetrachloroethylene	100	S
Pentylacetate	100	S	Tetrahydrofuran	100	S
Perchloroethylene	100	S	Tin chloride	Unknown	S
Petrol @ 15% alcohol	Unknown	S	Toluene	100	S
Petroleum	100	S	Trichloroacetic acid	Unknown	S
Phenol	Unknown	S	Trichloroethylene	100	l
Phosphoric acid	85	S	Triethylamine	Unknown	S
Potassium cyanide	Unknown	S	Turpentine oil	100	S
Potassium fluoride	Unknown	S	Vegetable oil	100	S
Potassium hydroxide	45	S	Water	100	S
Potassium permanganate	20	S	Weak acids	Unknown	S
Potassium sulfate	Unknown	S	Weak bases	Unknown	l
Propanol	100	S	Wine	Unknown	S
Propylene oxide	100	S	Xylene	100	S
Pyridine	Unknown	l	Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

representative of all the polyphenylene sulfides. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Fire resistance

Most polyphenylene sulfides are fire resistant with oxygen indices ranging from 45 up to 57 and a UL94 rating of V0. Rarely, a few compounds are reported to have a UL94 rating of HB with an oxygen index of 25.

4.22.6 Electrical properties

Polyphenylene sulfides are good insulators even in a hot environment, with high dielectric resistivities and low or moderate loss factors. Special grades are marketed for electrical applications.

4.22.7 Joining, decoration

Welding is possible by certain thermal processes, by ultrasound, by friction and induction. Special grades with improved weldability are marketed.

Because of the high resistance to chemicals, gluing is not possible with solvents but suitable cyanoacrylate, epoxy and polyurethane adhesives can be used leading to strengths significantly inferior to those of PPS. Preliminary tests are essential.

All precautions must be taken concerning health and safety according to the local laws and regulations.

4.22.8 Trade name examples

Crastone, Fortron, Primef, Ryton, Supec, Tedur, XTel.

4.22.9 Property tables

Table 4.81 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.81 Polyphenylene sulfide: examples of properties

	PPS		PPS 20–30% GF		PPS 40% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.35	1.35	1.5	1.5	1.6	1.7
Shrinkage (%)	0.6	1.4	0.2	0.5	0.2	0.5
Absorption of water (%)	0.01	0.07	0.02	0.05	0.04	0.05
Mechanical properties						
Shore hardness, D	90	95	90	>95	95	>95
Rockwell hardness, M	70	85	80	103	100	104
Stress at yield (MPa)	50	80	130	150	120	150
Strain at yield (%)	1	4	1	2	1	4
Tensile strength (MPa)	50	80	130	150	120	150
Elongation at break (%)	1	4	1	2	1	4
Tensile modulus (GPa)	3.3	4	6	11	8	14
Flexural modulus (GPa)	3.8	4.2	6	12	12	15
Notched impact strength ASTM D256 (J/m)	5	25	35	70	60	100
Tensile strength retention at 200°C (%)					24	39
Modulus retention at 200°C (%)	40	60			40	60
Thermal properties						
HDT B (0.46 MPa) (°C)	170	200	270	278	270	280
HDT A (1.8 MPa) (°C)	100	135	250	260	260	270
Continuous use temperature (°C)	200	220	200	240	200	240
Glass transition temperature (°C)	88	93	88	93	88	93
Melting temperature (°C)	275	290	275	290	275	290
Thermal conductivity (W/m.K)			0.3	0.3	0.3	0.3
Coefficient of thermal expansion (10^{-5}/°C)	3	5	1	4	1	3
Electrical properties						
Volume resistivity (ohm.cm)			10^{16}	10^{16}	10^{16}	10^{16}
Dielectric constant			3.8	3.8	4	4
Loss factor (10^{-4})			100	100	13	20
Dielectric strength (kV/mm)			31	31	17	17
Arc resistance (s)			85	85	34	34

(*Continued*)

Table 4.81 (Continued)

	PPS		PPS 20–30% GF		PPS 40% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Fire behaviour						
Oxygen index (%)	47	47	25	32		
UL94 rating	V0	V0	HB	V0		

	PPS 20% Carbon fibres		PPS Glass fibres & mineral fillers		PPS Conductive & glass fibres	
Miscellaneous properties						
Density (g/cm^3)	1.4	1.4	1.8	2	1.7	1.8
Shrinkage (%)			0.3	0.7	0.3	1.0
Absorption of water (%)	0.04	0.05	0.02	0.08	0.03	0.07
Mechanical properties						
Shore hardness, D			88	>95	90	>95
Rockwell hardness, M			66	102	70	100
Stress at yield (MPa)			60	150	60	90
Strain at yield (%)			1	3	0.5	3
Tensile strength (MPa)	180	180	60	150	60	90
Elongation at break (%)	2	2	1	3	0.5	3
Tensile modulus (GPa)	17	17	10	17	17	19
Flexural modulus (GPa)			10	17	16	18
Notched impact strength ASTM D256 (J/m)			25	70	40	80
Tensile strength retention at 200°C (%)			25	35		
Thermal properties						
HDT B (0.46 MPa) (°C)			200	280	230	>260
HDT A (1.8 MPa) (°C)	260	260	170	260	225	260
Continuous use temperature (°C)	200	240	200	240	200	220
Glass transition temperature (°C)			88	93	88	93
Melting temperature (°C)			275	290	275	290
Thermal conductivity (W/m.K)	0.4	0.5	0.6	0.6	0.3	0.4
Coefficient of thermal expansion (10^{-5}/°C)	1	2	1	2	1	9
Electrical properties						
Volume resistivity (ohm.cm)	10^{3}	10^{3}	10^{15}	10^{16}	1	10^{3}
Dielectric constant			5	5		
Loss factor (10^{-4})			70	580		
Dielectric strength (kV/mm)			13	13		
Arc resistance (s)			116	182		
Fire behaviour						
Oxygen index (%)			53	53	45	48
UL94 rating	V0	V0	V0	V0	V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Good behaviour
Weak acids	Good behaviour
Strong acids	Fair behaviour except with oxidizing acids
Weak bases	Limited behaviour
Strong bases	Limited behaviour
Solvents	At room temperature, polyphenylene sulfide generally resists most alcohols, aliphatic and aromatic hydrocarbons, greases, oils, gasoline, ketones, esters, ethers, glycols Behaviour with halogenated solvents, bases, oxidizing acids, amines, aromatic oxygenated solvents can be limited When the temperature rises, polyphenylene sulfide can be attacked by hot strong acids and bases, chlorinated solvents, oxidizing agents, halogens, amines
Food contact	Possible for special grades

4.23 Polyetheretherketones, polyetherketones and polyaryletherketones (PEEK, PEK, PAEK)

The polyarylketone family comprises three main chemical entities:

- polyetheretherketones – PEEK
- polyaryletherketones – PAEK
- polyetherketones – PEK.

Figure 4.104 shows examples of formulae.

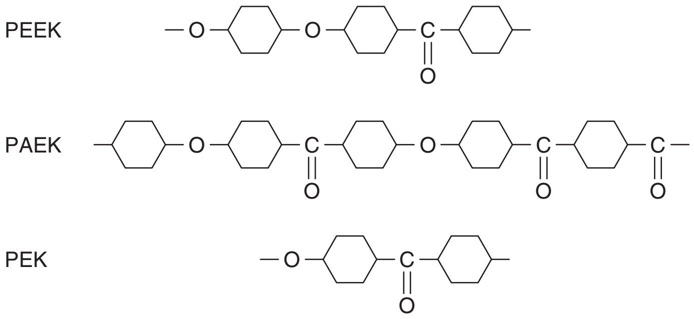


Figure 4.104. Examples of polyarylketone formuale

The properties described hereafter are, unless otherwise specified, those of the polyetheretherketones. PEK are characterized by a highly crystalline character, a better heat resistance and a better chemical behaviour.

In the following we will often use polyarylketone for all these ketones.

4.23.1 General properties

Advantages

Polyarylketones are appreciated for their: good mechanical, chemical and electrical properties, high service temperatures (250°C), rigidity, good creep behaviour, wear resistance, fatigue endurance, fair shrinkage and moisture uptake, high purity of special grades, high-energy radiation resistance, possibility of food contact.

Drawbacks

Polyarylketones are handicapped by their light and UV sensitivity, requiring efficient protection for outdoor exposure; the cost, which is justified by the performances; an insufficient fire resistance in some instances, but special grades are marketed.

Special grades

They can be classified according to the type of processing, specific properties or targeted applications:

- extrusion, injection, compression, extrusion moulding, powder coating, low or standard viscosity . . .
- high temperature, high rigidity, food contact, glass and carbon fibre reinforced, high purity, antistatic . . .
- for electrical applications, bearings, food industry, films, coating, filaments . . .

Costs

As for all plastics, the costs fluctuate greatly with the crude oil price, and are only given to provide a general idea. They are typically of the order of several tens of Euros to a hundred Euros per kilogram.

Processing

All the molten-state methods are usable but the main ones are extrusion, injection, compression, extrusion moulding, machining, welding. Specific grades can be used for powder coating.

Consumption

The consumption of polyarylketones varies according to the country and the source. Global consumption can be estimated between 2000 and 4000 tonnes per year, and can be approximately divided into three main sectors:

- 40% for industry
- 30% for automotive & transport
- 20% for E&E.

This is an example and other data can be found elsewhere depending on the source and country.

Applications

(See Chapter 2 for further information.)

Polyarylketones are engineering plastics used only for specialized and technical applications. The main applications areas are:

- Industrial
  - impeller wheels for regenerative pumps, pump rotors . . .
  - multi-pin connectors . . .
  - glue-gun bushings . . .
  - quick coupling systems . . .
  - laundry system wheels . . .
  - conductivity sensors . . .
  - seals, compressor valve plates . . .
  - heat exchanger parts . . .
- Automotive
  - piston components, seals, washers . . .
  - bearings . . .
  - transmission components, transmission thrust washers, braking and air-conditioning systems, ABS brake systems . . .
  - engine control systems . . .
  - truck oil screens . . .
  - starting discs in bus gears . . .
  - linings . . .
- Electrical engineering
  - wire insulation for extremely high-temperature applications, cable couplings and connectors, sub-sea connectors, coaxial connector jacks, sub-sea controlled environment connectors . . .

  - wafer wands, wafer transport carriers . . .
  - surface-mounted trimming potentiometers . . .
  - appliances: handles, cooking equipment . . .
- Aircraft
  - airbus interior components, bow-shaped luggage compartment retainers . . .
  - cable conduits, cable clips, ventilation wheels inside aviation fans, suction manifold of aviation pumps . . .
  - electrical wire harnesses isolated by monofilaments, sleeves . . .
  - convoluted tubing . . .
  - wire insulation . . .
  - pump casings and impellers . . .
- Medicine
  - prosthetics . . .
  - surgical and dental instruments (up to 3000 autoclave sterilization cycles) . . .
  - endoscopes . . .
  - port access systems . . .
  - haemodialysers, dialysis machine components . . .
- Food processing equipment
  - automatic espresso machines, high-tech coffee machines . . .
  - food pump seals . . .
  - beverage bottling components . . .
- Monofilaments
  - woven products for filters, belting and meshes . . .
  - wire insulation . . .
- Films
  - submersible pump insulation, dry transformer insulation . . .
  - flexible surface heaters . . .
  - speaker cones and coils . . .
  - gaskets, oilfield pipe flanges and gaskets . . .
  - speciality laminates, composite adhesive films . . .
  - high-temperature labels . . .
  - integrated circuit packaging (HDD) trays . . .

4.23.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at up to 250°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- For a given grade of polyarylketone, compared to the value at ambient temperature, the percentage retention of tensile or flexural strength is roughly:
  - 50% up to 70% at 100°C
  - 27% up to 39% at 150°C
  - 8% at 250°C.
- For a high-temperature PEEK grade (PEEK-HT), compared to the value at ambient temperature, the percentage retention of tensile or flexural strength is roughly 15% at 250°C.

- For a carbon fibre reinforced PEEK, compared to the value at ambient temperature, the percentage retention of tensile or flexural strength or modulus is roughly 20–30% at 250°C.
- For another neat grade, compared to the value at ambient temperature, the percentage retention of modulus is roughly:
  - ○ 68% at 150°C
  - ○ 20% at 180°C
  - ○ 7% at 250°C.
- For a PEEK-HT, compared to the value at ambient temperature, the retention percentage of modulus is roughly 75% at 150°C.
- HDTs under 1.8 MPa range from:
  - ○ 140°C up to 170°C for neat PEEK.
  - ○ 290°C up to 350°C for a fibre-reinforced grade.

Figure 4.105 displays two examples of tensile strength retention versus temperature for a neat and a carbon fibre reinforced polyetherketone, showing the rather fast decay up to 180°C followed by a stabilization.

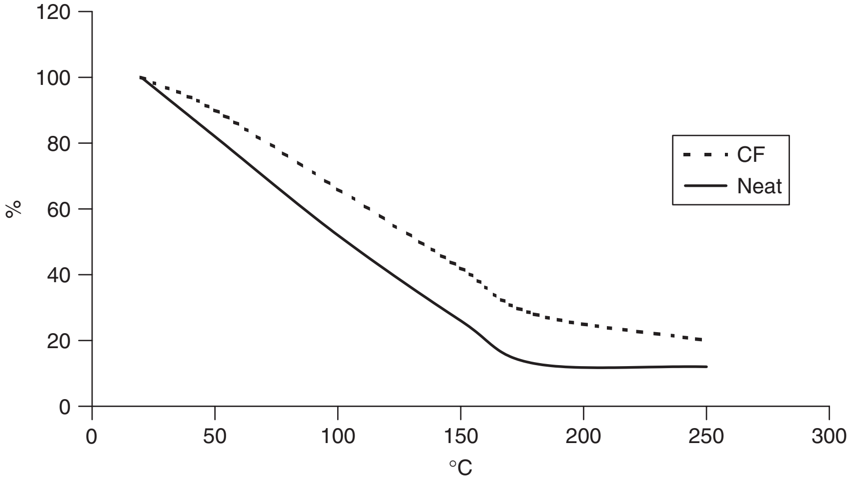


Figure 4.105. Neat & CF PEEK examples of tensile strength retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially heat-sensitive characteristics.

Half-lives of specific PEEK grades based on tensile strength are:

- up to 2.2 years at 250°C
- 18 days at 310°C.

Half-lives of specific PEEK grades based on elongation at break are much lower, for example:

- 1 year at 200°C
- 10 days at 310°C.

The behaviour at low temperatures is good, depending on the grades and the mechanical constraints experienced.

Generally, notched Izod impact strengths slowly decrease between room temperature and −40°C retaining, for example, 80–85% of the original value.

Glass transition temperatures are roughly 143°C for a general-purpose grade up to 157°C for a special heat-resistant grade.

These results relate to some grades only and cannot be generalized.

4.23.3 Optical properties

Semicrystalline polyarylketones are opaque with refractive indices of about 1.68–1.77.

Amorphous films with refractive indices of about 1.65–1.71 can be obtained by a special processing method.

These results relate to some grades only and cannot be generalized.

4.23.4 Mechanical properties

The mechanical properties are good with medium to low elongations at break and more limited strains at yield. Moduli and hardnesses are in a high range but notched impact strengths are in a medium range. The abrasion resistance of polyarylketones, generally good, depends on the roughness, type and morphology of the contacting counterpart sliding surface. The wear resistance and coefficient of friction of special grades are suitable for tribological applications.

Friction

Some self-lubricating grades of polyarylketones containing specific additives, and possibly reinforced with glass or carbon fibres, are marketed. The coefficients of friction are good, for example 0.1 at room temperature, and remain unchanged at high temperature: 0.12 at 200°C, for example.

PV limits are in a good range, similar to those of PES and a little inferior to those of polyimide, especially at high temperature

These results relate to a few grades only and cannot be generalized.

Dimensional stability

Alterations by moisture exposure are fair; shrinkage and coefficient of thermal expansion are rather low; creep resistance is good, the more so the higher the fibre content.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular or reinforcement orientation. For given samples of neat grades, they are evaluated at 0.38–0.42. For anisotropic parts, data of 0.30–0.34 are quoted for the thinnest dimension.

These examples cannot be generalized.

Creep

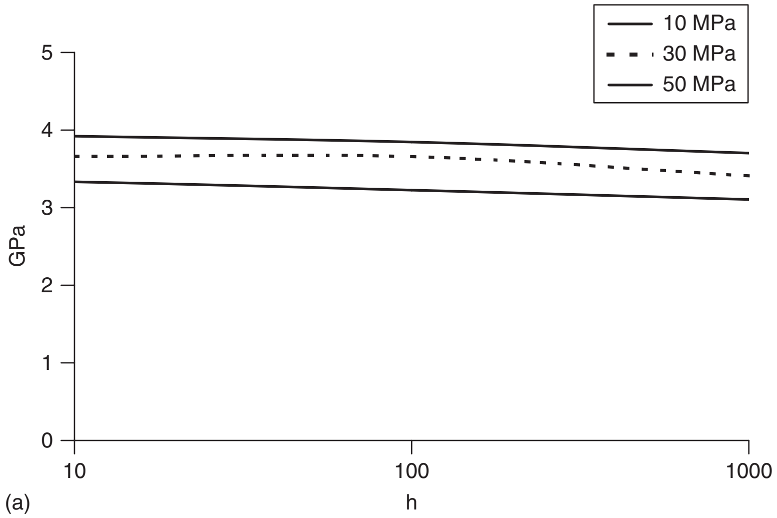
Creep behaviour is good even when the temperature rises. Neat PEEKs have rather high moduli that involve rather low strains for moderate loading. Consequently, creep moduli are also in a good range at room temperature but they decrease more slowly than the majority of other thermoplastics when the temperature rises. Reinforcement with fibres leads to high moduli and, consequently, high creep moduli.

Figure 4.106(a) shows the decrease in creep modulus for PAEK when the load increases from 10 MPa up to 50 MPa at room temperature.

Figure 4.106(b) shows:

- the slow decrease of the creep modulus at room temperature
- the moderate difference between creep at 22°C and 100°C
- the broader difference of creep between 100°C and 150°C but the fair level of creep modulus at 100°C and even at 150°C.

These results relate to a few grades only and cannot be generalized.



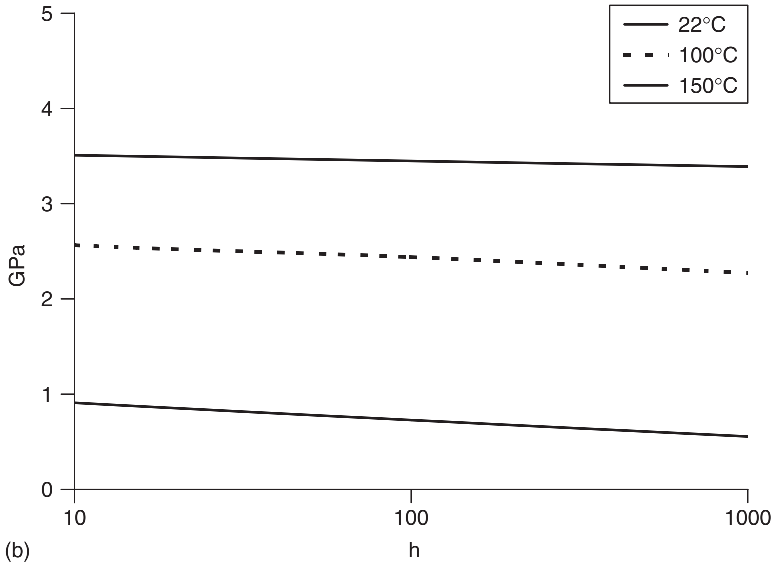


Figure 4.106. (a) PAEK examples of creep modulus (GPa) versus time (h) under 10 to 50 MPa at room temperature; (b) PAEK examples of creep modulus (GPa) versus time (h) under 20 MPa at various temperatures

4.23.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For three given grades of neat and glass or carbon fibre reinforced PEEK, Figure 4.107 displays examples of SN or Wöhler's curves.

These results are examples only and they cannot be generalized.

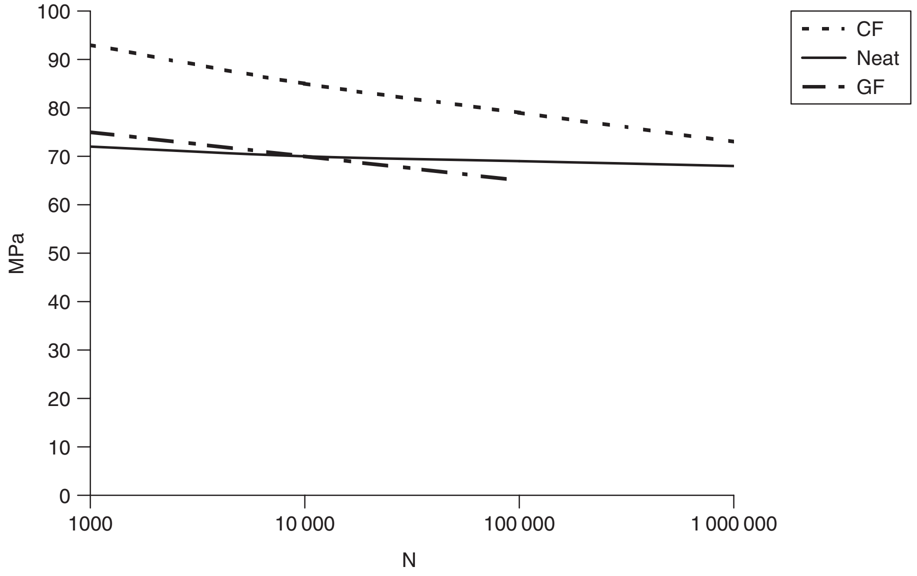


Figure 4.107. SN curves of neat PEEK, examples of maximum stress (MPa) versus number of cycles at rupture (N)

Weathering

Polyarylketones are inherently UV-sensitive and must be protected for outdoor exposure.

High-energy radiation

The resistance to gamma radiation is excellent without significant degradation after more than 1000 Mrad, exceeding even the behaviour of polystyrene. With alpha and beta radiations, resistance would be higher than 10 000 Mrad.

Chemicals

The resistance to moisture, hot water and pressurized water vapour is good, with no hydrolysis. The polyarylketones can withstand multiple steam sterilizations.

Suitably formulated compounds are usable in contact with food.

Polyarylketones resist acids at low concentrations, alcohols, aliphatic and aromatic hydrocarbons, greases, oils, gasoline, bases, most chlorinated solvents, ketones, esters, amines, and aldehydes.

They are attacked by chlorine water, oxidizing agents, concentrated sulfuric and nitric acids, halogens, and phenols.

Table 4.82 displays some general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the polyarylketones. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.82 Polyetherketones: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour
Acetic acid	≥10	S
Acetone	100	S
Aluminium chloride	Solution	S
Aluminium sulfate	Unknown	S
Ammonium hydroxide	30	S
Ammonium sulfate	50	S
Aqua regia	Unknown	l
Arsenic acid	Unknown	S
ASTM1 oil	100	S
ASTM2 oil	100	S
ASTM3 oil	100	S
Barium chloride	Saturated	S
Benzaldehyde	100	S
Benzene	100	S
Bromine (liquid)	100	n
Calcium chloride	Unknown	S
Carbon tetrachloride	100	S
Chlorine (dry gas)	100	S
Chlorine water	Unknown	n
Chloroform	100	S
Chromic acid	Unknown	S
Cyclohexane	100	S
Diethylamine	100	S
Diethyleneglycol	100	S
Diethylether	100	S
Dimethylamine	100	S
Dimethylformamide	100	S
Ethanol	Unknown	S
Ethylacetate	100	S
Ethylamine	100	S
Ethylene glycol	100	S
Fluorine	100	l
Formic acid	40	S
Formic acid	85	l
Glycerol	100	S
Hexane	100	S
Hydrobromic acid	48	n
Hydrochloric acid	10–37	S
Hydrofluoric acid	40	n
Hydrogen peroxide	30	S
Hydrogen sulfide gas	Unknown	S
Iron(III) chloride	Unknown	S
Isooctane (Fuel A)	100	S
Isopropanol	100	S
Lactic acid	90	S
Lead acetate	10	S
Liquid paraffin	100	S
Magnesium chloride	Unknown	l
Magnesium sulfate	Unknown	S
Methanol	100	S
Methylene chloride	100	S
Methylethylketone	100	S
Mineral oil	100	S
Molasses	Unknown	S
Nickel chloride	Unknown	S
Nitric acid	10	S
Nitric acid	≥65	n
Nitrobenzene	100	S
Oleic acid	Unknown	S
Olive oil	100	S
Ozone	Unknown	S
Perchloroethylene	100	S
Petroleum	100	S
Phenol	Unknown	l
Phosphoric acid	85	S
Potassium cyanide	Unknown	S
Potassium fluoride	Unknown	S
Potassium hydroxide	45	S
Potassium permanganate	20	S
Potassium sulfate	Unknown	S
Propanol	100	S
Sea water	100	S
Silicone oil	100	S
Silver nitrate	Unknown	S
Sodium borate	Unknown	S
Sodium carbonate	10	S
Sodium chloride	25	S
Sodium cyanide	Unknown	S
Sodium hydroxide	10–55	S
Sodium nitrate	Solution	S
Styrene	100	S
Sulfamic acid	Solution	S
Sulfuric acid	10	S
Sulfuric acid	≥70	n
Sulfurous anhydride (gas)	Unknown	S
Tin chloride	Unknown	S
Toluene	100	S
Transformer oil	100	S
Trichloroethane	100	S
Trichloroethylene	100	S
Triethylamine	Unknown	S
Vegetable oil	100	S
Water	100	S
White spirit	100	S
Wine	Unknown	S
Xylene	100	S
Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Fire resistance

Polyarylketones, with oxygen indices of 24, are not truly fire resistant. Compounding can improve these performances and numerous grades reach a UL94 rating of V0 with oxygen indices superior to 35.

4.23.6 Electrical properties

Polyarylketones are good insulators even in hot and wet environments, with high dielectric resistivities and low loss factors. Special grades are marketed for electrical applications.

4.23.7 Joining, decoration

Welding: ultrasound and friction give good results if sufficient energy is used.

Joining is possible with adhesives such as epoxies, cyanoacrylates, silicones. Surface treatments are very useful. Preliminary tests are essential.

All precautions must be taken concerning health and safety according to local laws and regulations.

Decoration: vacuum metallization gives good results.

4.23.8 Trade name examples

APC (aromatic polymer composite), Hostatec, Ultrapek, Victrex PEEK

4.23.9 Property tables

Table 4.83 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.83 Polyarylketones: examples of properties

	PEEK		PEEK HT		PAEK	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.27	1.32	1.32	1.32	1.3	1.3
Shrinkage (%)	1.1	1.1			0.8	1.2
Absorption of water (%)	0.1	0.5			0.1	0.1
Mechanical properties						
Shore hardness, D	85	>95	85	>95	86	>95
Rockwell hardness, R	110	>120	108	108	120	>120
Rockwell hardness, M	55	100	55	100	55	98
Tensile strength (MPa)	70	100	110	110	85	100
Elongation at break (%)	30	150	3	20	30	50
Tensile modulus (GPa)	3.6	3.9			3.5	4
Flexural modulus (GPa)	3.7	3.9	4	4	3.5	4
Notched impact strength ASTM D256 (J/m)	80	85			80	140
Modulus retention at 200°C (%)	8	23				
Thermal properties						
HDT B (0.46 MPa) (°C)					250	300
HDT A (1.8 MPa) (°C)	140	160	165	165	160	170
Continuous use temperature (°C)	250	250	250	>250	250	250

(*Continued*)

Table 4.83 (Continued)

	PEEK		PEEK HT		PAEK	
	Min.	Max.	Min.	Max.	Min.	Max.
Glass transition temperature (°C)	143	143	157	157		
Melting temperature (°C)	334	334	374	374	320	380
Thermal conductivity (W/m.K)	0.25	0.25				
Specific heat (cal/g/°C)	0.32	0.32				
Coefficient of thermal expansion (10^{-5}/°C)	4	6			4	5
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{17}	10^{16}	10^{17}		
Dielectric constant	3.2	3.2	3.3	4		
Loss factor (10^{-4})	30	30	35	35		
Dielectric strength (kV/mm)	20	20				
Fire behaviour						
Oxygen index (%)	24	35				
UL94 rating	V1	V0	V0	V0		
	PEEK 30% GF		PEEK 30% CF		PAEK 30% GF	
Miscellaneous properties						
Density (g/cm^3)	1.49	1.54	1.44	1.44	1.5	1.5
Shrinkage (%)	0.2	1	0.1	1.4	0.1	1
Absorption of water (%)	0.06	0.12	0.06	0.10	0.07	0.07
Mechanical properties						
Shore hardness, D	90	>95	90	>95	90	>95
Rockwell hardness, M	70	100	70	100	70	102
Stress at yield (MPa)	150	180	200	220	150	180
Strain at yield (%)	2	3	1	3	2	4
Tensile strength (MPa)	150	180	200	220	150	180
Elongation at break (%)	2	3	1	3	2	4
Tensile modulus (GPa)	9	10	13	20	9.5	12
Flexural modulus (GPa)	9	10.3	13	20	9.5	12
Notched impact strength ASTM D256 (J/m)	95	130	85	110	95	100
Thermal properties						
HDT B (0.46 MPa) (°C)			323	323	340	360
HDT A (1.8 MPa) (°C)	290	315	315	320	320	350
Continuous use temperature (°C)	250	250	250	250	250	250
Glass transition temperature (°C)	143	143	143	143		
Melting temperature (°C)	334	334	334	334	320	380
Thermal conductivity (W/m.K)	0.43	0.43	0.9	0.9		
Coefficient of thermal expansion (10^{-5}/°C)	1.5	2	1.5	4	1	2
Electrical properties						
Volume resistivity (ohm.cm)			10^5	10^5		

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV-sensitive, needs efficient stabilization
Weak acids	Good behaviour
Strong acids	Attacked by oxidizing and concentrated acids
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Polyarylketones resist acids at low concentrations, alcohols, aliphatic and aromatic hydrocarbons, greases, oils, gasoline, bases, most chlorinated solvents, ketones, esters, amines, aldehydes They are attacked by chlorine water, oxidizing agents, concentrated sulfuric and nitric acids, halogens, phenols
Food contact	Possible for special grades

4.24 Polyetherimide (PEI)

Polyetherimide is an amorphous thermoplastic having the formula shown in Figure 4.108.

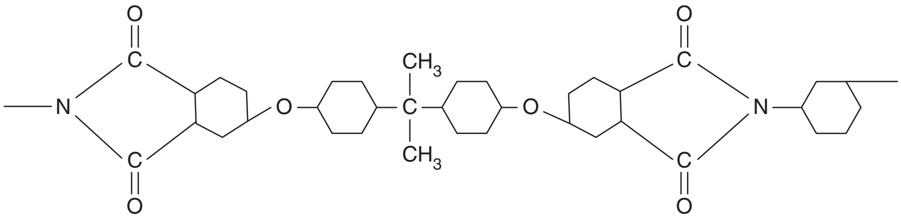


Figure 4.108. Example of polyetherimide formula

4.24.1 General properties

Advantages

Polyetherimide is appreciated for: good mechanical and electrical properties; high service temperatures (up to 170°C or 180°C); rigidity; good creep behaviour; fatigue endurance; low shrinkage and moisture uptake; inherent flame retardancy and low smoke emission in the event of fire; transparency to visible light, infrared and microwaves; inherent resistance to UV and weathering; good resistance to hydrolysis and steam sterilization; high-energy radiation resistance; possibility of food contact; FDA, KTW and USP VI compliant.

Drawbacks

Polyetherimides are handicapped by the cost (though justified by the performances), a high density, an insufficient chemical resistance in some cases, the small number of grades and sources.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- extrusion, injection, compression, low warpage, low viscosity, better flow . . .
- high temperature, food contact, glass and carbon fibre reinforced, improved chemical resistance, wear resistant, improved dimensional stability, antistatic . . .
- for electrical applications, bearings, food industry, aircraft, automotive lighting . . .

Costs

As for all plastics, the costs fluctuate greatly with the crude oil price, and are only given to provide a general idea. They are typically of the order of a few tens of Euros to several tens of Euros per kilogram.

Processing

All the molten-state methods are usable but the main ones are extrusion, injection, compression, machining and welding.

Consumption

The consumption of polyetherimide varies according to the country and the source. Global consumption can be estimated between 5000 and 10 000 tonnes per year, and can be approximately divided into three main sectors:

- 50% for industrial
- 20% for automotive & transport
- 20% for E&E.

This is an example and other data can be found elsewhere according to the source and country.

Applications

(See Chapter 2 for further information.)

Polyetherimide is an engineering plastic used only for specialized and technical applications. The main applications are:

- Industrial
  - water-pump impellers, expansion valves . . .
  - hot-water reservoirs, heat exchange systems . . .
  - fire helmets . . .
  - tableware and catering . . .
  - reusable food service, food trays, soup mugs, steam insert pans or gastronorm containers, cloches . . .
  - microwavable bowls, utensils . . .
  - ovenware, cooking utensils and re-usable airline casseroles . . .
- Automotive
  - transmission components . . .
  - throttle bodies . . .
  - ignition components, sensors and thermostat housings . . .
  - automotive lighting, headlight reflectors, foglight reflectors . . .
  - bezels and light bulb sockets . . .
- Electrical & electronics
  - electrical control units . . .
  - wire insulation . . .
  - reels . . .
  - integrated circuits . . .
  - connectors, high heat connectors . . .
  - computer components, mobile phone internal antennae . . .
  - RF-duplexers or micro-filters, EMI shielding . . .
  - fibre optic connectors, optical transceivers . . .
  - lighting applications, reflectors, reflectors with dichroic coating without primer . . .
- Aircraft
  - air and fuel valves . . .
  - steering wheels . . .
  - food tray containers, cooking utensils and re-usable airline casseroles . . .
  - interior cladding parts, structural components, semi-structural components . . .
- Medical and laboratory applications
  - reusable medical devices, sterilization trays . . .
  - stopcocks . . .

- dentist devices . . .
- pipettes . . .
- Foam cores for lightweight sandwich panels . . .
- Filaments for fire-resistant padding . . .

4.24.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at up to 170°C or 180°C.

The UL temperature indices of specific polyetherimide grades can range from 170°C up to 180°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- For a given grade of polyetherimide, compared to the value at ambient temperature, the percentage retention of tensile or flexural strength is roughly:
  - 60% at 100°C
  - 40% at 150°C
  - 35% at 180°C.
- For a carbon fibre reinforced PEI, compared to the value at ambient temperature, the percentage retention of tensile or flexural strength or modulus is roughly 55% at 180°C.
- For other grades, compared to the value at ambient temperature, the percentage retention of moduli is roughly:
  - 85–95% at 100°C
  - 70–90% at 150°C
  - 67–90% at 180°C.
- HDTs under 1.8 MPa range from 190°C up to 210°C.

Figure 4.109 displays two examples of tensile strength retention versus temperature for neat and carbon fibre reinforced polyetherimides, showing the steady decay up to 180°C.

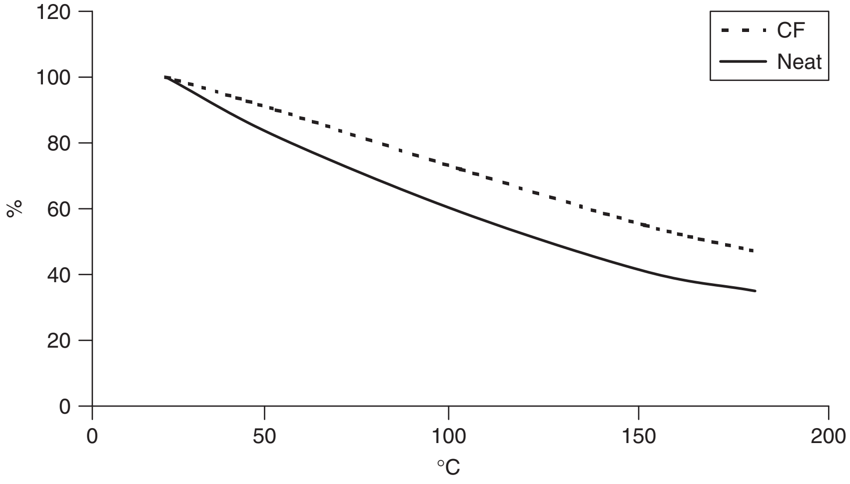


Figure 4.109. Neat & CF PEI examples of tensile strength retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially heat-sensitive characteristics.

The behaviour at low temperatures is good, depending on the grades and the mechanical constraints experienced.

Generally, polyetherimide displays notch sensitivity and stress concentrators must be avoided when designing. Notched Izod impact strengths slowly decrease between room temperature and −30°C retaining, for example, 80–100% of the original value.

The glass transition temperature is high, roughly 215°C.

These results relate to some grades only and cannot be generalized.

4.24.3 Optical properties

Amorphous polyetherimides are transparent to visible and infrared light with a slight amber colour and refractive indices of about 1.63–1.69.

These results relate to some grades only and cannot be generalized.

4.24.4 Mechanical properties

The mechanical properties are good with medium to low elongations at break and more limited strains at yield. Moduli and hardnesses are in a high range but notched impact strengths are in a medium range. Polyetherimide displays notch sensitivity and stress concentrators must be avoided when designing.

Special grades with better wear resistance and coefficient of friction are marketed for tribological applications.

Dimensional stability

Alterations by moisture exposure are fair; shrinkage and coefficient of thermal expansion are rather low; creep resistance is good, the more so the higher the fibre content.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular or reinforcement orientation. For given PEI samples, Poisson's ratios are evaluated at:

- 0.44 for an unreinforced resin
- 0.4 for a 20% glass fibre reinforced grade
- 0.37 for a 40% glass fibre reinforced grade.

These examples cannot be generalized.

Creep

Creep behaviour is good even when the temperature rises. Neat PEI has rather high moduli that involve rather low strains for moderate loading. Consequently, creep moduli are also in a good range at room temperature and they decrease more slowly than the majority of other thermoplastics when the temperature rises. Reinforcement with fibres leads to high moduli and, consequently, high creep moduli.

Figure 4.110(a) shows the decrease in creep modulus for PEI when the load increases from 35 MPa up to 50 MPa at room temperature.

Figure 4.110(b) shows:

- The slow decrease of the creep modulus at 82°C.
- The moderate difference between creep at 23°C and 82°C.

These results relate to a few grades only and cannot be generalized.

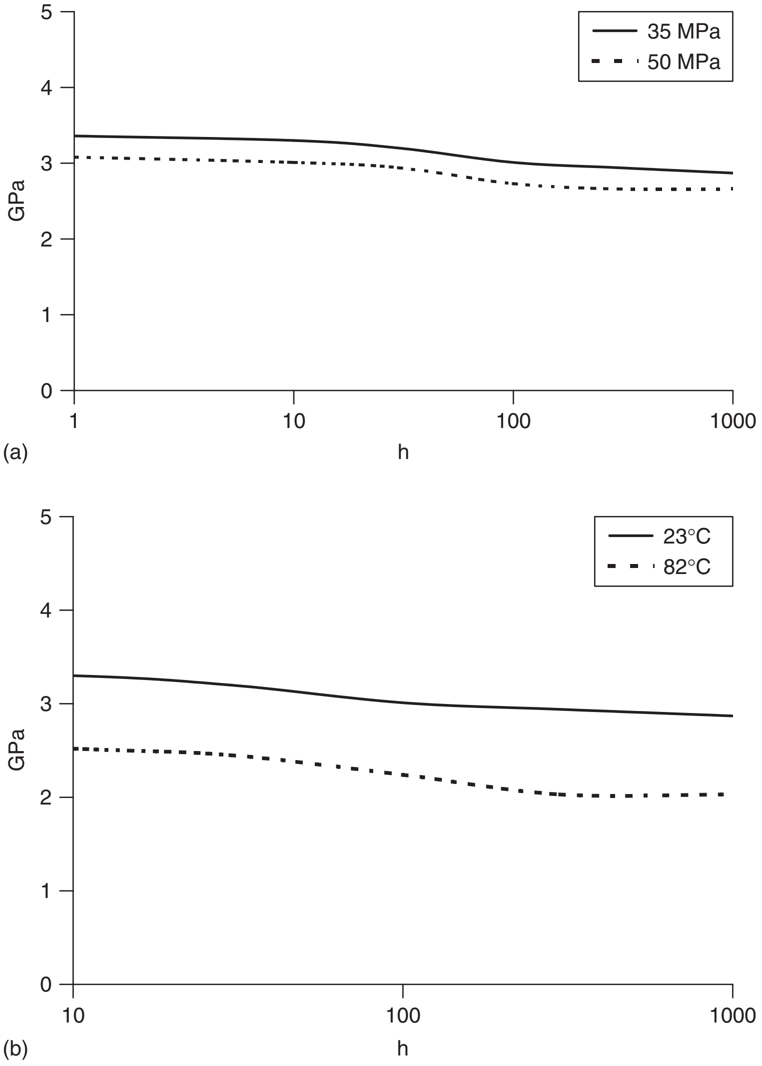


Figure 4.110. (a) PEI examples of creep modulus (GPa) versus time (h) under 35 & 50 MPa at room temperature; (b) PEI examples of creep modulus (GPa) versus time (h) under 35 MPa at 23°C & 82°C

4.24.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

Figure 4.111 displays examples of SN or Wöhler's curves for three given grades of neat and glass (GF) or carbon fibre (CF) reinforced PEI.

These results are examples only and they cannot be generalized.

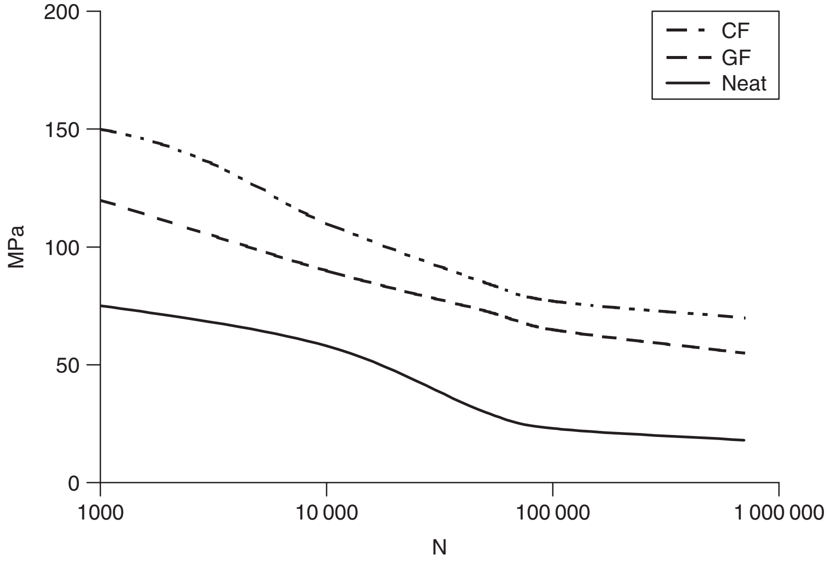


Figure 4.111. SN curve of PEI, examples of maximum stress (MPa) versus number of cycles at rupture (N)

Weathering

Polyetherimides are inherently resistant to UV and hydrolysis.

High-energy radiation

The resistance to gamma radiation is good without significant degradation after 500 Mrad; tensile strength retention is 94%.

Chemicals

The resistance to moisture, hot water and steam is good, with no hydrolysis. The polyetherimides can withstand multiple steam sterilizations. After 10 000 h in boiling water, a PEI retains 95% of its tensile strength. PEI resists repeated cycles of exposure to pressurized steam alternating with periods of vacuum at room temperature.

Suitably formulated compounds are usable in contact with food.

PEI resists mineral acids, dilute bases (pH less than 9), freons, oils, greases, gasoline, most fuels, certain hydrocarbons and fully halogenated hydrocarbons, most cooking oils and greases, most detergents and disinfectants. Ammonium hydroxide is the only common chemical producing a noticeable attack, with a lower tensile strength retention and more-pronounced swelling.

They are attacked by certain hydrocarbons, partially chlorinated solvents, and ketones.

Table 4.84 displays some results concerning tensile strength retention and weight gain after 100-day immersion in various chemicals at room temperature for given grades, which are not necessarily representative of all the polyetherimides. These general indications concerning short-term immersions should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.84 Polyetherimide: examples of tensile strength retention and weight gain after 100-day immersion at room temperature

Chemical	Concentration (%)	Tensile strength retention (%)	Weight gain (%)
Acetic acid	20	95	1.1
Ammonium hydroxide	10	68	1.8
Chromic acid	15	94	0.7
Citric acid	40	96	1.1
Cyclohexylamine	1	97	1.1
Deionized water	100	94	1.2
Formic acid	10	94	1.3
Hydrochloric acid	20	99	0.6
Nitric acid	20	96	1.1
Phosphoric acid	20	97	1.0
Potassium carbonate	30	97	0.8
Potassium hydroxide	10	97	1.5
Sodium hydroxide	10	97	1.0
Sulfuric acid	20	97	0.9
Tin chloride	10	97	1.0
Zinc chloride	10	96	1.1

Fire resistance

Polyetherimides are inherently fire resistant, with oxygen indices superior to 47 and a UL94 V0 rating. Compounding can improve these performances and certain grades reach an oxygen index of 50. In the event of fire, smoke emissions are low.

4.24.6 Electrical properties

Polyetherimides are good insulators even in hot and wet environments, with high dielectric resistivities and low loss factors. PEI is transparent to microwaves, which makes it usable for microwavable parts and utensils. Special grades are marketed for electrical applications.

4.24.7 Joining, decoration

Welding: ultrasound, friction, vibration and induction techniques give good results. Hot plate welding is not recommended.

Joining is possible with suitable adhesives. Preliminary tests are essential.

All precautions must be taken concerning health and safety according to local laws and regulations.

Decoration: painting, vacuum metallization by vapour deposition, sputtering, plating, dichroic coating give good results.

4.24.8 Trade name examples

Hydel, Lubricomp, RTP, Siltem, Stat-Kon, Tempalux, Ultem.

4.24.9 Property tables

Table 4.85 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.85 Polyetherimide: examples of properties

Filler	PEI		PEI Milled glass fibre		PEI Mineral	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.27	1.3	1.5	1.6	1.4	1.5
Shrinkage (%)	0.7	0.8	0.2	0.4	0.5	0.7
Absorption of water (%)	0.2	0.3			0.2	0.3
Mechanical properties						
Shore hardness, D	95	>95			95	>95
Rockwell hardness, R	>120	>120			>120	>120
Rockwell hardness, M	109	112			90	120
Stress at yield (MPa)	100	110	85	85	90	100
Strain at yield (%)	7	7	3	3	6	6
Tensile strength (MPa)	90	100	85	85	90	100
Elongation at break (%)	60	60	3	3	6	6
Tensile modulus (GPa)	3	3	7	7	5	7
Flexural modulus (GPa)	3	3.3	9	7	5	7
Modulus retention at 100°C (%)	85	90				
Modulus retention at 150°C (%)	65	70				
Notched impact strength ASTM D256 (J/m)	50	60			40	60
Thermal properties						
HDT B (0.46 MPa) (°C)	195	210	205	210	200	210
HDT A (1.8 MPa) (°C)	190	200	190	195	200	210
Continuous use temperature (°C)	170	180	170	180	170	180
Glass transition temperature (°C)	215	215	215	215	215	215
Thermal conductivity (W/m.K)	0.22	0.22	0.3	0.3		
Coefficient of thermal expansion (10^{-5}/°C)	5	6	2	3	2	5
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{17}	10^{15}	10^{16}	10^{15}	10^{15}
Dielectric constant	3.1	3.2			3	4
Loss factor (10^{-4})	13	25			10	15
Dielectric strength (kV/mm)	28	33			20	25
Arc resistance (s)	128	128			140	140
Fire behaviour						
Oxygen index (%)	47	47			48	48
UL94 rating	V0	V0	V0	V0	V0	V0
	PEI 30% GF		CF		Conductive	
Miscellaneous properties						
Density (g/cm^3)	1.5	1.6	1.3	1.4	1.3	1.4
Shrinkage (%)	0.2	0.4	0.2	0.4		
Absorption of water (%)	0.1	0.2				
Mechanical properties						
Shore hardness, D	95	>95				
Rockwell hardness, M	90	125				

Table 4.85 (Continued)

	PEI 30% GF		CF		Conductive	
Stress at yield (MPa)	160	160	200	200		
Strain at yield (%)	3	3	1	2		
Tensile strength (MPa)	160	160	200	200	200	210
Elongation at break (%)	3	3	2	2	2	2
Tensile modulus (GPa)	9	9	16	16		
Flexural modulus (GPa)	9	9	13.5	13.5	12	13
Modulus retention at 100°C (%)	95	95				
Modulus retention at 150°C (%)	90	90				
Notched impact strength ASTM D256 (J/m)	90	100			70	70
Thermal properties						
HDT B (0.46 MPa) (°C)	205	212	220	220	210	215
HDT A (1.8 MPa) (°C)	200	210	210	210	200	210
Continuous use temperature (°C)	170	180	170	180	170	>180
Glass transition temperature (°C)	215	215	215	215	215	215
Thermal conductivity (W/m.K)	0.29	0.33	0.36	0.36		
Coefficient of thermal expansion (10^{-5}/°C)	2	6	0.7	6	2	2.5
Electrical properties						
Volume resistivity (ohm.cm)	10^{14}	10^{16}			10^{4}	10^{6}
Dielectric constant	3	4				
Loss factor (10^{-4})	15	53				
Dielectric strength (kV/mm)	25	30				
Arc resistance (s)	85	85				
Fire behaviour						
Oxygen index (%)	50	50				
UL94 rating	V0	V0	V0	V0	V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV and hydrolysis resistant
Weak acids	Good behaviour
Strong acids	Good behaviour with dilute acids
Bases	Good behaviour limited to pH<9
Solvents	PEI resists mineral acids, dilute bases (pH less than 9), freons, oils, greases, gasoline, most fuels, certain hydrocarbons and fully halogenated hydrocarbons, most cooking oils and greases, most detergents and disinfectants They are attacked by certain hydrocarbons, partially chlorinated solvents, ketones
Food contact	Possible for special grades

4.25 Polyamide-imide (PAI)

Polyamide-imide is an amorphous thermoplastic having the formula shown in Figure 4.112.

4.25.1 General properties

Advantages

Polyamide-imides are appreciated for: good mechanical and electrical properties; high service temperatures (up to 220°C with possible long service times at 260°C); rigidity; good creep behaviour; fatigue endurance; low shrinkage and moisture uptake; inherent flame retardancy; chemical resistance; usability down to −196°C.

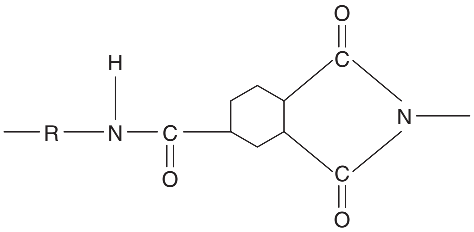


Figure 4.112. Example of polyamide-imide formula

Drawbacks

Polyamide-imides are handicapped by the cost (justified by the performances), a high density, the small numbers of grades and sources. PAI can slowly absorb some water in a wet environment, which has a plasticizing effect and can lead to a significant linear expansion.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- extrusion, injection, compression, machining, sonic welding . . .
- glass and carbon fibre reinforced, improved impact strength, wear resistant, improved electrical properties, better fatigue endurance, ESD . . .
- for electrical applications, bearings, aircraft, automotive . . .

Costs

As for all plastics, the costs fluctuate greatly with the crude oil price, and are only given to provide an idea. They are generally of the order of several tens of Euros to a hundred Euros per kilogram.

Processing

All the molten state methods are usable but the main ones are extrusion, injection, compression, machining.

Consumption

The consumption of polyamide-imide varies according to the country and the source, but is too low to be listed in statistics. It can be approximately divided into four main sectors:

- automotive & transport
- aircraft
- E&E
- industry.

Applications

(See Chapter 2 for further information.)

Polyamide-imide is an engineering plastic used only for specialized and technical applications.

The main applications are:

- non-lubricated bearings, seals, bearing cages, rotating and sliding components for automotive and industry, bushings, seal rings, wear pads, piston rings . . .
- ball bearings for America's Cup yachts . . .
- hook joints for transmission seal rings . . .
- tag axle assembly of cement trucks and heavy vehicles . . .
- vanes in air motor . . .
- reciprocating compressor parts . . .
- gears, valve plates, intake valves . . .
- impellers, rotors . . .
- material-handling components . . .
- terminal strips . . .
- ceramic-coated piston for 5-HP engine . . .
- insulators . . .
- ESD for integrated circuits, hard disk drives, circuit boards . . .
- parts for high-speed electronic printing and reproduction equipment . . .
- burn-in sockets . . .
- fibres for heat and fire protection; clothing for fighter pilots, army and police forces; smoke filtration . . .

4.25.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at up to 220°C, with the possibility of long use times at 260°C.

The UL temperature indices vary widely with the grade. Some of them reach 220°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- For a neat grade of polyamide-imide, compared to the value at ambient temperature, the percentage retention of flexural strength is roughly:
  - 72% at 150°C
  - 46% at 230°C
  - 35% at 260°C.
- For a carbon fibre reinforced polyamide-imide, compared to the value at ambient temperature, the percentage retention of flexural strength is roughly:
  - 77% at 150°C
  - 61% at 230°C
  - 55% at 260°C.
- For a neat PAI grade, compared to the value at ambient temperature, the percentage retention of moduli is roughly:
  - 77% at 150°C
  - 61% at 230°C
  - 55% at 260°C.
- For a carbon fibre reinforced polyamide-imide, compared to the value at ambient temperature, the percentage retention of moduli is roughly:
  - 88% at 150°C
  - 80% at 230°C
  - 77% at 260°C.
- HDTs under 1.8 MPa are of the order of 280°C.

Figure 4.113 displays three examples of flexural strength retention versus temperature for neat, carbon fibre reinforced and glass fibre reinforced polyamide-imides. The three curves are not distinguishable; note the steady decay up to 260°C.

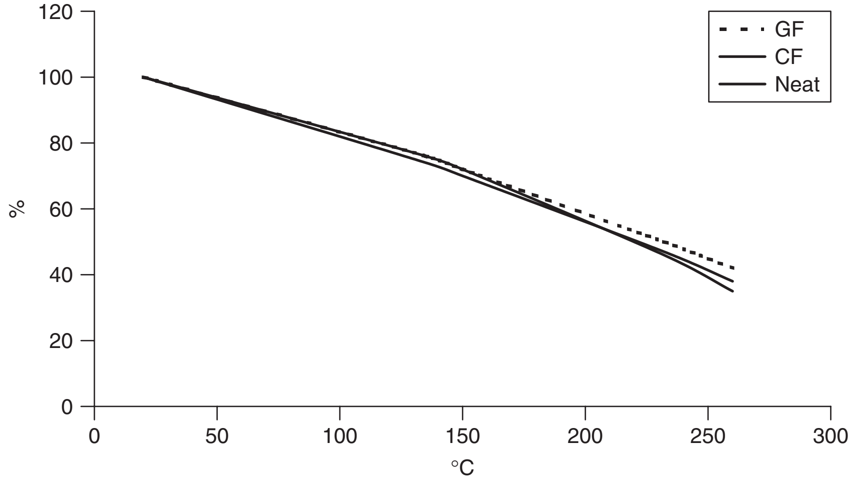


Figure 4.113. PAI examples of flexural strength retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially heat-sensitive characteristics.

Figure 4.114 displays the tensile strength of two PAIs after ageing in air at 260°C. Note that, after a maximum near 1500 h, tensile strengths gently decrease to reach 140–170 MPa after 10 000 h, which is a high value.

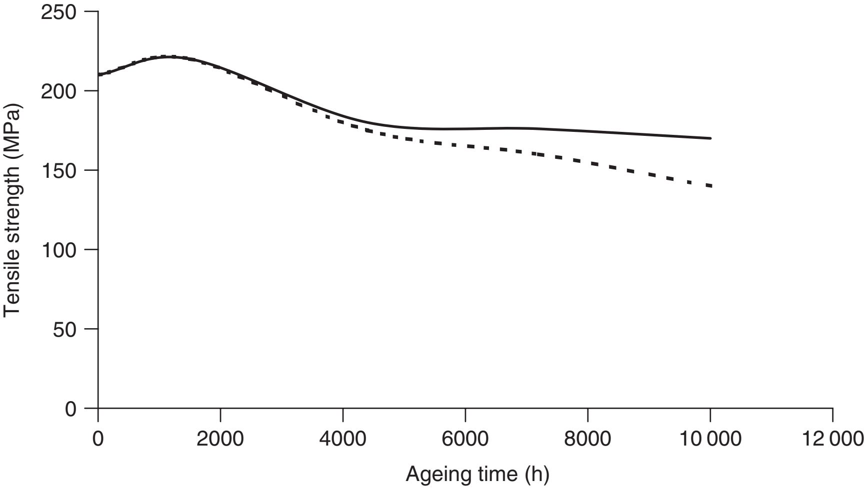


Figure 4.114. PAI examples of tensile strength (MPa) versus ageing time (h) at 260°C

The behaviour at low temperatures is good, depending on the grades and the mechanical constraints experienced.

Generally, polyamide-imide is usable down to −196°C and displays medium notched Izod impact strengths, which slowly decrease down to −50°C retaining, for example, 60% of the original value.

The glass transition temperature is high, roughly 275°C.

These results relate to some grades only and cannot be generalized.

4.25.3 *Optical properties*

Amorphous polyamide-imides are opaque.

4.25.4 *Mechanical properties*

The mechanical properties are good with medium to low elongations at break and more limited strains at yield. Moduli and hardnesses are in a high range and notched impact strengths are in a medium range.

Special grades with optimized wear resistance and coefficient of friction are marketed for tribological applications.

Friction

Some self-lubricating grades of polyamide-imides containing specific additives, and possibly reinforced with glass or graphite fibres, are marketed. The coefficients of friction are good: for example, 0.2 at room temperature for a neat grade and less for self-lubricated grades.

PV limits are in a high range, for example, 1.5–3 MPa.m/s.

Certain bearings are claimed to be operational at 200°C and above.

These results relate to a few grades only and cannot be generalized.

Dimensional stability

Alterations by moisture exposure are fair for short exposure times; shrinkage and coefficient of thermal expansion are rather low; creep resistance is good, the more so the higher the fibre content.

Long exposures to water or moisture can lead to a significant swelling, which leads to a significant linear expansion, for example 0.2% after 5000 h in air at 50% RH.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular or reinforcement orientation. For given PAI samples, Poisson's ratio is evaluated at:

- 0.45 for an unreinforced resin
- 0.43 for a glass fibre reinforced grade
- 0.39 for a graphite and PTFE filled grade or a carbon fibre reinforced grade.

These examples cannot be generalized.

Creep

Creep behaviour is good even when the temperature rises. Neat PAI has high moduli that involve low strains for moderate loading. Consequently, creep moduli are also in a good range at room temperature and they decrease more slowly than the majority of other thermoplastics when the temperature rises. Reinforcement with fibres leads to high moduli and, consequently, high creep moduli.

Figure 4.115(a) shows the decrease in creep modulus for PAI when the load increases from 70 MPa up to 105 MPa at room temperature. Note the high load level and the medium creep time.

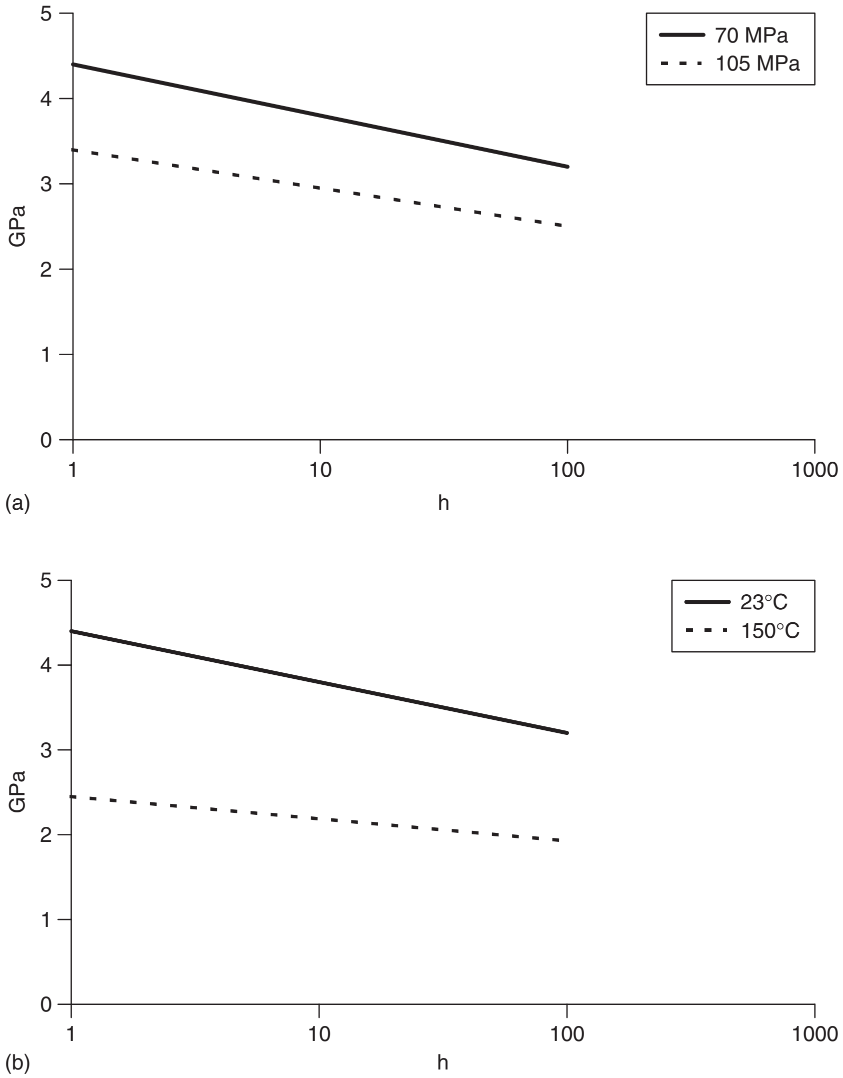


Figure 4.115. (a) PAI examples of creep modulus (GPa) versus time (h) under 70 & 105 MPa at room temperature; (b) PAI examples of creep modulus (GPa) versus time (h) under 70 MPa at 23°C & 150°C

Figure 4.115(b) shows:

- the slow decrease of the creep modulus at 150°C
- the moderate difference between creep at 23°C and 150°C. Note the high load and temperature (150°C).

These results relate to a few grades only and cannot be generalized.

4.25.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For three given grades of neat and GF or CF reinforced PAI, Figure 4.116 displays examples of SN or Wöhler's curves.

These results are examples only and they cannot be generalized.

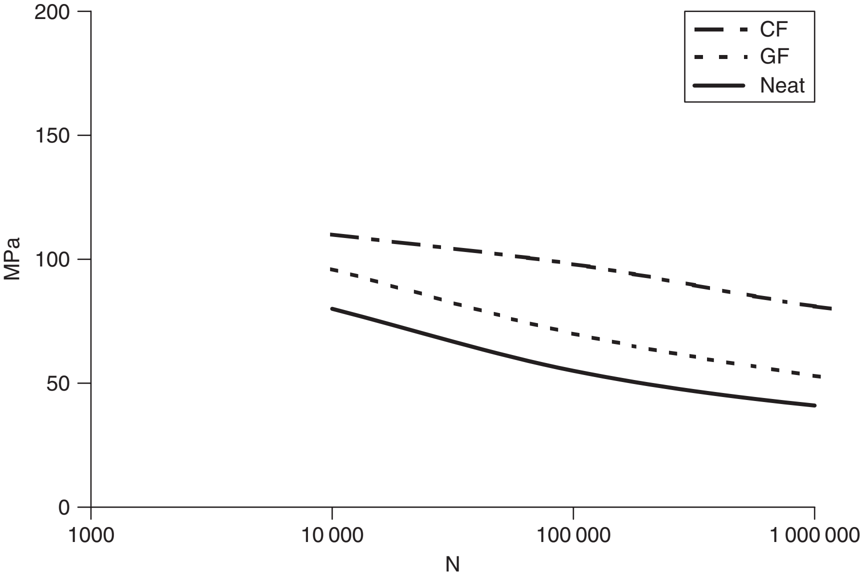


Figure 4.116. SN curves of PAI, examples of maximum stress (MPa) versus number of cycles at rupture (N)

High-energy radiation

The resistance to gamma radiation is good with acceptable degradation after 1000 Mrad exposure. For a given grade, property retentions are:

- 94% for the tensile strength
- 84% for the elongation at break.

Chemicals

The resistance to moisture, hot water and pressurized steam is good without hydrolysis, but long exposures to water or moisture can lead to a significant water uptake, which plasticizes the material.

For example after 5000 h in air at 50% RH, the water uptake is of the order of 2% and:

- linear expansion is of the order of 0.2%
- HDT decreases by about 40°C.

Polyamide-imides resist most acid and base solutions at low concentrations, alcohols, aldehydes, esters, aliphatic and aromatic hydrocarbons, greases, oils, gasoline, certain chlorinated hydrocarbons, and ketones.

They are attacked to a greater or lesser degree by concentrated bases and certain dilute bases, chlorine water and strong oxidizing agents, concentrated acids, dilute sulfuric and nitric acids, halogens, certain chlorinated solvents, and amines.

Table 4.86 displays some general assessments of behaviour for given grades after prolonged immersion in a range of chemicals at room temperature. The results are not necessarily representative of all the polyamide-imides. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.86 Polyamide-imide: examples of chemical behaviour at room temperature

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Acetic acid	10	S	Chlorine dioxide	Unknown	n
Acetic acid	>96	l	Chlorine water	Unknown	l
Acetic aldehyde	100	S	Chloroacetic acid	Unknown	l
Acetic anhydride	100	S	Chlorobenzene	100	S
Acetone	100	S	Chloroform	100	S
Acetophenone	100	S	Chromic acid	Unknown	S
Acetyl chloride	100	S	Citric acid	10	S
Aluminium chloride	Solution	S	Copper sulfate	Unknown	S
Aluminium sulfate	Unknown	S	Cresol	100	S
Ammonium hydroxide	30	n	Cyclohexane	100	S
Ammonium sulfate	50	S	Cyclohexanol	100	S
Amyl acetate	100	S	Cyclohexanone	100	S
Amyl alcohol	100	S	Dichloroethylene	100	S
Aniline	100	n	Diethylamine	100	l
Aqua regia	Unknown	n	Diethylether	100	S
ASTM1 oil	100	S	Dimethylformamide	100	l
ASTM2 oil	100	S	Dioctylphthalate	100	S
ASTM3 oil	100	S	Dioxan	100	S
Barium chloride	Saturated	S	Ethanol	Unknown	S
Benzaldehyde	100	S	Ethylacetate	100	S
Benzene	100	S	Ethylchloride	100	S
Benzylchloride	100	S	Ethylene glycol	100	S
Benzyl alcohol	100	S	Fluorine	100	n
Boric acid	Unknown	S	Formic acid	40	S
Butanol	100	S	Formic acid	85	n
Butyl acetate	100	S	Furfural	100	S
Butylchloride	100	S	Glycerol	100	S
Calcium chloride	Unknown	S	Hexane	100	S
Carbon sulfide	100	S	Hydrobromic acid	48	n
Carbon tetrachloride	100	S	Hydrochloric acid	10	l
Castor oil	100	S	Hydrochloric acid	36	n
Cellosolve	100	S	Hydrofluoric acid	40	n
Chlorine (dry gas)	100	l	Hydrogen peroxide	30	l

Table 4.86 (Continued)

Chemical	Concentration (%)	Estimated behaviour	Chemical	Concentration (%)	Estimated behaviour
Hydrogen peroxide	90	n	Potassium hydroxide	45	n
Hydrogen sulfide gas	Unknown	l	Potassium permanganate	20	n
Iron(III) chloride	Unknown	S	Potassium sulfate	Unknown	S
Isooctane (Fuel A)	100	S	Pyridine	Unknown	n
Lead acetate	10	S	Sea water	100	S
Linseed oil	100	S	Silver nitrate	Unknown	S
Liquid paraffin	100	S	Sodium borate	Unknown	S
Magnesium chloride	Unknown	S	Sodium carbonate	10	S
Mercury chloride	Unknown	S	Sodium chloride	25	S
Methanol	100	S	Sodium hydroxide	10–55	n
Methylbromide	100	S	Sodium hypochlorite	20	n
Methylene chloride	100	n	Sodium nitrate	Solution	S
Methylethylketone	100	S	Sulfuric acid	10–70	l
Mineral oil	100	S	Sulfuric acid	⩾96	n
Nickel chloride	Unknown	S	Sulfurous anhydride (gas)	Unknown	S
Nitric acid	10	l	Tin chloride	Unknown	S
Nitric acid	⩾65	n	Toluene	100	S
Nitrobenzene	100	S	Transformer oil	100	S
Oxalic acid	Unknown	l	Trichloroethylene	100	n
Perchloroethylene	100	l	Turpentine oil	100	S
Petroleum	100	S	Vegetable oil	100	S
Phenol	Unknown	S	Water	100	S
Phosphoric acid	85	n	Wine	Unknown	S
Potassium cyanide	Unknown	S	Xylene	100	S
Potassium fluoride	Unknown	S	Zinc chloride	Unknown	S

S: satisfactory; l: limited; n: not satisfactory

Fire resistance

Polyamide-imides are inherently fire resistant with oxygen indices superior to 42 and a UL94 V0 rating. In the event of fire, smoke emissions are low.

4.25.6 Electrical properties

Polyamide-imides are good insulators even in hot environments, with high dielectric resistivities. Special grades are marketed for electrical applications.

4.25.7 Joining, decoration

Welding: the ultrasound technique is suitable.

Joining is possible with suitable adhesives. Preliminary tests are essential.

All precautions must be taken concerning health and safety according to the local laws and regulations.

4.25.8 Trade name examples

Kermel, Torlon.

4.25.9 Property tables

Table 4.87 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.87 Polyamide-imide: examples of properties

	PAI		PAI 30% Glass fibre		PAI Carbon fibres	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.4	1.42	1.6	1.6	1.48	1.5
Shrinkage (%)	0.6	1	0.1	0.3	0.2	0.3
Absorption of water (%)	0.1	0.3	0.1	0.3		
Mechanical properties						
Shore hardness, D	95	>95	95	>95		
Rockwell hardness, M	86	100	95	110		
Tensile strength (MPa)	130	195	105	210	203	203
Elongation at break (%)	15	15	3	7	6	6
Tensile modulus (GPa)	4.2	5	11	15	22	23
Flexural modulus (GPa)	4	5	11	15	19	20
Notched impact strength ASTM D256 (J/m)	110	150	40	80	47	47
Thermal properties						
HDT A (1.8 MPa) (°C)	278	278	280	280	282	282
Continuous use temperature (°C)	220	220	220	220	220	220
Glass transition temperature (°C)	275	275	275	275	275	275
Thermal conductivity (W/m.K)					0.53	0.53
Coefficient of thermal expansion (10^{-5}/°C)	2	4	1	3	1	1
Electrical properties						
Volume resistivity (ohm.cm)	10^{17}	10^{18}	10^{14}	10^{18}		
Dielectric constant	3.9	4.2	4.2	6.3		
Loss factor (10^{-4})	10	310	220	500		
Dielectric strength (kV/mm)	23	24	32	33		
Fire behaviour						
Oxygen index (%)	45	45	51	51	52	52
UL94 rating	V0	V0	V0	V0	V0	V0
	Graphite powder		Mineral-filled		For bearings	
Miscellaneous properties						
Density (g/cm^3)	1.4	1.5	1.5	1.6	1.4	1.5
Shrinkage (%)					0.1	0.5
Absorption of water (%)	0.2	0.3	0.2	0.2	0.1	0.4
Mechanical properties						
Shore hardness, D					95	>95
Rockwell hardness, M					95	110
Stress at yield (MPa)					125	165
Strain at yield (%)					7	9
Tensile strength (MPa)	160	170	147	148	84	165
Elongation at break (%)	7	7	5	5	3	9
Tensile modulus (GPa)	6	7			5	7
Flexural modulus (GPa)	6	7	7	8	5	7
Notched impact strength ASTM D256 (J/m)	60	65	70	75	50	80
Thermal properties						
HDT A (1.8 MPa) (°C)	279	280	270	270	280	280
Continuous use temperature (°C)	220	220	220	220	220	220

Table 4.87 (Continued)

	Graphite powder		Mineral-filled		For bearings	
Glass transition temperature (°C)	275	275	275	275	275	275
Thermal conductivity (W/m.K)	0.54	0.54			0.53	0.53
Coefficient of thermal expansion (10^{-5}/°C)	1	2	1	2	2	3
Electrical properties						
Volume resistivity (ohm·cm)	10^{15}	10^{16}			10^{15}	10^{16}
Dielectric constant	5.4	6			5	8
Loss factor (10^{-4})	370	420			370	630
Fire behaviour						
Oxygen index (%)	44	44			44	44
UL94 rating	V0	V0	V0	V0	V0	V0

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Weak acids	Good to limited behaviour according to the concentration
Strong acids	Good behaviour with certain dilute acids, attacked by concentrated acids, dilute sulfuric and nitric acids
Bases	Good behaviour only with low concentration solutions, attacked by certain bases
Solvents	Polyamide-imides resist alcohols, aldehydes, esters, aliphatic and aromatic hydrocarbons, greases, oils, gasoline, certain chlorinated hydrocarbons, ketones They are attacked by chlorine water, strong oxidizing agents, halogens, certain chlorinated solvents, amines

4.26 Polyimides (PI)

The polyimide resins are obtained in two ways:

- Condensation polyimides or SP-polyimides: from the solvent-phase reaction of an aromatic tetra-acid with a diamine. Despite the thermoplastic form they are infusible and generally insoluble. Consequently, the producer can only mould this type. It is particularly convenient for the manufacture of thin parts and films, coatings . . .
- BMI or aminobismaleimides or addition polyimides: from the reaction of a diamine and a bismaleimide to make a prepolymer that is then cured by an excess of diamine. This type is particularly convenient for the manufacture of thick parts.

All the polyimides are thermostable. They do not melt before decomposition at high temperature. In thermogravimetric analysis, the decomposition starts at more than 400°C.

The properties are not differentiated enough to be treated separately. However, one of the methods leads to products of higher thermal resistance, but with more limited processing.

Polyimides are high-performance technical polymers mainly used for their short- and long-term thermal stability.

4.26.1 General properties

Advantages

Very good short- and long-term heat stability allowing continuous use up to 260°C and peak service up to 480°C, according to the duration and the grade; good mechanical properties, limited creep, low coefficient of friction and high abrasion resistance of the friction grades; resistance to numerous organic chemicals: stability of the electrical properties, depending on the temperature; resistance to high-energy radiation; limited vacuum outgassing after moisture elimination.

The polyimides are typical polymers for very-high-performance applications.

Drawbacks

The high prices, frequently long and energy-intensive production cycles, processing difficulties, and health & safety considerations during manufacture are justified by the high performances. The light stability, arc resistance and base and acid behaviours can be limited.

Special grades

They can be classified according to the processing methods, specific properties, or targeted applications:

- for specific processing: compression, transfer or injection moulding; prepregs, filament winding; impregnation, stratification, encapsulation, varnishing.
- reinforced or modified grades: glass or carbon fibres, glass beads; high, medium or low flow; for crystallization . . .
- for specific applications: self-lubricating filled with graphite, graphite and fibres, PTFE etc . . . for friction parts; for electronics.

The semi-products are, for example: blanks, films, filaments, rods.

Costs

As for all plastics, the costs fluctuate greatly with the crude oil price, and are only given to provide a general idea. They are typically of the order of several tens of Euros to a hundred Euros per kilogram for raw materials and much more for films, filaments, rods, blanks and parts.

Processing

For condensable polyimides, the current processing methods are applicable only by the polyimide producer that sells finished parts, blanks, rods, sheets, films . . . Machining is an important method for processing the polyimide blanks.

The main processing methods for addition polyimides are: machining; compression, transfer and injection moulding; encapsulation, impregnation, stratification, filament winding, varnishing, sintering.

Consumption

The consumption of polyimides by industrialized countries is not listed in the economic statistics. The global consumption can be estimated between 5000 and 10 000 tonnes per year, and can be approximately divided into three main sectors:

- more than 50% for industry
- 20% for E&E
- A few percent for automotive & transport.

It is estimated that the growth in PI consumption slightly exceeds the overall growth rate for plastic consumption.

Applications

(See Chapter 2 for further information.)

Polyimides are engineering plastics used only for specialized and technical applications.

The applications are always high-tech. The price and the difficulty of transformation limit the use of polyimides to well-targeted applications taking advantage of the high performance of these materials.

Some examples of operational or development parts are listed below.

- Aeronautical and space
  - bearings, grooved couplings in self-lubricating polyimide
  - jet engine cones, hydraulic fluid tanks for jet engines, stiffeners of acoustic panels, spacers for engine acoustic panels, protection hoods, empennages, supports for satellite antennas
  - honeycombs
  - parts intended to function in space vacuum
  - soundproofing and thermal insulation of missiles, planes and helicopters; cryogenic protection on satellites, piping insulation, protections for embarked equipment in polyimide foams.
- Automotive
  - self-lubricated discs for windscreen wipers, synchronization rings of heavy lorry gearboxes
  - base plates of cigar-lighters, bases of car lamps
  - heat shields, insulation shields for sparkplug leads in polyimide sheet.
- Office automation
  - plate bearings for printers, cable guides for printer heads; bearings and sockets for photocopiers; sliding parts and guiding rollers for high-speed printers and photocopiers . . .
  - paper/print drum separation arms, drive wheels for photocopiers, drive rollers.
- Electrical & electronics
  - insulating elements and spacers for electron accelerators and cathode-ray tubes
  - overmoulding of motor collectors, bodies of generator coils, overmoulding of coils, coil frames, insulation of rotor axis
  - printed circuit boards usable up to 300°C
  - terminal plates and terminals, lamp bases, connectors, parts of circuit breakers
  - insulating collars for chain saws, insulating elements and crossings for electric blowtorches
  - drive wheels for microwave ovens, handles for electric ovens and other household appliances, parts for spit-roasters, air vents for slide projectors
  - syntactic foams for microwave and RF applications.
- Industrial
  - honeycombs for structural sandwich composites
  - paper for fire-resistant uses
  - brakes on textile winding machine, pump pads, joint seatings, manipulator inserts for glass bottle demoulding, gears of variable speed transmissions, toothed wheels

  - ○ piston rings of ethylene compressors, dry bearings, sliding plates, guides for cast solid films in self-lubricated polyimide
  - ○ guiding rollers of grinder bands, sealing discs of valves in an industrial Freon compressor, segments of air compressors
  - ○ racks and handling cases for printed circuit board treatments, valve seats, piston rings for hydraulic installations for the chemical industry
  - ○ cryogenic insulation in polyimide foams.
- Vacuum technology
  - ○ seals and other parts for high-vacuum installations usable up to 300°C without lubrication
  - ○ joints and linings for vacuum pumps.
- Miscellaneous
  - ○ non-flammable scenery, coloured-filter holders for studios and theatres, spotlights, fire-resistant wallpaper
  - ○ voice coil insulation for stereo loudspeaker in or including Nomex paper
  - ○ disposable cookware in Nomex paper
  - ○ microspheres for syntactic foams.

4.26.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at up to 250–260°C, but in some cases are lower at 170–180°C. Higher peak temperatures, up to 480°C, can be tolerated.

The UL temperature indices vary broadly with the grade. Some are claimed to be 170°C. Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

The property retention when the temperature rises is generally excellent but depends on the matrix, the nature and level of fillers and reinforcements, and the base properties.

For example:

- For various grades, the percentage retention of strength relative to the value at ambient temperature is roughly:
  - ○ 57% for compressive strength at 240°C
  - ○ 50–85% for tensile strength at 250°C
  - ○ 44% for flexural strength at 250°C
  - ○ 54–68% for flexural strength at 260°C.
- For various grades, the percentage retention of moduli relative to the values at ambient temperature are roughly:
  - ○ 55% for flexural modulus at 250°C
  - ○ 60–85% or even 90% for a non-specified modulus at 250°C
  - ○ 52–61% for flexural modulus at 260°C.

The HDT A (1.8 MPa) are always high, greater than 250°C and up to 360°C according to the polyimide and the reinforcement.

Figure 4.117 displays three examples of flexural modulus retention versus temperature for various polyimides; note the low or moderate decay up to 250°C.

For long-term heat ageing, property retention depends on the property and grades considered. Impact strength and elongation at break are especially heat-sensitive characteristics.

Figure 4.118 shows three examples, for three different polyimide grades, of the half-lives (50% mechanical performance retention) in hours versus the air-ageing temperature indicated in °C.

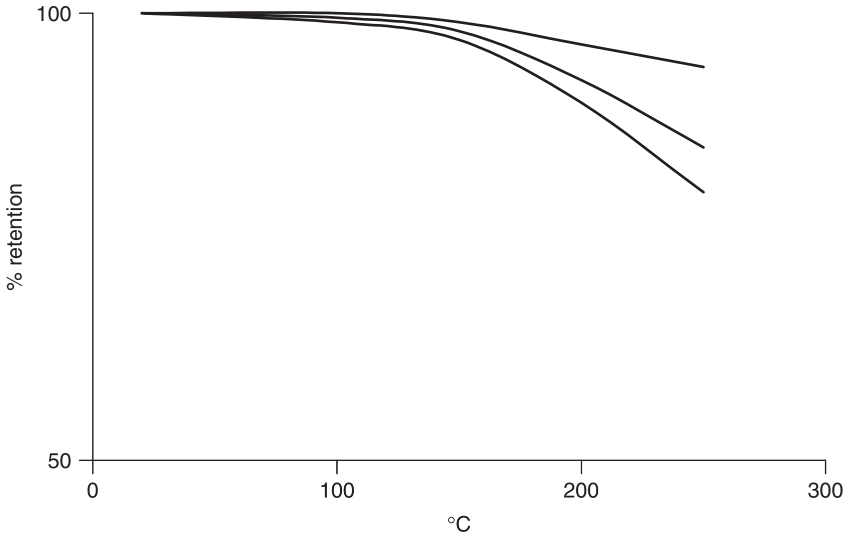


Figure 4.117. Polyimides: examples of flexural modulus retention versus temperature

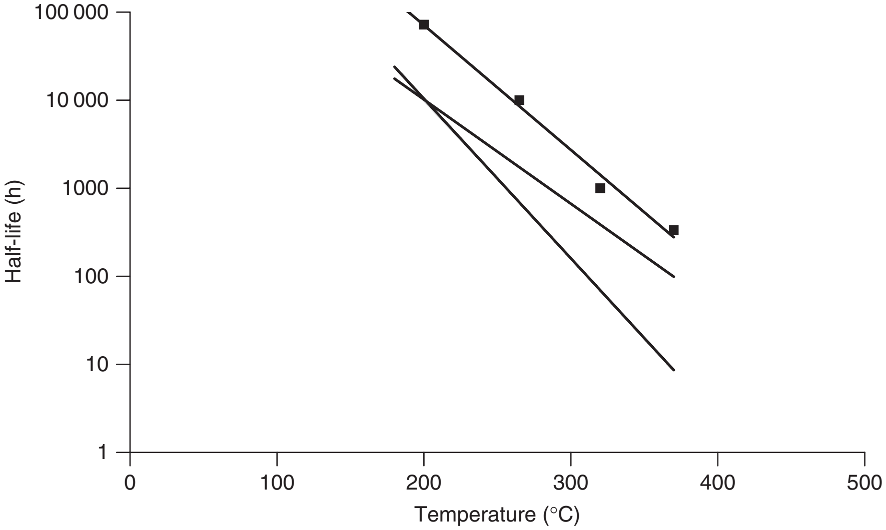


Figure 4.118. Polyimides: examples of half-life versus temperature

The results are correctly simulated by an Arrhenius law with predicted 25 000-hour-service temperatures between approximately 165°C and 235°C.

NASA is developing a special polyimide (PETI-5) for the High Speed Civil Transport (Mach 2.4) whose lifespan is more than 60 000 hours at 177°C with excellent property retention at this temperature.

The behaviour of polyimides is generally also good at low temperatures, allowing use from −60°C down to −250°C, according to the grades and the stresses.

As films, certain polyimides remain functional at cryogenic temperatures, −269°C for example.
Typical glass transition temperatures for polyimides are 300°C and above.
These results relate to some grades only and cannot be generalized.

4.26.3 Optical properties

Generally, thick parts are opaque and yellow to brown. Certain films are transparent with, for given grades:

- refractive indices of 1.66 to 1.7
- haze of 0.1%
- light transmission of 64%.

These results relate to some grades only and cannot be generalized.

4.26.4 Mechanical properties

The mechanical properties are good with rather low elongations at break and medium moduli for neat grades. Property retention is good when the temperature rises. The abrasion resistance depends on the roughness, type and morphology of the contacting counterpart sliding surface. The wear resistance and coefficient of friction of special grades are suitable for antifriction applications.

Friction

Special grades can be filled with graphite and possibly carbon or aramid fibres, PTFE, or molybdenum sulfide.

The PV limit can be medium or high with low coefficient of friction and low wear rate, as shown in Table 4.88, which gives some examples for PV ranging from 0.09 MPa.m/s to 4 MPa.m/s. However, significantly higher values, up to thousands of MPa.m/s, are quoted for certain sources with very high wear.

Figure 4.119 illustrates the evolution of the friction coefficient of a given polyimide grade versus temperature under a pressure of 14 MPa and a velocity of 2.5 cm/s, that is, a PV of 0.35 MPa.m/s.

Table 4.88 Polyimides: examples of tribological properties

PV (MPa·m/s)	Pressure, P (MPa)	Velocity, V (m/s)	Coefficient of friction	Wear rate after 1000 h (mm)
0.09			0.1–0.3	
0.15	0.3	0.5	0.1–0.3	0.04–0.5
0.24	0.4	0.6	0.1–0.3	Unknown
0.33	0.3	1.1	0.1–0.3	0.1–2.1
0.35	0.35	1	0.1–0.2	0.2–0.8
0.35	14	0.025	0.2–0.3	Unknown
0.875	Unknown	Unknown	0.12–0.24	Unknown
3.5	Unknown	Unknown	0.08–0.12	Unknown
4	1	4	0.07	Unknown
1252	Unknown	Unknown	0.08	80
25 000	Unknown	Unknown	Unknown	1.5–30

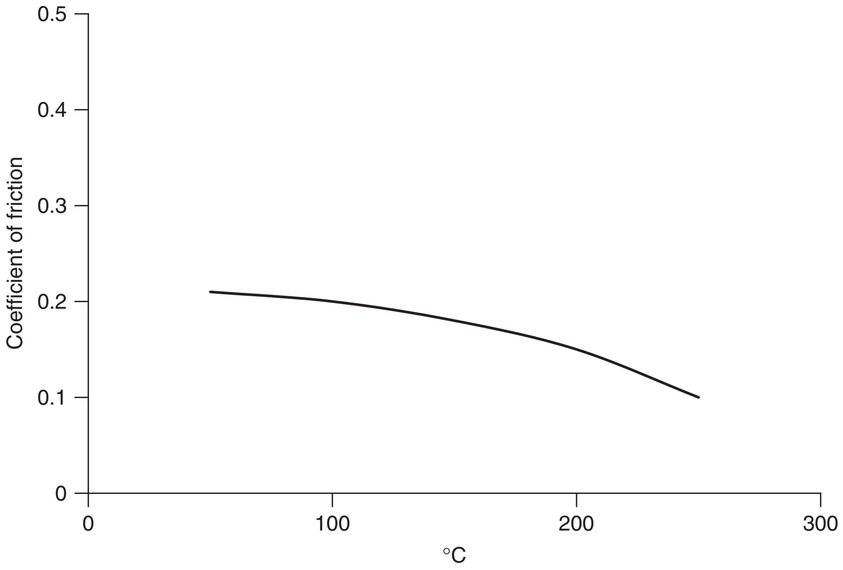


Figure 4.119. Polyimides: example of coefficient of friction versus temperature

These results relate to a few grades only and cannot be generalized.

Dimensional stability

The shrinkage is generally limited, the coefficient of thermal expansion is often moderate or low, the creep is good but, on the other hand, the absorption of water or moisture can be relatively significant. Thus, dimensional stability in a dry atmosphere is good, but can be degraded in water or in the presence of moisture. Figure 4.120 illustrates the differences in linear dilation of a given grade according to the relative humidity of the ambient atmosphere.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the used grade and its processing, the temperature, the possible reinforcements, the testing direction with regard to the molecular or reinforcement orientation. For given grades, they are evaluated at 0.32–0.4.

These examples cannot be generalized.

Creep

Creep behaviour is good even when the temperature rises. Neat polyimides have medium moduli that involve rather low strains for moderate loading. Consequently, creep moduli are also in a good range at room temperature but they decrease more slowly than the majority of other thermoplastics when the temperature rises. Reinforcement with fibres leads to high moduli and, consequently, high creep moduli.

Figure 4.121 presents, for a given grade, some examples of the evolution of the creep modulus for various conditions of load and temperature. Note the creep modulus of 0.6 GPa after 1000 hours under a 17 MPa load at 300°C.

These results relate to a few grades only and cannot be generalized.

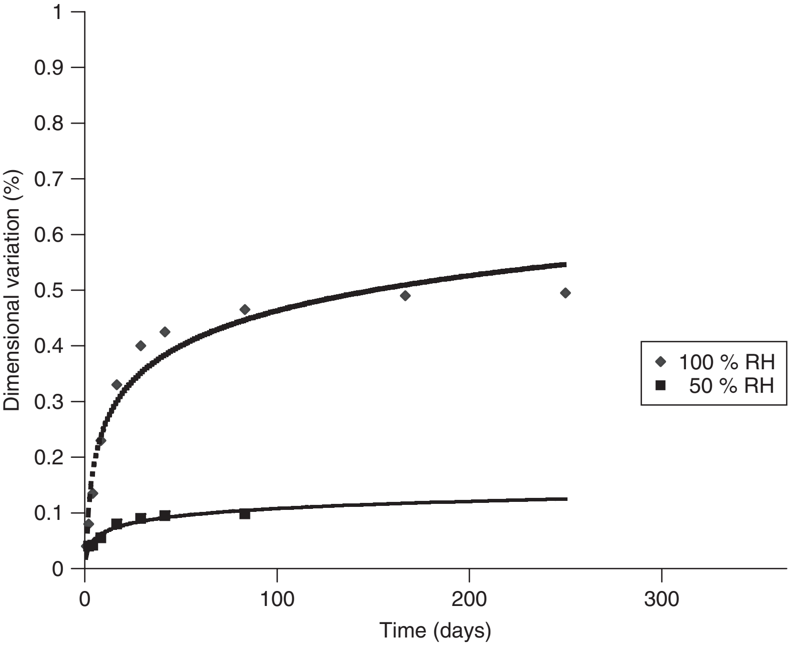


Figure 4.120. Polyimides: examples of linear dimensional variation (%) versus time (days)

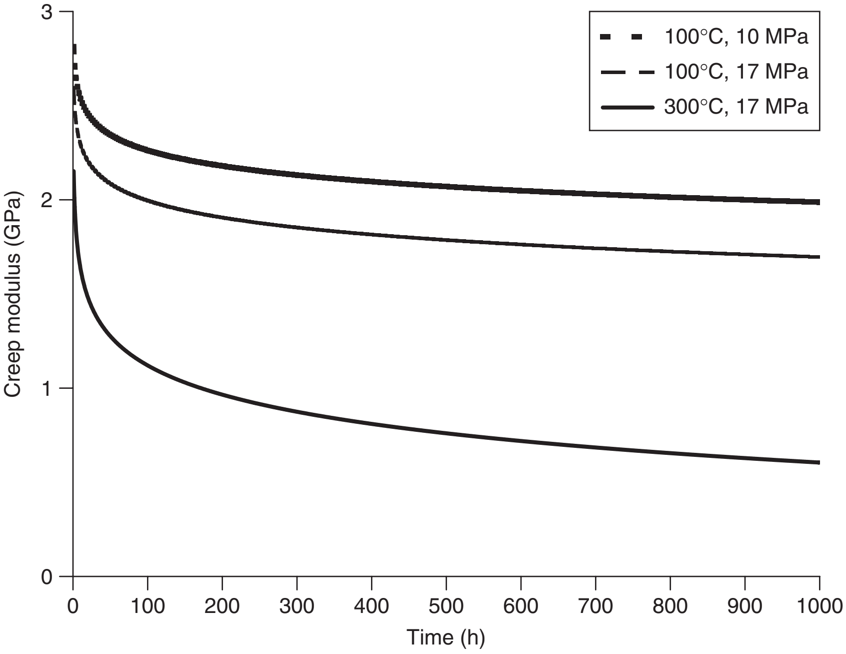


Figure 4.121. Polyimides: examples of creep modulus (GPa) versus time (h) at 100°C and 300°C

4.26.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

Figure 4.122 displays examples of SN curves for two grades, with the maximum stress in traction/compression at 30 Hz frequency versus the number of loading cycles.

Figure 4.123 shows two examples of curves of the maximum stress for 10^7 cycles in traction and compression at a frequency of 30 Hz, versus the test temperature.

These results relate to tested grades only and cannot be generalized.

Weathering

Weathering can cause decreases in some properties such as strength and elongation at break. Preliminary tests are necessary for outdoor-exposed parts.

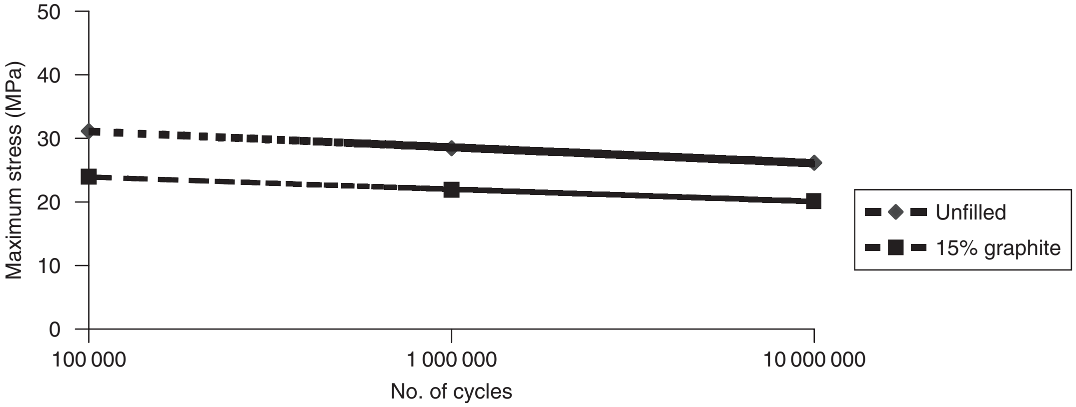


Figure 4.122. Polyimide: two examples of SN curves; maximum stress (MPa) versus loading cycle number

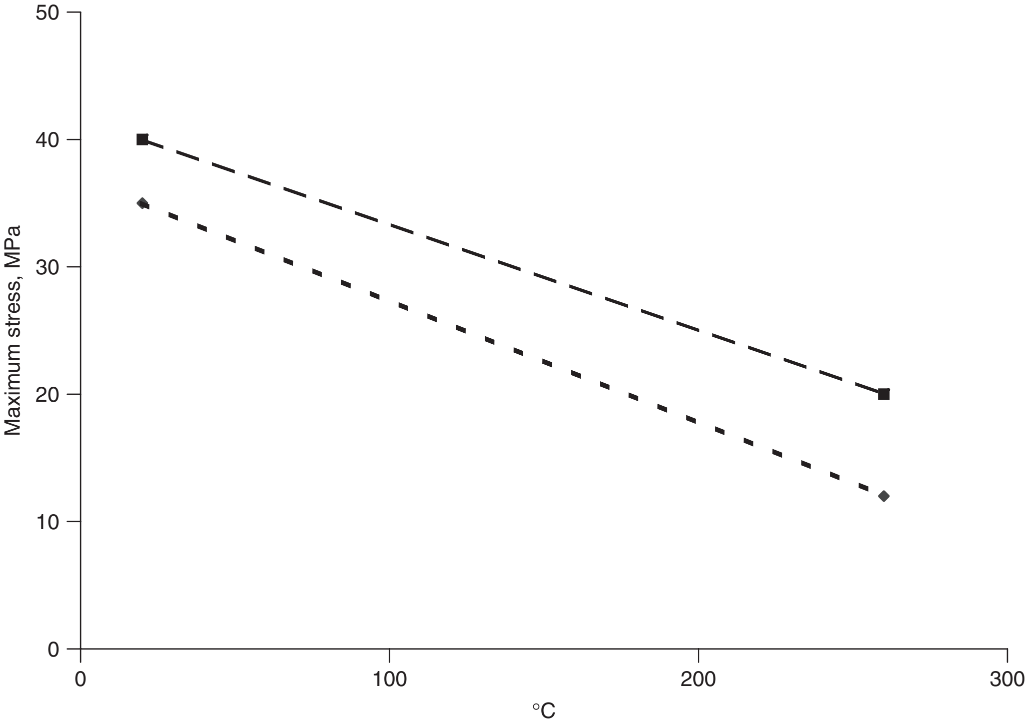


Figure 4.123. Dynamic fatigue of polyimide: two examples of maximum stress (MPa) at 10^7 cycles versus temperature

Figure 4.124 shows two examples of the retention of tensile strength and elongation at break for a film exposed to the Weather-Ometer.

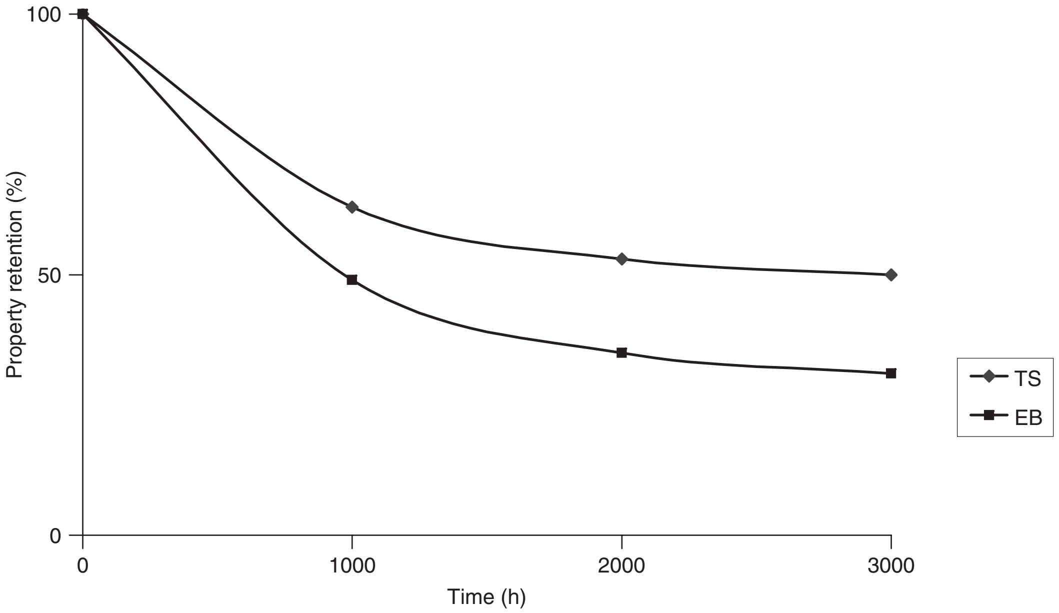


Figure 4.124. Polyimide: retention of tensile strength and elongation at break versus Weather-Ometer exposure time (h)

High-energy radiation

Certain polyimides resist high-energy radiation well. For example, the properties of certain grades are still suitable after exposure to 10^3 and 10^4 Mrad.

These results are examples only and they cannot be generalized.

Chemicals

The polyimides absorb water and moisture to greater or lesser degrees. This plasticizes them, involving immediate decreases of 10–25% in characteristics, depending on the grades and the conditions. In long exposures, the effect is more significant and the type of polyimide is of prime importance. As examples, for two given grades, the retention of tensile strength after immersion in boiling water is:

- 55% after 500 hours for one grade
- 77% after 3000 hours for the other.

The following swellings were noted for four different grades:

- 1.5% after 7 days in boiling water
- 0.1–2% after 300 days in ambient air at 50% RH
- 0.5% after 300 days in ambient air at 100% RH.

Generally, the weak acid behaviour is good at ambient temperature, but limited at higher temperature. Resistance to strong acids and bases is poor even at ambient temperature.

The behaviour with organic materials is generally good, except for alkaline products (amines, for example) and certain specific chemicals such as metacresol and hot nitrobenzene, which cause significant swelling (75–85%, for example).

Table 4.89 displays some general assessments, strength decreases and weight change percentages after immersion in various chemicals for one month to more than one year at ambient temperature for given grades, which are not necessarily representative of all the polyimides. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.89 Polyimides: examples of chemical behaviour at room temperature

Chemical	Duration (days)	Concentration (%)	Estimated behaviour	Swelling (%)	Strength decrease (%)
Acetic acid	7	5		0.8	
Acetic acid	Long	10	l		
Acetic acid	100	20		1.2	5
Acetic acid	Long	>96	l		
Acetic aldehyde	Long	100	S		
Acetic anhydride	Long	100	S		
Acetone	Long	100	S		
Acetonitrile	Long	100	S		
Acetophenone	Long	100	S		
Acetyl chloride	Long	100	S		
Aluminium chloride	Long	Sol	S		
Aluminium sulfate	Long	Unkn	S		
Amines	Long	Unkn	n		
Ammonium hydroxide	7	10	n	1	23
Ammonium hydroxide	100	10	n	1.8	32
Ammonium hydroxide	Long	Conc.	n		
Ammonium sulfate	Long	50	S		
Amyl acetate	Long	100	S		
Amyl alcohol	Long	100	S		
Aniline	Long	100	n		
Antimony chloride	Long	10	S		
ASTM1 oil	Long	100	S		
ASTM2 oil	Long	100	S		
ASTM3 oil	7	100		0	
ASTM3 oil	Long	100	S		
Barium chloride	Long	Satur	S		
Benzaldehyde	Long	100	S		
Benzene	Long	100	S		
Benzyl chloride	Long	100	S		
Benzyl alcohol	Long	100	S		
Boric acid	Long	Unkn	S		
Bromine (liquid)	Long	100	l		
Butanol	Long	100	n		
Butyl acetate	Long	100	S		
Butyl amine	Long	Unkn	S		
Butyl chloride	Long	100	S		
Calcium chloride	Long	Unkn	S		
Carbon sulfide	Long	100	S		
Carbon tetrachloride	Long	100	S		
Cellosolve	Long	100	S		

(*Continued*)

Table 4.89 (Continued)

Chemical	Duration (days)	Concentration (%)	Estimated behaviour	Swelling (%)	Strength decrease (%)
Chlorine water	Long	Unkn	l		
Chlorobenzene	Long	100	S		
Chloroform	Long	100	l		
Chromic acid	Long	Unkn	n		
Citric acid	100	40		1.1	4
Citric acid	Long	10	S		
Copper sulfate	Long	Unkn	S		
Cresol	Long	100	S		
Cyclohexane	Long	100	S		
Cyclohexanol	Long	100	S		
Cyclohexanone	Long	100	S		
Cyclohexylamine	100	1		1.1	3
Diethyl amine	Long	100	l		
Diethylene glycol	Long	100	n		
Dimethyl formamide	Long	100	l		
Dioctyl phthalate	Long	100	S		
Dioxan	Long	100	S		
Engine oil 200°C	30	100			30
Ethanol	Long	96	S		
Ethanol	Long	Unkn	n		
Ether	Long	100	S		
Ethyl acetate	Long	100	S		
Ethyl chloride	Long	100	S		
Ethylene glycol	Long	100	n		
Fluorine	Long	100	l		
Formaldehyde	Long	37	l		
Formic acid	100	10		1.3	6
Formic acid	Long	85	n		
Freon	7	100		0.2	
Freon 12	Long	100	S		
Furfural	Long	100	S		
Glycerol	Long	100	n		
Grease	Long	Unkn	S		
Hexane	Long	100	S		
Hydraulic fluid	Long	100	S		
Hydrobromic acid	Long	48	n		
Hydrochloric acid	100	20	l	0.6	1
Hydrochloric acid	Long	36	n		
Hydrochloric acid	5	37			30
Hydrofluoric acid	Long	40	n		
Hydrogen peroxide	Long	30	n		
Isooctane (Fuel A)	Long	100	S		
Isopropanol	Long	100	n		
Kerosene	Long	100	S		
Methanol	Long	100	n		
Methylethylketone	Long	100	S		
Mineral oil	Long	100	S		
Nitric acid	7	10	l		20–26
Nitric acid	100	20		1.1	4
Nitric acid	5	70	n		60
Oxalic acid	Long	Unkn	l		
Perchloroethylene	Long	100	l		
Petrol	Long	100	S		
Phenol	Long	Unkn	l		

Table 4.89 (Continued)

Chemical	Duration (days)	Concentration (%)	Estimated behaviour	Swelling (%)	Strength decrease (%)
Phosphoric acid	Long	85	n		
Potassium carbonate	100	30		0.8	3
Potassium hydroxide	100	10		1.6	3
Potassium hydroxide	Long	45	n		
Potassium permanganate	Long	20	n		
Potassium sulfate	Long	Unkn	S		
Propanol	Long	100	n		
Pyridine	Long	Unkn	n		
Sea water	Long	100	S		
Silicone oil	Long	Unkn	S		
Silver nitrate	Long	Unkn	S		
Sodium borate	Long	Unkn	S		
Sodium chloride	Long	25	S		
Sodium cyanide	Long	Unkn	S		
Sodium hydroxide	7	10			20–30
Sodium hydroxide	Long	10	n		
Sodium hydroxide	Long	55	n		
Styrene	Long	100	S		
Sulfuric acid	90	1		2–4	18
Sulfuric acid	7	10	n	1	12–31
Sulfuric acid	100	20	n	0.9	3
Sulfuric acid	Long	70	n		
Textile detergent	7	0.2–2		1	
Toluene	Long	100	S		
Trichloroethylene	Long	100	S		
Water	Long	100	S		
White spirit	Long	100	S		
Xylene	Long	100	S		
Zinc chloride	100	10		1.1	4

S: satisfactory; l: limited; n: non-satisfactory
Long: the duration is undefined but of the order of years
Conc: concentrated solution; Satur: Saturated solution; Sol: Solution; Unkn: Unknown

Vacuum outgassing

After elimination of moisture, the vacuum outgassing of certain polyimides is sufficiently low to be usable in space.

Fire resistance

The oxygen indices are in the range of 30 to 53. Specific formulations make it possible to obtain V0 UL94 fire rating.

4.26.6 Electrical properties

The insulating properties basically depend on the filler: graphite-filled grades can have resistivity values as low as 100 ohm.cm.

For insulating grades, electrical properties except arc resistance are good and remain relatively stable with changing temperature.

As an example, for a given grade, between 50 Hz and 10^6 Hz, and between 25°C and 200°C, the following variations are quoted:

- 4.7 to 5 for the permittivity
- 0.003 to 0.018 for the loss tangent.

However, the resistivity is significantly more sensitive to temperature and, for another grade, decreases from 10^{16} to 10^{12} when the temperature increases from ambient to 260°C, while in another example the resistivity changes from 10^{17} at 38°C to 10^{11} at 315°C.

4.26.7 Joining, decoration

Welding and joining with solvents cannot be used.

Adhesives alone, chosen following rigorous tests, allow joining. The joined parts should not be subjected to high stresses.

After cleaning by abrasion and with solvents, the polyimides can be stuck with a polyimide, epoxy or acrylic resin adhesive whose thermal resistance is compatible with the operating conditions. Preliminary tests are essential.

All precautions must be taken concerning health and safety according to the local laws and regulations.

4.26.8 Foams

Polyimide resins are:

- foamed to obtain very lightweight foams
- more rarely filled with artificial micro-balloons or spheres to make syntactic foams.

Flexible foams

Unlike typical industrial dense polymers, which are processed as carefully as possible to avoid the formation of bubbles, vacuoles and other inclusions, the alveolar materials result from intentionally introducing, in a controlled manner, a certain proportion of voids with the aims of:

- increasing flexibility
- improving the thermal or phonic insulating character
- making damping parts.

The alveolar materials consist of a polymer skeleton surrounding the cells, which may be closed or partially or completely open to neighbouring cells or to the outside.

The intrinsic properties come from those of the polyimides with:

- a reduction in the mechanical properties due to the small quantity of solid material and the high proportion of gas
- a reduction in the chemical behaviour due to the highly divided nature of the material. The thin cell walls immediately absorb liquids and gases and are rapidly damaged.

The polyimide foams are flexible and have a very low density (7 kg/m^3), associated with good fire behaviour, a broad service temperature range and good soundproofing and thermal insulation qualities. These materials are sensitive to diluted strong bases, concentrated salts and acids. Other foams have densities varying from 15–250 kg/m^3.

These foams find applications in:

- Aeronautics, space, armaments, shipbuilding
  - ○ soundproofing and thermal insulation of missiles, planes and helicopters
  - ○ protection of material embarked on space shuttles

  - cryogenic protection on satellites
  - piping insulation.
- Industrial
  - cryogenic applications.

Foam properties are shown in Table 4.90, which relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.90 Polyimide foams: property examples

Density (g/cm^3)	0.007	0.015–0.25
Density (kg/m^3)	7	15–250
Service temperatures (°C)	−195 to +260	−195 to +300
Thermal conductivity (W/m.K)	0.042	
Compression load to 40% (MPa)	0.005–0.009	0.015–0.050
Tensile strength (MPa)	0.050	0.050–0.250
Specific tensile strength (MPa/density)	7	3–1
Tensile strength after 1000 h at 260°C (MPa)	0.025	
Oxygen index (%)	43	

Syntactic foams

Syntactic foams are composites made of micro-balloons or hollow macrospheres bound into a plastic matrix. The polyimide syntactic foams are used in specific electronic equipment for microwave and RF applications. They act as structural, dielectric and heat-barrier materials.

Micro-balloons can be made of polyimides for special applications.

4.26.9 Trade name examples

Actymid, Aurum, Compimide, Cuming C-Stock, Duratron, Imidex, Kapton, Kerimid, Kinel, Meldin, Neopreg, Nolimid, Nomex, Sintimid, Upilex, Upimol, Vespel, Willmid.

4.26.10 Property tables

Table 4.91 relates to examples only and cannot be generalized. See also Table 4.90 for foam property examples. Data cannot be used for design purposes.

Table 4.91 Polyimides: property examples

	Condensation polyimides for moulding			
	Neat	Neat TP	30% Glass fibre	30% Carbon fibre
Density (g/cm^3)	1.33–1.43	1.33	1.56	1.43
Shrinkage (%)	0.8–0.9		0.4–0.5	0.2
Water absorption, 24 h (%)	0.2–0.4		0.2–0.3	0.2–0.33
Rockwell hardness, M	92–102		104	105
Rockwell hardness, E		47		
Tensile strength (MPa)	70–140	92	168	233
Elongation at break (%)	8–9	90	3	2
Tensile modulus (GPa)	2–3		12	21
Flexural strength (MPa)	96–200	135	246	326
Flexural modulus (GPa)	3–3.5	2.9	9–10	19–20

(*Continued*)

Table 4.91 (Continued)

	Condensation polyimides for moulding			
	Neat	Neat TP	30% Glass fibre	30% Carbon fibre
Compression modulus (GPa)	2–4	3.2		
Compression strength (MPa)	110–280		190–195	210
Poisson's ratio	0.4			
Notched impact D 256 (J/m)	80–90		120	108
Notched impact (kJ/m^2)	17			
HDT A (1.8 MPa) (°C)	235–300		242	247
CUT unstressed (°C)	180–250		180–250	180–250
Glass transition temperature (°C)	315			
Thermal conductivity (W/m.K)	0.1–0.4		0.37	0.49
Coefficient of thermal expansion (10^{-5}/°C)	4.5–5.6	5	1.7–5.3	0.6–4.7
Volume resistivity (ohm.cm)	10^{14}–10^{16}			
Dielectric constant	3–4	3.3		
Dissipation factor (10^{-4})	18–36			
Dielectric strength (kV/mm)	20–22			
Oxygen index (%)	44–53			
Self-lubricating grades	15% graphite	40% graphite	15% graphite + 10% PTFE	15% MoS_2
Specific applications			Friction	Friction
Density (g/cm^3)	1.4–1.5	1.6–1.7	1.4–1.6	1.6
Water absorption, 24 h (%)	0.2	0.14	0.2	0.23
Rockwell hardness, M	82–94	68–78	69–79	75–100
Tensile strength (MPa)	62–66	48–54	44–52	55–56
Elongation at break (%)	4–6	2–3	3–6	4
Flexural strength (MPa)	90–110	70–130	70	
Flexural modulus (GPa)	3–4	4–5	3	
Compression modulus (GPa)	2–3	3–4	1–2	
Compression strength (MPa)	100–140	90–110	77–105	
Notched impact D 256 (J/m)	43	38		
HDT A (1.8 MPa) (°C)		360		
CUT unstressed (°C)	180–260	200–250	200–250	180–260
Thermal conductivity (W/m.K)	0.4–0.9	0.9–2.1	0.4–0.8	
Coefficient of thermal expansion (10^{-5}/°C)	2.3–4	3.8	2.3–3	
Volume resistivity (ohm.cm)	10^{12}–10^{13}			
Dielectric constant	13–14			
Dissipation factor (10^{-4})	53–106			
	Thermoplastic PI Neat	Thermoplastic PI Self-lubricating grade		
Density (g/cm^3)	1.33	1.51		
Rockwell hardness, M		37		
Rockwell hardness, E	47			
Tensile strength (MPa)	92	107		
Elongation at break (%)	90	3		
Flexural strength (MPa)	135	96		
Flexural modulus (GPa)	2.9	6		
Notched impact (kJ/m^2)		80		
HDT A (1.8 MPa) (°C)		262		
Coefficient of thermal expansion (10^{-5}/°C)	5	2.5–6.2		
Dielectric constant	3.3	6.6		
PV limit (MPa.m/s)		17 (lubricated)		
Coefficient of friction		0.09		

Table 4.91 (Continued)

	Thermoset polyimides for moulding			
	Neat	Glass fibre reinforced	40% glass fibres	65% glass fibres
Density (g/cm^3)	1.4–1.5	1.5–1.9	1.6	1.9
Shrinkage (%)	0.1–1	0.1–0.6		
Water absorption, 24 h (%)	0.4–1.3	0.4–0.9	0.6	0.5
Rockwell hardness, M	110–120	115–126		
Tensile strength (MPa)	30–160	40–160	45–50	120–160
Elongation at break (%)	1	0.5–1		
Tensile modulus (GPa)	3–10	7–32		
Flexural strength (MPa)	45–250	90–350		250–350
Flexural modulus (GPa)	3–10	7–21	5–8	17–21
Compression modulus (GPa)	3			
Compression strength (MPa)	133–230	180–240	100–180	130–230
Poisson's ratio			0.4	0.4
Notched impact D 256 (J/m)	35–800	55–800		
HDT A (1.8 MPa) (°C)	>300	>300	320	330
CUT unstressed (°C)	180–250	180–250	200–250	200–250
Glass transition temperature (°C)		300		
Thermal conductivity (W/m.K)	0.2–0.5	0.3–0.5	0.3	0.5
Coefficient of thermal expansion (10^{-5}/°C)	1.5–5	1–5	1.5–3	1.4
Minimum service temperature (°C)		−250 to −60		−100 to −60
Volume resistivity (ohm.cm)		10^{14}–10^{16}	10^{15}–10^{16}	10^{14}–10^{15}
Dielectric constant		3–5	3–4	4–5
Dissipation factor (10^{-4})		10–400	150	90
Dielectric strength (kV/mm)		10–22		
Arc resistance (s)		Limited		
Oxygen index (%)		36–44		

Self-lubricating grades	Graphite	Graphite + aramid fibres	MoS_2 + PTFE	Graphite + MoS_2
Specific applications		Friction	Friction	Friction
Density (g/cm^3)	1.4–1.6	1.65	1.4	1.4–1.5
Shrinkage (%)	0.3–0.6	0.1–0.2	1	0.2–0.6
Water absorption, 24 h (%)	0.1–0.6	0.6	0.3–1.3	0.3–1.2
Rockwell hardness, M	100–110	94	113–115	95–110
Tensile strength (MPa)	30–65	30	10–35	30–40
Elongation at break (%)	1–6	0.3–0.4	0.5–1	<1
Tensile modulus (GPa)	3–8	8	2.4	
Flexural strength (MPa)	80–90	60	40–50	55–90
Flexural modulus (GPa)	6–8	7–8	2–3	4–5
Compression strength (MPa)	110–140	80–90	80–140	110–155
Notched impact D 256 (J/m)	14–45	35	14–16	14–17
HDT A (1.8 MPa) (°C)	310–360	>300	>300	360
CUT unstressed (°C)	180–260	200–260	180–250	180–250
Glass transition temperature (°C)	300	300	300	300
Thermal conductivity (W/m.K)	1.4–5	0.4–0.5	0.2–0.3	0.7–0.9
Coefficient of thermal expansion (10^{-5}/°C)	1–4	2.4–3.3	5–7	2.5
Minimum service temperature (°C)	−250 to −60			
Volume resistivity (ohm.cm)	10^{2}–10^{3}	10^{3}–10^{4}	10^{12}–10^{14}	
Dielectric constant	14		3–4	
Dissipation factor (10^{-4})	50		110–160	
Dielectric strength (kV/mm)	10		18–19	
Oxygen index (%)	36–50			30

(*Continued*)

Table 4.91 (Continued)

	Undefined polyimides for moulding			
	Neat	40% glass fibres and beads	Aramid fibres + MoS$_2$ + PTFE	Friction
Density (g/cm^3)	1.3–1.4	1.6	1.4	1.4–1.7
Shrinkage (%)		0.3–0.6	0.8–1	0.1–0.6
Water absorption, 24 h (%)	0.2–0.3			0.2
Rockwell hardness, M	92–120			
Tensile strength (MPa)	72–86	80	30	20–55
Elongation at break (%)	7–8	1	1	0.3–4
Tensile modulus (GPa)	3–4			2–11
Flexural strength (MPa)		110	45	
Flexural modulus (GPa)		8	3	
Notched impact D 256 (J/m)	80	55	35	14–40
Ratio of tensile modulus or strength 250°C/20°C (%)	50			50–85
HDT A (1.8 MPa) (°C)	360	>300	>300	>300
CUT unstressed (°C)	180–260	225	<225	180–260
Glass transition temperature (°C)	300–365	300	290	300–365
Thermal conductivity (W/m.K)	0.15–0.4	0.3	0.25	0.2–0.8
Coefficient of thermal expansion (10^{-5}/°C)	4–6	3	3.8–5	2–7
Minimum service temperature (°C)	−250 to −60			−250 to −60
Volume resistivity (ohm·cm)	10^{14}–10^{16}	10^{15}		10^{3}–10^{14}
Dielectric constant	3–5	4.1	3.3	3–14
Dissipation factor (10^{-4})	10–400			50–200
Dielectric strength (kV/mm)	10–22	14	19	10–19
Arc resistance (s)	Limited			
Oxygen index (%)	36–53	<45	<45	30–40

	Polyimides for laminates Neat polyimide
Density (g/cm^3)	1.2–1.3
Tensile strength at 23°C (MPa)	80–100
Tensile strength at 180°C (MPa)	50–70
Tensile strength at 200°C (MPa)	40–60
Tensile modulus at 23°C (GPa)	3.5–4.5
Tensile modulus at 180°C (GPa)	2.5–3
Tensile modulus at 200°C (GPa)	2–3
Elongation at break at 23°C (%)	2–3
Elongation at break at 180°C (%)	2–3
Elongation at break at 200°C (%)	2–5

Laminates	Carbon fibre UD Tested in fibre direction	Glass fibre
Density (g/cm^3)		1.9–2
Water absorption, 24 h (%)		0.3
Barcol hardness, M		70
Tensile strength at 23°C (MPa)	1210–1450	50–350
Tensile strength at 240°C (MPa)	1000–1300	
Tensile modulus at 23°C (GPa)	115–120	
Flexural strength at 23°C (MPa)	1850*	70–140
Flexural strength at 240°C (MPa)	1240*	
Flexural modulus at 23°C (GPa)	117*	14–28
Compression strength at 23°C (MPa)	1400	70–140
Compression strength at 240°C (MPa)	800	

Table 4.91 (Continued)

Laminates	Carbon fibre UD Tested in fibre direction	Glass fibre
Compression modulus at 23°C (GPa)	128	
Compression modulus at 240°C (GPa)	120	
ILSS (MPa)		14–15
Notched impact D 256 (J/m)		700
CUT unstressed (°C)	180–250	
Coefficient of thermal expansion (10^{-5}/°C)		1

*Perpendicular to the fibre direction: flexural strength is 53 MPa at 23°C and 29 MPa at 240°C; flexural modulus is 7 GPa at 23°C and 5 GPa at 240°C.

	Polyimide films
Density (g/cm^3)	1.33–1.42
Tensile strength (MPa)	100–230
Tensile strength at yield (MPa)	70
Elongation at break (%)	70–110
Tensile modulus (GPa)	2–3
UL94 fire rating	V0
Optical properties	
Haze (%)	0.1
Light transmission (%)	64
Refractive index	1.7

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same as the polyimide matrix.

Light	Limited behaviour, preliminary tests necessary
Weak acids	Limited behaviour with hot acids
Strong acids	Limited to poor behaviour even at ambient temperature
Bases	Attacked to a greater or lesser degree according to the nature, concentration and temperature
Solvents	Good general behaviour. Resistance to ethers, aromatics, esters. Attacked by certain alcohols, hot metacresol, nitrobenzene, alkaline organic products, amines
Water	Generally, absorbed water plasticizes polyimides. Possibly attacked by boiling water
Industrial fluids	Good resistance to hydraulic fluids, kerosene, mineral oils, certain Freons, silicone oils

CUT: continuous use temperature in an unstressed state

4.27 Liquid crystal polymers (LCP)

Liquid crystal polymers (LCP), of which aromatic polyesters are the most common type, are crystalline in the molten state and highly crystalline after cooling. These thermotropic (melt-orienting) thermoplastics are subject to a molecular alignment under processing shear stresses, which leads to a self-reinforcing effect, the polymer's rod-like macromolecules acting like reinforcing microfibres. This also results in a high degree of anisotropy, the more so the higher the shear stresses are during processing. The mechanical properties depend on the part geometry, particularly the thickness, and the processing conditions. Mould design is a very significant parameter in the final properties.

Certain properties, mainly the thermal characteristics and the rigidity, vary widely with the nature of the LCPs and we have chosen to classify them according to their processing temperatures.

Note that the quoted properties are generally measured in the most favourable direction.

4.27.1 General properties

Advantages

When properly designed and processed, LCPs are appreciated for: high strength and rigidity; low viscosity and high mouldability even for thin-walled parts; high service temperatures (200–240°C), high HDTs and soldering heat resistance; low shrinkage and low coefficient of linear expansion in the direction of flow; chemical and electrical properties; inherent fire resistance; good behaviour with UV and light; good creep behaviour; wear resistance; fatigue endurance; fair moisture uptake; transparency to microwaves and X-rays; high-energy radiation resistance; low outgassing; possibility of food contact; USP VI compliance.

Drawbacks

LCPs are handicapped by a high anisotropy of properties, shrinkage and thermal expansion; low weld strength; the cost, though justified by the performances; and unusual design rules.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- injection, high to low moulding temperatures, low warpage, low shrinkage, low coefficient of thermal expansion . . .
- high temperature, high rigidity, food contact, glass and carbon fibre reinforced, lubricated, USP VI compliant, antistatic . . .
- for electrical and electronics applications, food industry, for metallization, for filament production . . .

Costs

As for all plastics, the costs fluctuate greatly with the crude oil price, and are only given to provide a general idea. They are typically of the order of a few tens of Euros per kilogram.

Processing

All the molten-state methods are usable but the main ones are injection and welding.

Consumption

The consumption of LCPs varies from country to country and depends on the source. Global consumption can be estimated between 20 000 and 30 000 tonnes. LCPs are mainly used in electrical and electronics applications and, to a lesser degree, in industry and automotive. The following markets shares are quoted:

electrical & electronics	65–75%
industrial parts	8–20%
audio-visual	8–10%
automobile	1–5%
others	4%

This is an example and other data can be found elsewhere depending on the source and country.

Applications

(See Chapter 2 for further information.)

LCPs are engineering plastics used only for specialized and technical applications.

- Electrical/electronics, lighting, telecommunications
  - bobbins, coils . . .
  - sockets, switches, relays, electrical and electronic connectors, fuse holders, closures . . .
  - chip carriers . . .
  - sensors, LED housings . . .
  - surface mount devices, surface mount interconnection devices, PCMCIA card frames . . .
  - high-performance motor components . . .
  - imaging devices . . .
  - guides . . .
  - hard-disk drive components . . .
- Automotive
  - components for ignition systems . . .
  - components for fuel handling, fuel or gas barrier structures . . .
  - transmission system components, pump components . . .
  - sensors . . .
  - lamp sockets . . .
- Medical applications
  - surgical instruments, dental tools . . .
  - sterilizable trays and equipments . . .
  - drug delivery systems and diagnostics . . .
  - miniature hearing aid parts . . .
- Miscellaneous
  - components for aerospace, sensors, imaging and optoelectronic components . . .
  - optical devices, optical lens components . . .
  - fibre optics components, fibre optics connectors . . .
  - dual-oven cookware, ovenware . . .
  - miniature gears for watches . . .

4.27.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at up to 200–240°C. The UL temperature indices vary broadly with the grade and can:

- be lower than 100°C
- reach 220°C for electrical and mechanical properties including impact, or 240°C for electrical and mechanical properties excluding impact.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- For given grades, compared to the value at ambient temperature, the percentage retention of tensile or flexural strength is roughly:
  - 25–40% at 175°C
  - 0–15% at 260°C.
- For other grades, compared to the value at ambient temperature, the percentage retention of modulus is roughly:
  - 35–53% at 175°C
  - 0–17% at 260°C.

- HDTs under 1.8 MPa depend on the nominal processing temperature of the grade, for example:
  - ○ from 310°C up to 355°C for glass fibre reinforced grades mouldable at 380–400°C
  - ○ from 250°C up to 285°C for glass fibre reinforced grades mouldable at 350°C
  - ○ from 230°C up to 250°C for glass fibre reinforced grades mouldable at 280–330°C.

Figure 4.125 displays examples of tensile or flexural strength retention versus temperature for reinforced LCPs, showing the significant differences in behaviour for the four tested grades.

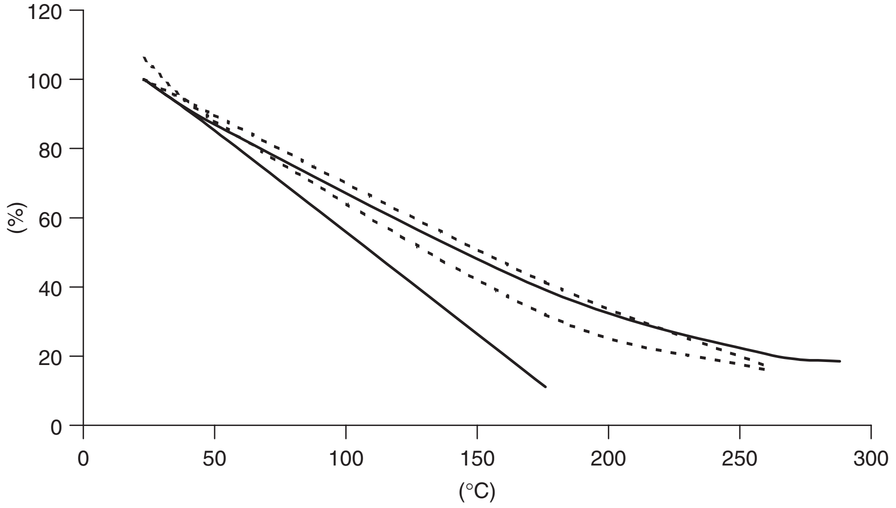


Figure 4.125. LCP examples of tensile or flexural strength retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Impact strength and elongation at break are especially heat-sensitive characteristics.

After 3000 h exposure in hot air, for convenient grades, property retention based on tensile strength is:

- more than 90% at 150°C
- more than 80% at 204°C
- more than 60% at 270°C.

For the same conditions, unnotched impact strength retention is, for example:

- more than 70% at 150°C
- more than 60% at 204°C
- more than 30% at 270°C.

The behaviour at low temperatures is good, depending on the grades and the mechanical constraints experienced.

Certain LCPs are usable at cryogenic temperatures, −196°C for example. Notched Izod impact strengths can slowly decrease between room temperature and −196°C retaining, for example, 70% of the original value.

Glass transition temperatures are roughly 120°C for a general-purpose grade.

These results relate to some grades only and cannot be generalized.

4.27.3 Optical properties

Highly crystalline LCPs are opaque.

4.27.4 Mechanical properties

The mechanical properties are good but depend on the shear stresses during processing and consequently on the thickness of the part.

Figure 4.126 ((a) and (b)) shows tensile strength and modulus versus temperature for samples that are identical except for the thickness, which is 1 mm for one and 4 mm for the other. The gap decreases when the temperature rises but at room temperature is 26% for strengths and 45% for moduli.

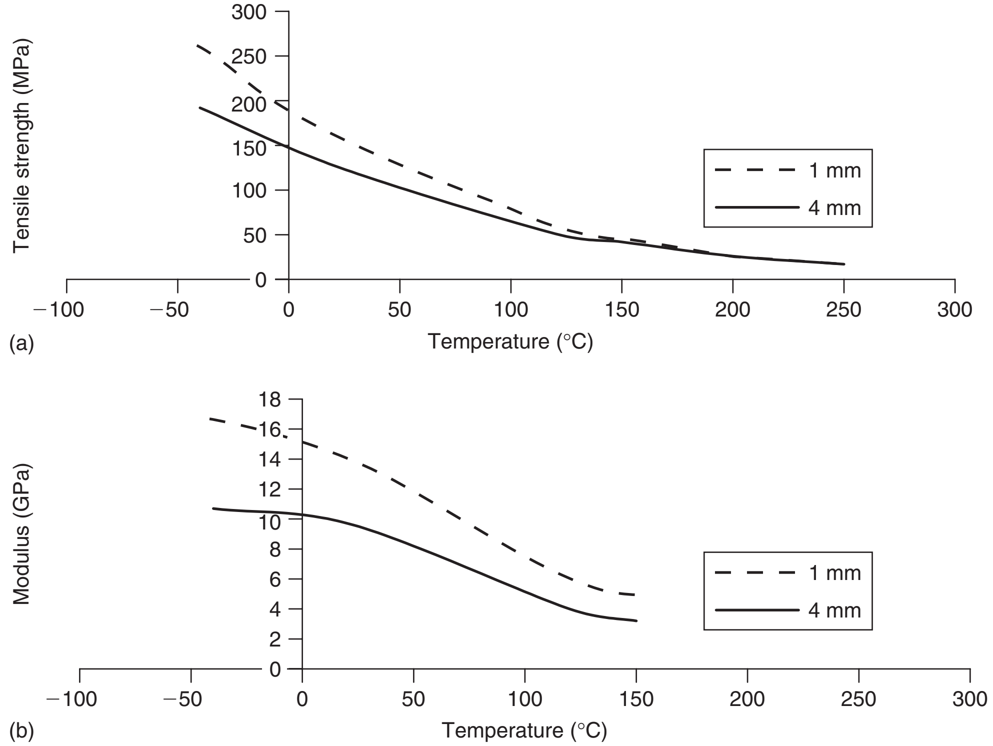


Figure 4.126. (a) LCP examples of tensile strength (MPa) versus temperature (°C) for 1 & 4 mm thick samples; (b) LCP examples of modulus (GPa) versus temperature (°C) for 1 & 4 mm thick samples

Elongations at break are low, while moduli and hardnesses are in a high or very high range due to the self-reinforcement of the polymer crystals. Notched impact strengths are also in a good range.

The parts are anisotropic in the bulk and according to the processing direction.

The abrasion resistance of LCPs, generally good, depends on the roughness, type and morphology of the contacting counterpart sliding surface. The wear resistance and coefficient of friction of special grades are suitable for tribological applications.

Dimensional stability

Alterations by moisture exposure are fair. Shrinkage and coefficient of thermal expansion are anisotropic with values typical of crystalline polymers. Creep resistance is good.

For example, the coefficient of thermal expansion can be:

- 0.2 in the processing direction and 6 in the perpendicular direction for a glass fibre reinforced grade
- −0.3 in the processing direction and 4 in the transverse direction for a carbon fibre reinforced grade
- 1.7 in the machine direction and 6 in the transverse direction for a mineral-filled grade.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular or reinforcement orientation. For given samples of glass fibre reinforced grades, they are evaluated at 0.42–0.49.

Creep

Creep behaviour is good even when the temperature rises. Neat LCPs have high moduli that involve rather low strains for moderate loading. Consequently, creep moduli are also in a good range at room temperature but they decrease more slowly than the majority of other thermoplastics when the temperature rises.

Let us remember that the properties of LCPs are dependent on processing shear and, consequently, creep modulus varies with sample geometry.

Figure 4.127 shows the creep modulus of several grades of glass fibre reinforced LCPs in various conditions of sample geometry, loading and temperature. The two samples tested

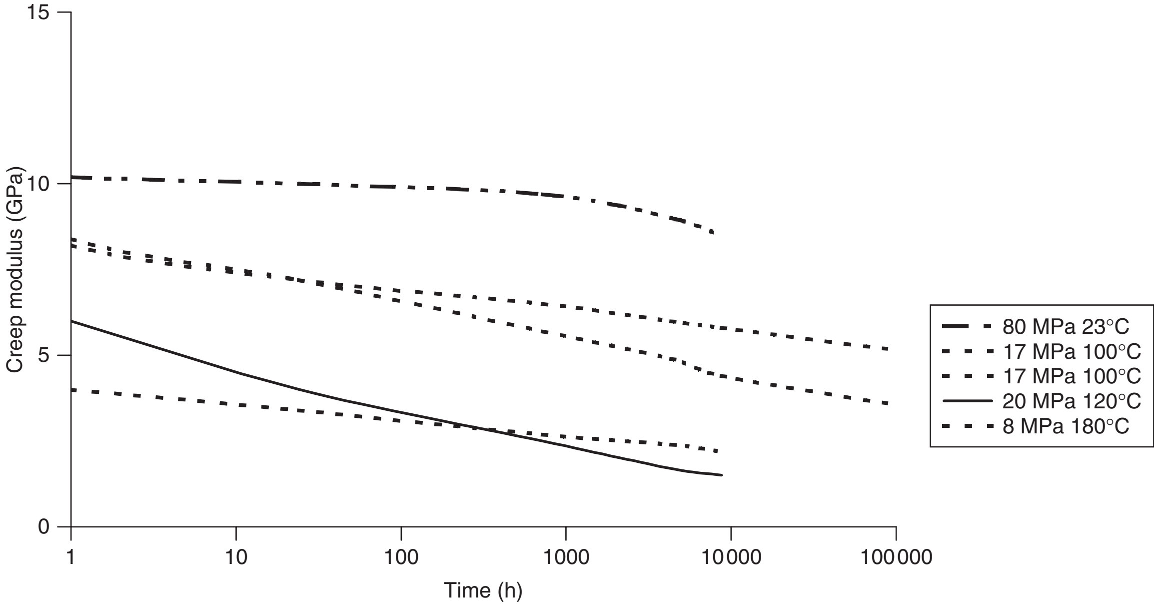


Figure 4.127. LCP: examples of creep modulus (GPa) versus time (h) under 8 to 80 MPa at temperatures from 23 to 180°C

under 17 MPa at 100°C are made of the same material but their thicknesses are different and consequently processing shears are different, which explains the different moduli.

These results relate to a few grades only and cannot be generalized.

4.27.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

Figure 4.128 displays examples of SN or Wöhler's curves for two given grades of mineral and glass fibre (GF) reinforced LCPs.

These results are examples only and they cannot be generalized.

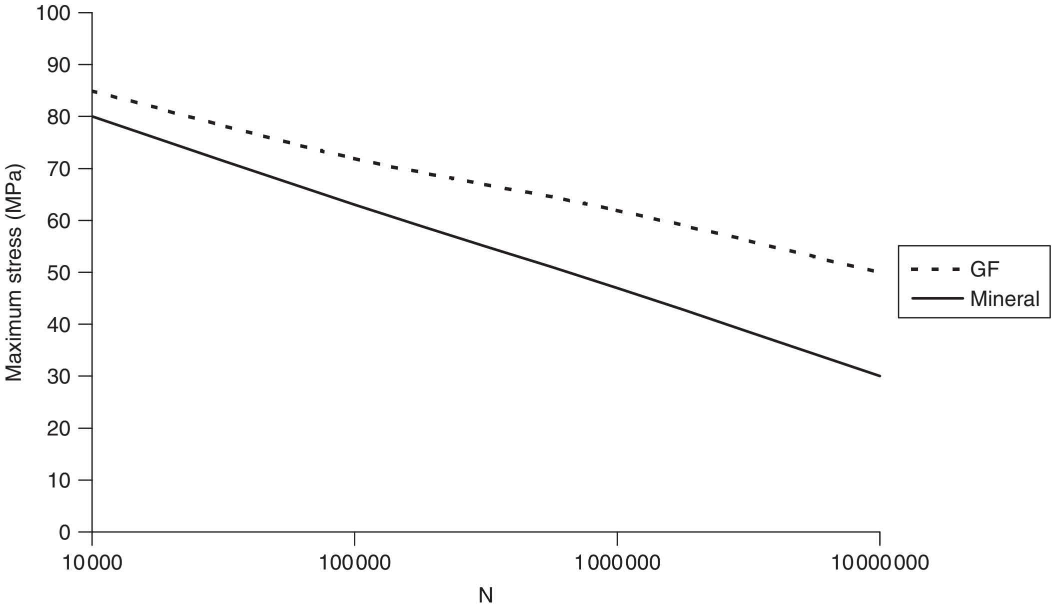


Figure 4.128. SN curve of reinforced LCPs: examples of maximum stress (MPa) versus number of cycles at rupture (N)

Weathering

LCPs are slightly altered by one year of outdoor exposure, with a light surface chalking, but after a 2000 h exposure in a Weather-Ometer, retention of mechanical properties is superior to 90%.

High-energy radiation

The resistance to gamma radiation is excellent without significant degradation after more than 500 Mrad.

Chemicals

The resistance to moisture and water is good, but with very hot water or pressurized steam, the behaviour can vary from satisfactory to unsatisfactory depending on the grade, the chemical nature of the LCP and the filler or reinforcement. For example, after 1000 h in water or steam at 120°C, for three different grades:

- retention of modulus varies from 50% up to 100%
- retention of tensile strength varies from 60% up to 97%.

Suitably formulated compounds are usable in contact with food.

Chemical resistance broadly depends on the chemical nature of the LCP and the following estimations must be carefully interpreted and should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

At room or moderate temperature, LCPs generally resist acids at low concentrations, aliphatic and aromatic hydrocarbons, greases, oils, pure gasoline, acetone, most chlorinated hydrocarbons, and most brake fluids.

The behaviour depends on the type of LCP and can be limited or unsatisfactory with certain concentrated acids, antifreezes, bases, oxygenated gasolines, very hot water and steam, amines, methanol, and phenol.

Table 4.92 displays some general assessments for given grades after short or long immersions in a range of chemicals at various temperatures. The results are not necessarily representative of all the LCPs. Some results appear conflicting because of the diversity of LCP chemical structures. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.92 LCPs: examples of chemical behaviour for various times and temperatures

Chemical	Concentration (%)	Time (days)	Temperature (°C)	Estimated behaviour
Acetic acid	100	20	23	S
Acetic acid	100	30	118	S to l
Acetone	100	180	23	S
Acetone	100	180	56	S
Acetonitrile	100	120	23	S
Antifreeze	100	30	50	S
Antifreeze	100	83	104	l to n
Antifreeze/water	50/50	30	50	S
Antifreeze/water	50/50	30	121	l to n
Brake fluid	100	83	104	l
Brake fluid	100	30	50	S
Brake fluids (Castrol)	100	30	121	S to l
Brake fluids (Castrol)	100	90	121	l to n
Brake fluids (Napa brand)	100	30	23	n
Chlorinated gas	Unknown	180	23	S
Chlorine water	Saturated	180	23	S
Chromic acid	50	180	50	S to l
Chromic acid	70	30	88	S to l
Dimethylformamide	100	180	66	S
Diphenylamine	100	180	66	S
Diphenylcarbonate	100	10	250	n
Ethanol	100	30	52	S
Ethyl acetate	100	180	77	S
Ethylenediamine	100	180	23	S to l
Ethylenediamine	100	30	100	n
Fluorhydric acid (anhydrous)	Unknown	30	23	n
Formic acid	Unknown	30	104	S
Formic acid	Unknown	270	104	l
Formic acid	Unknown	455	104	n

Table 4.92 (Continued)

Chemical	Concentration (%)	Time (days)	Temperature (°C)	Estimated behaviour
Fuel C (50/50 iso-octane/toluene)	100	90	121	l
Fuel C (50/50 iso-octane/toluene)	100	30	121	S
Fuel C + 20% ethanol	100	125	60	S to l
Fuel M-85	100	20	121	n
Gasoline (pure)	100	83	82	S to l
Gasoline (pure)	100	30	121	S
Gasoline (pure)	100	90	121	S
Gasoline (Unleaded + 10% methanol)	100	90	93	S to l
Gasoline (Unleaded + 10% methanol)	100	15	121	n
Gasoline (Unleaded + 10% methanol)	100	30	121	l
Gasoline (Unleaded + 10% methanol)	100	90	121	n
Hexafluoroisopropanol	100	10	25	n
Hexane	100	10	23	S
Hydraulic fluid	100	90	121	S to l
Hydraulic fluid	100	30	149	S
Hydrochloric acid	37	30	88	S to l
Hydrochloric acid	37	120	88	l
Iso-octane	100	120	23	S
Iso-octane	100	14	60	S
Methanol	100	30	64	S
Methanol	100	90	64	S to l
Methanol	100	45	110	n
Methylene chloride	100	180	40	S
Monochloroacetic acid	Unknown	180	50	S
Morpholine (200 ppm/water vapour)	0.02	10	132	S
Motor oil	100	30	50	S
Motor oil	100	83	104	S to l
Motor oil	100	30	121	S
Motor oil	100	90	121	S to l
Nitric acid	50	120	23	S
Nitric acid	50	60	70	S
Nitric acid	50	180	70	S to l
Nitric acid	70	30	88	l to n
Nitrobenzene	100	30	66	S
Nitroglycerine	100	30	66	S
Pentafluorophenol	100	10	60	n
Phenol	100	100	100	S to l
Silicone oil	100	30	200	S
Skydrol	100	30	71	S
Sodium hydroxide	5	90	23	S
Sodium hydroxide	5	180	23	S to l
Sodium hydroxide	5	30	70	S
Sodium hydroxide	5	180	70	l to n
Sodium hydroxide	10	180	23	S to l
Sodium hydroxide	10	30	88	S to n
Sodium hydroxide	30	30	88	n
Sodium hypochlorite	12.5	28	23	l
Sodium hypochlorite	12.5	28	70	n
Sulfuric acid	20	30	23	S
Sulfuric acid	35	14	23	l to n
Sulfuric acid	50	180	88	S to n
Sulfuric acid	93	8	23	l to n
Sulfuric acid	93	30	121	n
Tetrahydrofuran	100	120	23	S

(*Continued*)

Table 4.92 (Continued)

Chemical	Concentration (%)	Time (days)	Temperature (°C)	Estimated behaviour
Toluene	100	180	111	S
Transmission fluid (automatic)	100	30	50	S
Transmission fluid (automatic)	100	83	104	S to l
Trichloroethane	100	90	66	S
Urea	46	60	88	l to n
Washer fluid	Unknown	83	82	S to l
Water	100	10	121	S
Water	100	60	121	S to n
Water vapour	100	16	121	l
Water vapour	100	70	121	S to l
Zinc chloride	Unknown	83	82	S

S: satisfactory; l: limited; n: not satisfactory

For films, in several series of experiments concerning various thicknesses of various polymers, permeability coefficients have been calculated for a reference thickness of 40 μm. Units differ for the various gases but are comparable for the different polymers tested with the same gas. The following data (without units) are only given to provide a general idea and cannot be used for designing any parts or goods.

- Water vapour: LCP has a low permeability, evaluated from 0.05 up to 0.4 for a full range of 0.05 up to 400 for the overall tested plastics.
- Oxygen: LCP has a low permeability, evaluated at 1 up to 2 versus a full range of <1 up to 11 000 for the overall tested plastics.

Fire resistance

LCPs with oxygen indices of 35 and more are inherently fire resistant and reach a V0 UL94 rating.

4.27.6 Electrical properties

LCPs are good insulators even in hot and wet environments with high dielectric resistivities. Electricity and electronics are the main market for LCPs and special grades are marketed for it. Moreover they are transparent to microwaves.

4.27.7 Joining, decoration

Welding by ultrasound is used.

Joining is possible with adhesives such as epoxies, acrylates, cyanoacrylates, polyurethanes. Surface treatments can be useful. Preliminary tests are essential.

All precautions must be taken concerning health and safety according to the local laws and regulations.

Decoration: electroplating and vacuum metallization give good results.

4.27.8 Trade name examples

Laxtar, Sumikasuper, Titan, Vectra, Vectran, Xydar, Zenite.

4.27.9 Property tables

Table 4.93 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.93 LCPs: examples of properties

	Neat LCP Low modulus		Neat LCP High modulus		Neat LCP High temperature	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.4	1.4	1.4	1.4	1.4	1.4
Shrinkage (%)	0	0.6	0	0.6		
Absorption of water (%)	0.02	0.03	0.02	0.03	0.01	0.01
Mechanical properties						
Shore hardness, D	90	90	>95	>95	82	85
Rockwell hardness, R	>120	>120	>120	>120	112	112
Rockwell hardness, M	60	60	100	100	40	60
Tensile strength (MPa)	156	165	180	188	140	145
Elongation at break (%)	2	3	1	2	2	3
Tensile modulus (GPa)	10	10	19	21	10	10
Flexural modulus (GPa)	8	9	12	15	8	9
Notched impact strength, ASTM D256 (J/m)	520	520	415	415	450	450
Thermal properties						
HDT B (0.46 MPa) (°C)	180	180	200	200	310	310
HDT A (1.8 MPa) (°C)	168	168	182	182	275	275
Continuous use temperature (°C)	200	240	200	240	200	240
Melting temperature (°C)	280	280	280	280	325	325
Coefficient of thermal expansion (10^{-5}/°C)	−0.5	7.5	−0.5	4		
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{16}	10^{16}		
Dielectric constant	3	4	3	4		
Loss factor (10^{-4})	40	200	40	100		
Dielectric strength (kV/mm)	47	47	37	37		
Arc resistance (s)	137	137	74	74		
Fire behaviour						
Oxygen index (%)	35	35	50	50		
UL94 rating	V0	V0	V0	V0		
Moulding temperature	High		Medium		Low	
Reinforcement	30% GF		30% GF		30% GF	
Miscellaneous properties						
Density (g/cm^3)	1.6	1.7	1.6	1.7	1.6	1.7
Shrinkage (%)	0.02	1.3	0.2	1.2	0	0.4
Absorption of water (%)	0.02	0.09	0.02	0.02	0.02	0.02
Mechanical properties						
Shore hardness, D	75	78	79	80	81	82
Rockwell hardness, R	89	91	103	103	107	107
Rockwell hardness, M	<20	25	20	30	30	40
Tensile strength (MPa)	117	182	146	164	127	220
Elongation at break (%)	2	6	2	5	1	5
Tensile modulus (GPa)			12	15	11	24
Flexural modulus (GPa)	12	14	11	13	11	19
Notched impact strength, ASTM D256 (J/m)	108	176	108	137	71	150
Thermal properties						
HDT B (0.46 MPa) (°C)					250	260
HDT A (1.8 MPa) (°C)	310	355	250	284	232	254
Continuous use temperature (°C)	200	240	200	240	200	240
Melting temperature (°C)	370	390	320	360	280	320
Thermal conductivity (W/m.K)	0.46	0.53	0.45	0.46	0.47	0.48
Coefficient of thermal expansion (10^{-5}/°C)	0.2	8	0.3	9	−0.1	8

(*Continued*)

Table 4.93 (Continued)

Moulding temperature Reinforcement	High 30% GF		Medium 30% GF		Low 30% GF	
Electrical properties						
Volume resistivity (ohm.cm)	10^{13}	10^{15}	10^{13}	10^{15}	10^{13}	10^{16}
Dielectric constant	3	5	3	5	3	5
Loss factor (10^{-4})	40	350	127	340	60	320
Dielectric strength (kV/mm)	37	37	37	50	37	50
Arc resistance (s)	128	209	130	150	66	137
Fire behaviour						
Oxygen index (%)	41	48	37	48	37	49
UL94 rating	V0	V0	V0	V0	V0	V0
Poisson's ratio	0.44	0.49	0.45	0.46	0.42	0.45

Reinforcement	30% Mineral		30% CF		Conductive	
Miscellaneous properties						
Density (g/cm^3)	1.6	1.7	1.5	1.5	1.6	1.6
Shrinkage (%)	0.1	0.4	0	0.3		
Absorption of water (%)			0.03	0.03		
Mechanical properties						
Shore hardness, D	88	90	92	>95		
Rockwell hardness, R	>120	>120	>120	>120		
Rockwell hardness, M	65	65	80	100		
Tensile strength (MPa)	125	186	158	241	138	140
Elongation at break (%)	3	5	1	2	1	2
Tensile modulus (GPa)	10	14	28	37	13	14
Flexural modulus (GPa)	10	12	22	32	12	13
Notched impact strength, ASTM D256 (J/m)	160	294	35	70	77	77
Thermal properties						
HDT A (1.8 MPa) (°C)	183	244	220	240	224	225
Continuous use temperature (°C)	200	240	200	240	200	240
Melting temperature (°C)	280	280	280	280	280	280
Coefficient of thermal expansion (10^{-5}/°C)	1	6	−0.3	7		
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{3}	10^{4}	10^{6}	10^{8}
Dielectric constant	3	4	16	32		
Loss factor (10^{-4})	10	290	250	260		
Dielectric strength (kV/mm)	38	41				
Arc resistance (s)	100	100				
Fire behaviour						
Oxygen index (%)	37	37				
UL94 rating	V0	V0	V0	V0		

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Fair behaviour, light chalking and fair retention of properties after 1 year exposure
Weak acids	Good behaviour
Strong acids	Behaviour depends on acid type and concentration
Bases	Satisfactory to unsatisfactory behaviour according to the base and concentration
Solvents	Chemical resistance broadly depends on the chemical nature of the LCP and the following estimations must be carefully interpreted and should be verified by consultation with the producer of the selected grades and by tests under operating conditions At room or moderate temperature, LCPs generally resist acids at low concentrations, aliphatic and aromatic hydrocarbons, greases, oils, pure gasoline, acetone, most chlorinated hydrocarbons, most brake fluids Behaviour depends on the type of LCP and can be limited or unsatisfactory with certain concentrated acids, antifreezes, bases, oxygenated gasolines, very hot water and steam, amines, methanol, phenol
Food contact	Possible

4.28 Polybenzimidazole (PBI)

Polybenzimidazole (PBI) is an infusible thermoplastic, perhaps the most advanced polymer from the thermal and mechanical points of view but, on the other hand, processing is the monopoly of its producer.

4.28.1 General properties

Advantages

PBI is appreciated for: high service temperatures (260–425°C), high strength and rigidity at high temperatures, high HDT; non-fusibility; good behaviour at low temperature; low coefficient of linear expansion; chemical and electrical properties; hydrolysis resistance; inherent fire resistance; good creep behaviour; wear resistance; fatigue endurance; fair short-term moisture uptake; ultrasonic transparency; low outgassing except moisture; ionic purity.

Drawbacks

PBI is handicapped by its high cost (which is justified by the performances); unsuitability of conventional processing methods; slow long-term moisture uptake; non-compliance with FDA and other similar regulations; lack of sources and grades.

Applications

(See Chapter 2 for further information.)

PBI is an engineering plastic used only for specialized and high-tech applications.

Consumption varies according to the country. It is mainly used in high-tech sectors: aircraft and aerospace, semiconductor and vacuum industries, electricity and electronics. For example:

- high heat bushings, valve seats, ball valve seats, contact seals, insulator bushings . . .
- thermal isolators, high-heat insulator bushings for hot runner plastic injection moulds . . .
- guide rollers . . .
- semiconductor industry, vacuum chamber applications, clamp rings for gas plasma etching equipment, wafer retaining rings for gas plasma etching, vacuum tips . . .
- wafer carriers . . .
- connectors, connectors for aircraft engines . . .
- filaments and fibres
- vacuum cups, fingers and holders for incandescent and fluorescent light bulbs . . .

4.28.2 Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated from 260°C up to 425°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . . For example:

- compared to the value at ambient temperature, the percentage retention of tensile or flexural strength is roughly:
  - near 90% at 200°C
  - 55–65% at 300°C
  - 25% at 400°C
- compared to the value at ambient temperature, the percentage retention of compression modulus is roughly:
  - 75% at 200°C
  - 45–55% at 300°C
  - 20–25% at 400°C.

HDTs under 1.8 MPa are, for example, from 427°C up to 435°C.

Figure 4.129 displays examples of tensile strength retention versus temperature for PBI. Note the unusually high temperature levels.

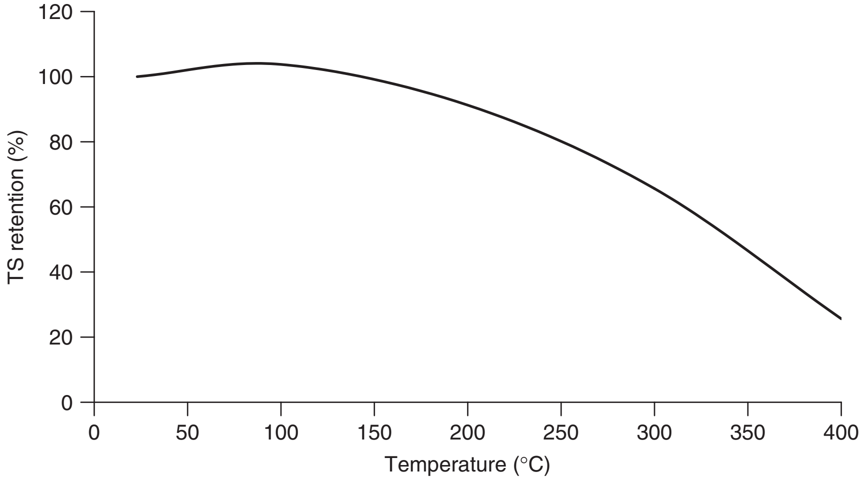


Figure 4.129. PBI examples of tensile strength retention (%) versus temperature (°C)

For long-term heat ageing, property retention depends on the property considered. Impact strength and elongation at break are especially heat-sensitive characteristics.

After 500 h exposure in hot air, retentions based on compressive strength are:

- near 100% at 260°C
- near 90% at 315°C
- near 40% at 370°C.

For the same conditions, weight losses are, for example:

- near 0% at 260°C
- near 10% at 315°C
- near 55% at 370°C.

The behaviour at low temperatures is good, depending on the mechanical constraints undergone. Mechanical properties vary little between room temperature and −70°C. Suitably designed parts are usable at cryogenic temperatures, −160°C for example. Notched Izod impact strengths are weak and parts must be designed to avoid stress concentrators.

Glass transition temperatures are roughly 400–425°C.

These results relate to some grades only and cannot be generalized.

4.28.3 Optical properties

PBI is black.

4.28.4 Mechanical properties

The mechanical properties are good but notched Izod impact strengths are weak and parts must be conveniently designed to avoid stress concentrators.

Elongations at break are low; moduli and hardnesses are in a high range.

The wear resistance is good, depending on the roughness, type and morphology of the contacting counterpart sliding surface.

Friction

The wear resistance and coefficient of friction are suitable for tribological applications.

Tribological properties for a PV of 1.75 MPa.m/s are, for example:

- static coefficient of friction: 0.19
- dynamic coefficient of friction: 0.24–0.27.

These results are examples only and cannot be generalized.

Dimensional stability

Alterations by short-term moisture exposures are fair but in long-term exposures PBI can slowly absorb significant amounts of water. The coefficient of thermal expansion is low. Creep resistance is good.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the processing, the temperature, and the direction of testing with regard to the molecular orientation. For given samples they are evaluated at 0.34.

These results are examples only and cannot be generalized.

Creep

Creep behaviour is good even when the temperature rises.

4.28.5 Ageing

Dynamic fatigue

The dynamic fatigue can be good for certain grades if care is taken to limit the strains by restricting the stresses to values in keeping with the modulus.

For example, the load leading to failure after 1 million cycles is estimated at 56 MPa, that is, 35% of the tensile strength at break.

This result is an example only and cannot be generalized.

Weathering

Resistance to weathering is estimated by certain sources to be limited.

Chemicals

The resistance to moisture and water is good but, with very hot water or pressurized steam, the behaviour can vary from satisfactory to unsatisfactory depending on the temperature, pressure and exposure time. In long-term exposures PBI can slowly absorb significant amounts of water.

At room or moderate temperature, PBI generally resists aliphatic and aromatic hydrocarbons, greases, oils, pure gasoline, acetone, most chlorinated hydrocarbons, certain alcohols, ketones, esters, ethers, and phenol.

Behaviour can be limited or unsatisfactory with certain dilute and concentrated acids, bases, very hot water and steam, and methanol.

Table 4.94 displays some results concerning general assessments after short immersions in a range of chemicals at various temperatures that are not representative of long-term exposures. Moreover, most conditions are unknown and some results appear conflicting. These

Table 4.94 PBI: examples of chemical behaviour at various times and temperatures

Chemical	Concentration (%)	Time (days)	Temperature (°C)	Estimated behaviour
Acetic acid	Dilute	Unknown	Unknown	S to l
Acetic acid	10	1	93	S
Acetic acid	10	30	93	l
Acetic acid	100	7	93	S
Acetone	100	Unknown	Unknown	S
Alcohols	100	Unknown	Unknown	S
Aliphatic hydrocarbons	100	Unknown	Unknown	S
Aromatic hydrocarbons	100	Unknown	Unknown	S
Chlorinated solvents	100	Unknown	Unknown	S
Diethyl ether	100	Unknown	Unknown	S
Dimethylacetamide	Unknown	1	93	n
Esters	100	Unknown	Unknown	S
Ethers	100	Unknown	Unknown	S
Gasoline	100	Unknown	Unknown	S
Gasoline	100	7	93	S
Greases	100	Unknown	Unknown	S
Hydrochloric acid	Dilute	Unknown	Unknown	S to l
Hydrochloric acid	Concentrated	Unknown	Unknown	n to l
Hydrochloric acid	10	1	93	S
Hydrochloric acid	10	7	93	n
Hydrochloric acid	37	1	93	l
Hydrochloric acid	37	7	93	n
Inorganic salt solutions	Unknown	Unknown	Unknown	S
Kerosene	100	7	93	S
Ketones	100	Unknown	Unknown	S
Methanol	100	Unknown	Unknown	S to l
Methanol	100	7	Reflux	S
Methanol	100	30	Reflux	l
Methylethylketone	100	7	Reflux	S
Methylene chloride	100	7	Reflux	S
Nitric acid	10	1	93	l
Nitric acid	10	7	93	n

Table 4.94 (Continued)

Chemical	Concentration (%)	Time (days)	Temperature (°C)	Estimated behaviour
Oils	100	Unknown	Unknown	S
Phenol	100	30	93	S
Phosphoric acid	35	1	93	S
Phosphoric acid	35	7	93	l
Phosphoric acid	35	30	93	n
Potassium chloride solution	Unknown	Unknown	Unknown	S
Sodium carbonate	10	30	93	S
Sodium chloride solution	Unknown	Unknown	Unknown	S
Sodium hydroxide	Dilute	Unknown	Unknown	l
Sodium hydroxide	Concentrated	Unknown	Unknown	n
Sodium hydroxide	15	1	93	S
Sodium hydroxide	15	7	93	l
Sodium hydroxide	15	30	93	n
Sodium hypochlorite	5	1	93	S
Sodium hypochlorite	5	30	93	l
Steam	100	Unknown	Unknown	l to n
Steam	100	30	343	l
Strong acids	Concentrated	Unknown	Unknown	n to l
Strong bases	Concentrated	Unknown	Unknown	n
Sulfuric acid	Concentrated	Unknown	Unknown	n to l
Sulfuric acid	30	1	93	S
Sulfuric acid	30	7	93	n
Toluene	100	Unknown	Unknown	S
Toluene	100	7	Reflux	S
Triethylene glycol	Unknown	30	232	S
Water	100	1	100	S
Water	100	30	100	l
Weak acids	Dilute	Unknown	Unknown	S to l
Weak bases	Dilute	Unknown	Unknown	l
Xylene	100	7	Reflux	S

S: satisfactory; l: limited; n: not satisfactory

results must be treated with particular caution. These general indications should be verified by consultation with the producer and by tests under operating conditions.

Fire resistance

PBI, with an oxygen index of 58, is inherently fire resistant and is compliant with a V0 UL94 rating.

4.28.6 Electrical properties

LCPs are good insulators even in hot environments, with high dielectric resistivities. The electrical and electronics sector is an important market for PBI.

4.28.7 Trade name examples

Celazole.

4.28.8 Property tables

Table 4.95 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.95 PBI: examples of properties

	Min.	Max.
Miscellaneous properties		
Density (g/cm^3)	1.3	1.3
Absorption of water (%)	0.4	0.4
Mechanical properties		
Shore hardness, D	>95	>95
Rockwell hardness, R	>120	>120
Rockwell hardness, M	>125	>125
Tensile strength (MPa)	140	160
Elongation at break (%)	3	3
Tensile modulus (GPa)	5	6
Flexural modulus (GPa)	5	7
Notched impact strength, ASTM D256 (J/m)	27	30
Thermal properties		
HDT A (1.8 MPa) (°C)	427	435
Continuous use temperature (°C)	260	425
Glass transition temperature (°C)	400	425
Brittle point (°C)	−160	−160
Thermal conductivity (W/m.K)	0.4	0.4
Coefficient of thermal expansion (10^{-5}/°C)	2	3
Electrical properties		
Volume resistivity (ohm.cm)	10^{14}	10^{15}
Dielectric constant	3.2	3.5
Loss factor (10^{-4})	10	140
Dielectric strength (kV/m)	21	22
Arc resistance (s)	186	186
Fire behaviour		
Oxygen index (%)	58	58
UL94 fire rating	V0	V0

Results concerning chemical resistance relate to short immersions at various temperatures that are not representative of long-term exposures. Moreover, most conditions are unknown and some results appear conflicting. The following estimations must be treated with particular caution. These general indications should be verified by consultation with the producer and by tests under operating conditions. General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	Limited behaviour
Acids	Behaviour depends on acid type and concentration
Bases	Behaviour depends on base type and concentration
Solvents	At room or moderate temperature, PBI generally resists aliphatic and aromatic hydrocarbons, greases, oils, pure gasoline, acetone, most chlorinated hydrocarbons, certain alcohols, ketones, esters, ethers, phenol Behaviour can be limited or unsatisfactory with certain dilute and concentrated acids, bases, very hot water and steam, methanol

4.29 Alloys

Thermoplastic families are diversified; however, their number is limited and consequently there are often wide gaps between the properties of two basic polymer families. To bridge the gap, it is possible to mix two families to form an alloy if they are compatible or if it is possible to compatibilize them with a third material.

The main effects targeted are:

- a decrease in the cost of high-performance thermoplastics without an unacceptable decrease in technical properties
- improvement of the technical properties of cheap thermoplastics with an acceptable increase in the cost
- processability improvement of difficult-to-process but good-performance thermoplastics.

For a suitable mixing of the two components, the properties of an alloy, including the cost, are generally intermediate between those of each component, as we can see in Figure 4.130 comparing several properties for an ABS, a PC and an ABS/PC alloy:

- mechanical: tensile strength (TS), elongation at break (EB) and notched impact strength
- thermo-mechanical: HDT A
- thermal: continuous use temperature (CUT).

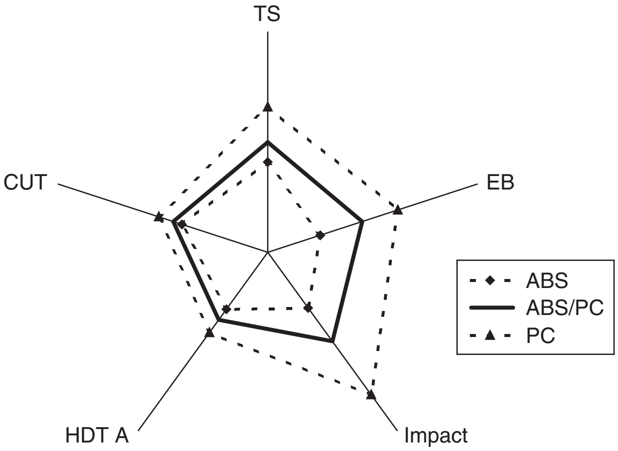


Figure 4.130. Property examples for ABS, PC and ABS/PC alloy

Alloys are numerous and some of them have already been covered, such as ABS – the most consumed – or PPE, which are really alloys with polystyrene or polyamide. Table 4.96 displays some examples without claiming to be exhaustive.

Applications

Some alloys have moderate consumptions such as:

- ABS: roughly 4 million tonnes
- PPE: roughly 350 000 tonnes
- PC alloys: roughly 300 000 tonnes.

Other alloys can be estimated at 500 000 tonnes.

All end-use sectors use all the alloys to some extent, but the main sectors are:

- automotive
- E&E
- appliances
- industry.

Table 4.96 Examples of thermoplastic alloys

- Alloys containing ABS
  - ABS/PC
  - ABS/PA
  - ABS/PVC
  - ABS/PBT
  - ABS/SMI, AES, AAS or ASA
  - ABS/PSU
  - ABS/PUR
  - ABS/polyolefin
- Alloys containing PC
  - PC/ABS
  - PC/PBT
  - PC/PET
  - PC/PMMA
  - PC/ASA
  - PC/PS
  - PC/SMA
  - PC/PSU
  - PC/PEI
  - PC/LCP
- Alloys containing PA
  - PA/ABS
  - PA/PPE
  - PA/PBT
  - PA/PP
  - PA/polyolefin
- Alloys containing polyester
  - PBT/PC
  - PET/PC
  - PBT/ABS
  - PBT/styrenics
  - PBT/PA
  - Polyester/polyolefin
- Alloys containing styrenics
  - Styrenics/ABS
  - ABS/PC
  - ASA/PC
  - PS/PC
  - SMA/PC
  - SMA/PVC
  - Styrenic/PBT
- Alloys containing acrylics
  - PMMA/PC
  - PMMA/PVC
- Alloys containing polyolefins
  - Polyolefin/polyester
  - PP/PA
  - Polyolefin/PA
  - Polyolefin/COC
  - PP/PPE
- Alloys containing PVC
  - PVC/ABS
  - PVC/PMMA
  - PVC/SMA
- Alloys containing PPE
  - PPE/PS and PPE/PA (already examined)
  - PPE/PP
  - PPE/PEI
- Alloys containing PUR
  - PUR/ABS
- Alloys containing PSU
  - PSU/ABS
  - PSU/PC
- Alloys containing PPS
  - PPS/PEI
- Alloys containing PEI
  - PEI/PC
  - PEI/PPE
  - PEI/PPS
- Alloys containing LCP
  - LCP/PC
- Alloys containing thermoplastic polyimide
  - Proprietary alloys
- Alloys containing polyarylate
  - Proprietary alloys

Automotive

- Automotive exteriors
  - bumper systems . . .
  - fenders, body panels, door panels . . .
  - radiator grilles, headlamp supports . . .
  - mirror housings . . .
  - exterior trims . . .
  - wheel covers
- Automotive interiors
  - instrument panels, consoles, air bag system components . . .
  - interior trims, mirror housings . . .
  - panel and knee bolsters . . .

- Under-the-hood, electrical & electronics components
  - bobbins, connectors, fuse junction systems, switches, sockets . . .
  - ignition components . . .

Electrical & electronics

- electronic enclosures . . .
- EMI shielding components . . .
- computer and business equipment components, housings . . .
- electronics components . . .
- connectors . . .

Miscellaneous

- gas barrier materials . . .
- packaging applications . . .
- bearings, tribological, antifriction applications . . .
- separation membranes . . .

4.29.1 ABS/PC alloys

Properties, processability and prices are intermediate between those of ABS and PC. Consumption is relatively appreciable.

Advantages

ABS/PC alloys are appreciated for their good mechanical properties, high impact strength, rigidity, good creep behaviour, fatigue resistance, attractive price/property ratios, fair dimensional stability, aesthetics, good low-temperature properties, broad range of service temperatures, easy processing, inertness to certain chemicals, weak absorption of water, fair density, good electrical insulation even in wet environments, feasibility of welding, versatility of processing methods, ease of joining.

Drawbacks

General drawbacks are the natural sensitivity to heat, UV, light and weathering, requiring efficient protection for outdoor exposure (stabilized grades are marketed); inherent easy combustion, but FR grades are marketed including halogen-free grades; cost, justified by the performances; creep when the temperature rises; sensitivity to environmental stress cracking and attack by some chemicals.

The costs are of the order of several Euros per kilogram, for example €5–6/kg for small shipments.

Application examples

- Automotive
  - instrument panels
  - grilles
  - wheel covers
  - snowmobile bodies . . .

- Electrical & electronics
  - electrical enclosures, electricity meter covers . . .
  - switches, plugs, sockets . . .
  - housings and internal components for desktop computers, laptops, photocopiers, printers, plotters, monitors . . .
- Appliances
  - washing machines, dryers and microwave ovens components . . .
  - mobile phone housings
  - smart cards . . .
- Miscellaneous
  - helmets . . .

Trade name examples: Bayblend, Multilon, Pulse, Strapon.

Table 4.97 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.97 Property examples of ABS/PC alloys compared to ABS and PC

	ABS		General-purpose ABS/PC		PC	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.00	1.15	1.12	1.16	1.2	1.2
Shrinkage (%)	0.4	0.9	0.5	0.7	0.5	0.7
Absorption of water (%)	0.1	0.8	0.15	0.3	0.1	0.2
Mechanical properties						
Shore hardness, D	75	85	80	85	85	95
Rockwell hardness, R	75	95	110	112	114	>120
Rockwell hardness, M	10	50	30	50	50	85
Stress at yield (MPa)	20	64	47	60	50	65
Strain at yield (%)			3	8	7	7
Tensile strength (MPa)	30	60	45	55	55	77
Elongation at break (%)	2	100	>50	125	100	150
Tensile modulus (GPa)	1	3	2	2.5	2.1	2.5
Flexural modulus (GPa)	1	3	2	2.5	2.1	2.5
Notched impact strength ASTM D256 (J/m)	100	500	500	650	650	950
Notched impact strength ASTM D256 at −40°C (J/m)			400	450		
Impact strength at 23°C (kJ/m^2)			48	80		
Impact strength at −20°C (kJ/m^2)			42	46		
Thermal properties						
HDT B (0.46 MPa) (°C)	90	125			130	145
HDT A (1.8 MPa) (°C)	80	120	100	132	130	140
Continuous use temperature (°C)	65	110			90	125
Brittle point (°C)	−40	−20			−25	−25
Thermal conductivity (W/m.K)	0.20	0.40			0.2	0.2
Specific heat (cal/g/°C)	0.30	0.40			0.3	0.3
Coefficient of thermal expansion (10^{-5}/°C)	6	10	8	8	6	7
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{16}	10^{16}	10^{15}	10^{16}
Dielectric constant	2.4	5			3	3
Loss factor (10^{-4})	20	350	35	35	7	100
Dielectric strength (kV/mm)	12	20	24	24	15	30
Fire behaviour						
Oxygen index (%)	18	19	22	24	24	25
UL94 fire rating	HB	HB	HB	HB	V2	V2

Table 4.97 (Continued)

ABS/PC alloys	FR grade		Halogen-free FR		10% glass fibre reinforced	
Miscellaneous properties						
Density (g/cm^3)	1.2	1.2	1.18	1.2	1.22	1.23
Shrinkage (%)	0.4	0.6	0.5	0.6	0.2	0.3
Mechanical properties						
Stress at yield (MPa)	62	62	63	63		
Strain at yield (%)	2	2	3	3		
Tensile strength (MPa)	50	50	48	48	84	84
Elongation at break (%)	3	4	80	80	3	3
Tensile modulus (GPa)	3.3	3.3	2.6	2.6	5.1	5.2
Flexural modulus (GPa)	3.2	3.3	2.6	2.6	5.1	5.2
Notched impact strength ASTM D256 (J/m)					106	106
Impact strength at 23°C (kJ/m^2)	22	22	15	15		
Thermal properties						
HDT B (0.46 MPa) (°C)	94	94	94	94	130	135
HDT A (1.8 MPa) (°C)	84	84	84	84	115	120
Coefficient of thermal expansion (10^{-5}/°C)	6	8	8	8		
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{16}	10^{16}		
Fire behaviour						
UL94 fire rating	V1	5 VB	5 VB	V0		

Summary of some general assessments concerning the chemical behaviour at room temperature of ABS and PC, which are not necessarily representative of ABS/PC alloys or of all grades of ABS and PC. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	ABS	PC
Light	UV protection is needed	UV protection is needed
Weak acids	Good behaviour	Good to limited behaviour
Strong acids	Limited to unsatisfactory behaviour	Good to unsatisfactory behaviour according to the concentration
Bases	Good to limited behaviour according to the nature and concentration	Good to unsatisfactory behaviour according to the nature and concentration
Solvents	Good to limited resistance against vegetable oils, saturated aliphatic hydrocarbons, polyglycols, and various foodstuffs Unsatisfactory against aldehydes, esters, ethers, ketones, aromatic and certain aliphatic hydrocarbons, chlorinated solvents, aromatic amines, polyglycol ethers . . .	Good to limited resistance against oils, greases, aliphatic hydrocarbons, certain alcohols Unsatisfactory against aldehydes, esters, ethers, ketones, aromatic hydrocarbons, chlorinated solvents, amines, certain alcohols, phenols . . .

4.29.2 ASA/PC alloys

Properties, processability and prices are intermediate between those of ASA and PC. The consumption is lower than that of ABS/PC.

Advantages

ASA/PC alloys are appreciated for their better behaviour and lower yellowing with UV, light and weathering, but UV protection is needed for long-term outdoor exposures; the good mechanical properties, high impact strength, rigidity, good creep behaviour, attractive price/property ratios, fair dimensional stability, aesthetics, good low-temperature properties for suitable grades; easy processing; inertness to certain chemicals; weak absorption of water; good electrical insulation even in wet environments; feasibility of welding.

Drawbacks

General drawbacks are a certain sensitivity to heat, UV, light and weathering, requiring efficient protection for long-term outdoor exposure (stabilized grades are marketed); inherent easy combustion, but FR grades are marketed including halogen-free ones; the cost, which is justified by the performances; creep when the temperature rises, unsuitability for long-term contact with very hot water; sensitivity to environmental stress cracking and attack by some chemicals.

The costs are of the order of several Euros per kilogram.

Application examples

- Automotive
    - rear light lenses and base plates . . .
    - mirror housings . . .
- Electricity & electronics, appliances
    - switches, junction box bases, motion sensors, transformer casings, motor housings . . .
    - television antennas, parabolic dishes . . .
    - cooking pots, espresso and coffee machine components . . .
    - extractor hood housings, alarm system housings, instrument panels for washing machines, microwave oven components . . .
    - sewing machine parts . . .
- Sports and recreation
    - golf cart parts . . .
    - ski boxes . . .

Trade name examples: Luran S, Terblend S.

Table 4.98 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.98 Property examples of ASA/PC alloys compared to ASA and PC

	ASA		ASA/PC alloys		PC	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.05	1.07	1.15	1.2	1.2	1.2
Shrinkage (%)	0.4	0.7	0.3	0.7	0.5	0.7
Absorption of water (%)	0.2	0.3	0.3	0.4	0.1	0.2
Mechanical properties						
Shore hardness, D	75	80			85	95
Rockwell hardness, R	83	100			114	>120
Rockwell hardness, M	<10	30			50	85
Stress at yield (MPa)	35	40	53	63	50	65
Strain at yield (%)			3	5	7	7
Tensile strength (MPa)	47	56			55	77
Elongation at break (%)	15	40			100	150
Tensile modulus (GPa)	2	2.6	2.3	2.6	2.1	2.5
Flexural modulus (GPa)	1.5	2.4			2.1	2.5
Notched impact strength ASTM D256 (J/m)	100	600			650	950
Impact strength at 23°C (kJ/m^2)			25	70		
Impact strength at −30°C (kJ/m^2)			7	15		

Table 4.98 (Continued)

	ASA		ASA/PC alloys		PC	
	Min.	Max.	Min.	Max.	Min.	Max.
Thermal properties						
HDT B (0.46 MPa) (°C)	80	101	100	130	130	145
HDT A (1.8 MPa) (°C)	75	96	72	109	125	140
Short-time service temperature (°C)			105	110		
Continuous use temperature (°C)	80	90			90	125
Brittle point (°C)					−25	−25
Thermal conductivity (W/m.K)	0.17	0.17	0.17	0.17	0.2	0.2
Specific heat (cal/g/°C)	0.33	0.33	0.3	0.33	0.3	0.3
Coefficient of thermal expansion (10^{-5}/°C)	5	11	7	9	6	7
Electrical properties						
Volume resistivity (ohm.cm)	10^{14}	10^{15}	10^{13}	10^{15}	10^{15}	10^{16}
Dielectric constant	3.3	3.8	3	3.4	3	3
Loss factor (10^{-4})	90	340	20	190	7	100
Dielectric strength (kV/mm)					15	30
Fire behaviour						
Oxygen index (%)	18	18			24	25
UL94 fire rating	HB	HB	HB	HB	V2	V2

	ASA/PC High impact, low modulus		ASA/PC High impact at low temperature		ASA/PC FR grade	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.14	1.14	1.15	1.15	1.2	1.3
Shrinkage (%)	0.5	0.7	0.3	0.7	0.4	0.8
Absorption of water (%)	0.20	0.30			0.2	0.3
Mechanical properties						
Stress at yield (MPa)	50	50	53	53	58	58
Strain at yield (%)	4	4	4	5	5	5
Tensile strength (MPa)	50	50	53	53	58	58
Elongation at break (%)	>50	>50	110	120	100	100
Tensile modulus (GPa)	2	2	2.3	2.3	2.5	2.5
Flexural modulus (GPa)	2	2			2.5	2.5
Creep modulus 0.5% 1 h (GPa)			2	2		
Creep modulus 0.5% 1000 h (GPa)			1.6	1.6		
Notched impact strength ASTM D256 (J/m)			600	600	500	500
Notched impact strength ASTM D256 at −30°C (J/m)			150	150	100	100
Impact strength at 23°C (kJ/m^2)	45	45	40	40	30	30
Impact strength at −20°C (kJ/m^2)					2	2
Impact strength at −30°C (kJ/m^2)	7	8				
Thermal properties						
HDT B (0.46 MPa) (°C)			125	125	130	130
HDT A (1.8 MPa) (°C)	105	105	106	106	115	115
Short-time service temperature (°C)			105	110	110	115
Thermal conductivity (W/m.K)			0.17	0.17	0.17	0.17
Coefficient of thermal expansion (10^{-5}/°C)			7	9	6	8
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{13}	10^{14}	10^{14}	10^{14}
Dielectric constant	3	3.1	3.2	3.4	3.2	3.3
Loss factor (10^{-4})	16	43	160	190	7	100
Dielectric strength (kV/mm)					110	170
Fire behaviour						
UL94 fire rating	HB	HB	HB	HB	V0	V0

4.29.3 ABS/PA alloys

Properties, processability and prices are intermediate between those of ABS and PA.

Advantages

ABS/PA alloys are appreciated for their good mechanical properties, high impact strength, attractive price/property ratios, aesthetics, good low-temperature properties for suitable grades, easy processing, high surface quality, inertness to certain chemicals, fair density, good electrical insulation even in wet environments, feasibility of welding, paintability, lower water uptake than PA.

Drawbacks

The general drawbacks are sensitivity to heat, UV, light and weathering, requiring efficient protection for long-term outdoor exposure (stabilized grades are marketed); inherent easy combustion, but FR grades are marketed including halogen-free ones; cost, though justified by the performances; creep when the temperature rises; sensitivity to attack by some chemicals.

The costs are of the order of several Euros per kilogram.

Application examples

- Automotive
  - instrument panels . . .
  - centre consoles, airbag covers, radio faceplates, glove compartments . . .
  - air vents, demister/defroster grilles . . .
  - door assemblies . . .
  - gear levers . . .
  - car bodies, spoilers . . .
  - bumpers . . .
  - motorcycle fairings, scooter exterior parts . . .
- Sports and recreation
  - ski and binding components, ski poles . . .
  - snowboards, gears for skaters . . .
- Consumer goods, appliances
  - power tool housings . . .
  - appliances, household housings . . .

Trade name examples: Technyl Alloy, Terblend N, Triax.

Table 4.99 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

4.29.4 Polypropylene/polyamide (PP/PA) alloys

Properties, processability and prices are intermediate between those of polypropylene and polyamide, mainly PA 6 and PA 66.

Advantages

PP/PA alloys are appreciated for their good mechanical properties, toughness, broad range of moduli, attractive price/property ratios, good low-temperature properties for suitable

Table 4.99 Property examples of ABS/PA alloys compared to ABS and PA

	ABS		General-purpose ABS/PA		PA	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.00	1.15	1.06	1.07	1.13	1.15
Shrinkage (%)	0.4	0.9	0.8	2	0.7	3
Absorption of water (%)	0.1	0.8	0.1	0.1	1	3
Mechanical properties						
Shore hardness, D	75	85			80	95
Rockwell hardness, R	75	95				
Rockwell hardness, M	10	50			30	85
Stress at yield (MPa)	20	64			45	85
Tensile strength (MPa)	30	60	40	41	50	95
Elongation at break (%)	2	100	270	290	150	300
Tensile modulus (GPa)	1	3	1.2	1.3	1.0	3.5
Flexural modulus (GPa)	1	3			0.8	3.0
Notched impact strength ASTM D256 (J/m)	100	500	950	1000	50	150
Impact strength at 23°C (kJ/m^2)			50	75		
Impact strength at −30°C (kJ/m^2)			10	18		
Thermal properties						
HDT B (0.46 MPa) (°C)	90	125	91	100	180	240
HDT A (1.8 MPa) (°C)	80	120	70	75	65	105
Continuous use temperature (°C)	60	110			80	150
Brittle point (°C)	−40	−20			−80	−65
Thermal conductivity (W/m.K)	0.2	0.4	0.29	0.31	0.25	0.25
Specific heat (cal/g/°C)	0.3	0.4			0.55	0.55
Coefficient of thermal expansion (10^{-5}/°C)	6	10	6	10	5	14
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{13}	10^{15}	10^{12}	10^{14}
Dielectric constant	2.4	5	3	6	4	5
Loss factor (10^{-4})	20	350	400	900	100	400
Dielectric strength (kV/mm)	12	20	13	40	20	30
Fire behaviour						
Oxygen index (%)	18	19	20	21	21	23
UL94 fire rating	HB	HB	HB	HB	HB	V2

	High impact		10% GF		20% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.07	1.07	1.12	1.12	1.2	1.2
Mechanical properties						
Stress at yield (MPa)	28	30	48	55	60	80
Strain at yield (%)	3	6	3	4	3	4
Elongation at break (%)	>50	>50	5	7	3	4
Tensile modulus (GPa)	1.2	1.6	3.3	3.3	4.2	5.5
Flexural modulus (GPa)	1.2	1.6	3.3	3.3	4.2	5.5
Impact strength at 23°C (kJ/m^2)	80	80	20	20	15	15
Impact strength at −30°C (kJ/m^2)	50	50	10	10	8	8
Thermal properties						
HDT B (0.46 MPa) (°C)	94	94	110	110	170	170
HDT A (1.8 MPa) (°C)	68	68	90	90	105	105
Coefficient of thermal expansion (10^{-5}/°C)	10	11	6	6	4	4

(*Continued*)

Table 4.99 (Continued)

	High impact		10% GF		20% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Electrical properties						
Volume resistivity (ohm.cm)	10^{13}	10^{15}	10^{13}	10^{15}	10^{13}	10^{15}
Dielectric constant	2.9	3.1	2.9	3.6	2.9	3.6
Loss factor (10^{-4})	450	450	130	500	130	500
Dielectric strength (kV/mm)	35	40	35	40	35	40
Fire behaviour						
UL94 fire rating	HB	HB	HB	HB	HB	HB

Summary of some general assessments concerning chemical behaviour at room temperature of ABS and polyamide, which are not necessarily representative of ABS/PA alloys or of all grades of ABS and PA. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	ABS	PA
Light	UV protection is needed	UV protection is needed
Weak acids	Good behaviour	Good to limited behaviour
Strong acids	Limited to unsatisfactory behaviour	Unsatisfactory behaviour
Bases	Good to limited behaviour according to the nature and concentration	Good to limited behaviour according to the nature and concentration
Solvents	Good to limited resistance against vegetable oils, saturated aliphatic hydrocarbons, polyglycols and various foodstuffs	Good to limited resistance against oils, greases, hydrocarbons, certain chlorinated solvents, cosmetics, aldehydes, some alcohols, ketones, esters, glycols
	ABS are attacked by aldehydes, esters, ethers, ketones, aromatic and certain aliphatic hydrocarbons, chlorinated solvents, aromatic amines, polyglycol ethers . . .	Polyamides are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols

grades, easy processing, inertness to certain chemicals, fair density, good electrical insulation even in wet environments, feasibility of welding, lower water uptake than PA, low permeability to gases and polar solvents.

Drawbacks

The general drawbacks are sensitivity to heat, UV, light and weathering, requiring efficient protection for outdoor exposure (stabilized grades are marketed); inherent easy combustion, but FR grades are marketed; cost (but justified by the performances); creep when the temperature rises; sensitivity to attack by some chemicals.

The costs are of the order of several Euros per kilogram.

Applications include extrusion, blown film, cable sheathing, blow moulding and extrusion, injection moulding. For example:

- tubes, mandrels, pipes, profiles, cables . . .
- hollow vessels, parts and containers . . .
- films, barrier films . . .
- engine air intake (sequential blow moulding) . . .

Trade name examples: Nylex, Orgalloy.

Table 4.100 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.100 Property examples of PP/PA alloys compared to PP and PA

	PP		PP/PA alloys		PA	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	0.90	0.91	1.03	1.05	1.13	1.15
Shrinkage (%)	1	3	1.4	2	0.7	3.0
Absorption of water (%)	0.01	0.1	0.5	1.4	1.0	3.0
Mechanical properties						
Shore hardness, D	70	83	50	76	80	95
Rockwell hardness, R						
Rockwell hardness, M					30	85
Stress at yield (MPa)	35	40	23	50	45	85
Strain at yield (%)			3	7		
Tensile strength (MPa)	20	40	30	56	50	95
Elongation at break (%)	150	600	>100	380	150	300
Tensile modulus (GPa)	1.1	1.6	0.3	2.3	1.0	3.5
Flexural modulus (GPa)	1.2	1.6	0.2	2.2	0.8	3.0
Notched impact strength ASTM D256 (J/m)	20	60	180	260	50	150
Impact strength at 23°C (kJ/m^2)			16	NB		
Impact strength at −20°C (kJ/m^2)			12	NB		
Thermal properties						
HDT B (0.46 MPa) (°C)	100	120	60	200	180	240
HDT A (1.8 MPa) (°C)	50	60	45	80	65	105
Continuous use temperature (°C)	120	130			80	150
Brittle point (°C)	−20	−10			−80	−65
Thermal conductivity (W/m.K)	0.15	0.21			0.25	0.25
Specific heat (cal/g/°C)	0.46	0.46			0.55	0.55
Coefficient of thermal expansion (10^{-5}/°C)	6	17	6	20	5	14
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{18}	10^{13}	10^{16}	10^{12}	10^{14}
Dielectric constant	2.3	2.3			4	5
Loss factor (10^{-4})	3	5	170	1100	100	400
Dielectric strength (kV/mm)	20	28	34	36	20	30
Fire behaviour						
Oxygen index (%)	17	18			21	23
UL94 fire rating	HB	HB	HB	HB	HB	V2

	PA 6/PP Low modulus		PA 6/PP Medium modulus		PA 6/PP High modulus	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.04	1.04	1.02	1.05	1.03	1.05
Absorption of water (%)	0.8	1.35	0.7	1	0.7	1.1
Mechanical properties						
Shore hardness, D	50	55	61	72	71	77
Stress at yield (MPa)	23	23	30	40	40	52
Strain at yield (%)	3.5	3.5	4	7	3	4
Tensile strength (MPa)	30	35	46	56	45	56
Elongation at break (%)	260	380	250	330	>100	300
Tensile modulus (GPa)	0.3	0.5	0.6	1.8	1.6	2.6
Flexural modulus (GPa)	0.2	0.8	0.5	1.4	1.3	2.32
Impact strength at 23°C (kJ/m^2)	NB	NB	23	NB	16	32
Impact strength at −20°C (kJ/m^2)	NB	NB	12	32	12	25

(*Continued*)

Table 4.100 (Continued)

	PA 6/PP Low modulus		PA 6/PP Medium modulus		PA 6/PP High modulus	
	Min.	Max.	Min.	Max.	Min.	Max.
Thermal properties						
HDT B (0.46 MPa) (°C)	60	60			80	130
HDT A (1.8 MPa) (°C)			45	45	50	75
Coefficient of thermal expansion (10^{-5}/°C)	17	18	<20	20	9	14
Electrical properties						
Volume resistivity (ohm.cm)	10^{13}	10^{14}			10^{15}	10^{16}
Loss factor (10^{-4})	500	1100			170	700
Dielectric strength (kV/mm)	36	36			36	38
Fire behaviour						
UL94 fire rating	HB	HB	HB	HB	HB	HB

	PA 6/PP 10% glass fibre		PA 6/PP 30% glass fibre	
	Min.	Max.	Min.	Max.
Miscellaneous properties				
Density (g/cm^3)	1.12	1.12	1.25	1.25
Absorption of water (%)	0.8	0.8	0.6	0.6
Mechanical properties				
Shore hardness, D	81	81	82	82
Stress at yield (MPa)	84	84		
Strain at yield (%)	3	4		
Tensile strength (MPa)	80	80	130	130
Elongation at break (%)	4	5	3	4
Tensile modulus (GPa)	3.3	3.3	7.5	7.5
Flexural modulus (GPa)	3	3.2	7	7.4
Impact strength at 23°C (kJ/m^2)	20	21	20	22
Impact strength at −20°C (kJ/m^2)	19	20	18	19
Thermal properties				
HDT B (0.46 MPa) (°C)	210	210	210	210
HDT A (1.8 MPa) (°C)	190	190	190	190
Coefficient of thermal expansion (10^{-5}/°C)			2	12
Electrical properties				
Volume resistivity (ohm.cm)	10^{15}	10^{15}	10^{15}	10^{15}
Loss factor (10^{-4})	240	650	230	660
Dielectric strength (kV/mm)	36	36	34	34
Fire behaviour				
UL94 fire rating	HB	HB	HB	HB

	PA 66/PP High modulus		PA 66/PP 20% glass fibre		PA 66/PP 35% glass fibre	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.04	1.04	1.18	1.18	1.31	1.31
Absorption of water (%)	0.7	0.7	0.5	0.5	0.4	0.4
Mechanical properties						
Shore hardness, D	77	77	82	82	83	83
Stress at yield (MPa)	51	52				
Strain at yield (%)	4	5				

Table 4.100 (Continued)

	PA 66/PP High modulus		PA 66/PP 20% glass fibre		PA 66/PP 35% glass fibre	
	Min.	Max.	Min.	Max.	Min.	Max.
Tensile strength (MPa)	50	50	110	110	160	160
Elongation at break (%)	>100	>100	4	5	3	4
Tensile modulus (GPa)	2.6	2.6	5.5	5.5	9	10
Flexural modulus (GPa)	2.1	2.3	5.1	5.2	8	9
Impact strength at 23°C (kJ/m^2)	17	20	16	16	22	23
Impact strength at −20°C (kJ/m^2)	12	13	10	10	20	20
Thermal properties						
HDT B (0.46 MPa) (°C)	160	160	240	240	245	245
HDT A (1.8 MPa) (°C)	80	80	220	220	225	225
Coefficient of thermal expansion (10^{-5}/°C)	6	11	3	11	1.7	10
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{15}	10^{16}	10^{15}	10^{16}
Loss factor (10^{-4})	170	320	170	310	150	310
Dielectric strength (kV/mm)	36	36	36	36	34	34
Fire behaviour						
UL94 fire rating	HB	HB	HB	HB	HB	HB

Summary of some general assessments concerning the chemical behaviour at room temperature of polypropylene and polyamide, which are not necessarily representative of PP/PA alloys or of all grades of PP and PA. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	PP	PA
Light	UV protection is needed	UV protection is needed
Weak acids	Good behaviour	Good to limited behaviour
Strong acids	Good behaviour except oxidizing acids	Unsatisfactory behaviour
Bases	Good behaviour	Good to limited behaviour according to the nature and concentration
Solvents	Good behaviour up to 60°C except aromatics, chlorinated solvents, certain oxidizing chemicals	Good to limited resistance against oils, greases, hydrocarbons, certain chlorinated solvents, cosmetics, aldehydes, some alcohols, ketones, esters, glycols Polyamides are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols

4.29.5 Thermoplastic polyester alloys

Most polyester alloys are polyester/polycarbonates and properties, processability and prices are intermediate between those of polyester and polycarbonate. A few alloys are polyester/ASA and properties, processability and prices are intermediate between those of polyester and ASA.

Advantages

Polyester/PC alloys are appreciated for their high impact resistance even at low temperatures; outstanding aesthetics characteristics; chemical resistance to fuels and some other fluids used for automotive applications; good UV resistance and colour retention of suitable grades; good mechanical properties; good creep behaviour; attractive price/property ratios; fair dimensional stability; easy processing; weak absorption of water; good electrical insulation even in wet environments; feasibility of welding.

Drawbacks

The general drawbacks are a certain sensitivity to heat, UV, light and weathering, requiring efficient protection for outdoor exposure (stabilized grades are marketed); inherent easy combustion, but FR grades are marketed including halogen-free ones; cost (but justified by the performances); creep when the temperature rises.

The costs are of the order of several Euros per kilogram.

Application examples

- Automotive
  - ○ bumpers, fascias . . .
  - ○ airbag covers and doors . . .
  - ○ wheel covers . . .
  - ○ headlamp bezels . . .
  - ○ brake and fuel line clips . . .
  - ○ tractor hoods and panels . . .
  - ○ outdoor recreational vehicle components . . .
  - ○ large structural parts, farming machine parts . . .
- Consumer goods
  - ○ lawnmower decks . . .
  - ○ chain-saw housings . . .
  - ○ business equipment housings . . .
  - ○ cellular phones . . .
- Electricity & electronics
  - ○ switches, connectors . . .
  - ○ power distribution boxes . . .
  - ○ telephone-line splice cases . . .
- Miscellaneous
  - ○ material-handling pallets . . .
  - ○ ski bindings . . .
  - ○ suitcase shells, transport boxes . . .

Trade name examples: Ultradur, Vandar, Xenoy, Xylex

Table 4.101 relates to examples only and cannot be generalized. Data cannot be used for designing.

4.29.6 ABS/PVC alloys

Properties, processability and prices are intermediate between those of ABS and PVC. Like PVC, these alloys are handicapped by their halogen content, which conflicts with ecological trends.

Advantages

ABS/PVC alloys are appreciated for their inherent flame resistance, but beware of toxic and corrosive fumes; good impact resistance; resistance to certain chemicals; good UV resistance of suitable grades; fair mechanical properties; attractive price/property ratios; fair dimensional stability; easier processing than PVC; weak absorption of water; good electrical insulation even in wet environments, feasibility of welding.

Table 4.101 Property examples of polyester/PC alloys compared to polyester and PC

	Polyester		Polyester/ PC alloys		PC	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.3	1.4	1.2	1.2	1.2	1.2
Shrinkage (%)	0.5	2.2	0.5	0.7	0.5	0.7
Absorption of water (%)	0.1	0.2	0.1	0.2	0.1	0.2
Mechanical properties						
Shore hardness, D	90	95	80	>95	85	95
Rockwell hardness, R	>120	>120	108	>120	114	>120
Rockwell hardness, M	70	80	30	109	50	85
Stress at yield (MPa)			37	53	50	65
Strain at yield (%)			4	7	7	7
Tensile strength (MPa)	40	50	41	57	55	77
Elongation at break (%)	50	200	>100	200	100	150
Tensile modulus (GPa)	2	3	1.6	2.2	2.1	2.5
Flexural modulus (GPa)	2	3	1.5	2.2	2.1	2.5
Notched impact strength ASTM D256 (J/m)	35	55	110	850	650	950
Notched impact strength ASTM D256 at −40°C (J/m)			25	450		
Impact strength at 23°C (kJ/m^2)			2	70		
Thermal properties						
HDT B (0.46 MPa) (°C)	115	150	110	>110	130	145
HDT A (1.8 MPa) (°C)	50	85	57	120	125	140
Continuous use temperature (°C)	80	140	90	140	90	125
Brittle point (°C)	−40	−40	−40	−25	−25	−25
Thermal conductivity (W/m.K)	0.21	0.21	0.2	0.2	0.2	0.2
Specific heat (cal/g/°C)	0.32	0.32			0.3	0.3
Coefficient of thermal expansion (10^{-5}/°C)	6	10	7	13	6	7
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{14}	10^{16}	10^{15}	10^{16}
Dielectric constant	3	3	3	3	3	3
Loss factor (10^{-4})	10	200	15	1000	7	100
Dielectric strength (kV/mm)	45	60	14	24	15	30
Fire behaviour						
Oxygen index (%)	21	24	20	25	24	25
UL94 fire rating	HB	HB	HB	V2	V2	V2

Unfilled alloys	General purpose		High impact		High temp.	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.22	1.22	1.2	1.22	1.2	1.22
Shrinkage (%)	0.5	2.2	0.7	1.1	0.5	0.8
Absorption of water (%)	0.06	0.14			0.1	0.1
Mechanical properties						
Shore hardness, D	80	>95				
Rockwell hardness, R	108	>120				
Rockwell hardness, M	30	109				
Stress at yield (MPa)	37	53	47	50	52	52
Strain at yield (%)	4	7	4	5	5	5
Tensile strength (MPa)	41	57	47	50	52	52
Elongation at break (%)	>100	200	>100	>100	>100	>100

(*Continued*)

Table 4.101 (Continued)

Unfilled alloys	General purpose		High impact		High temp.	
	Min.	Max.	Min.	Max.	Min.	Max.
Tensile modulus (GPa)	1.6	2.2	1.8	1.9	2.2	2.2
Flexural modulus (GPa)	1.5	2.2	1.8	1.9	2.2	2.2
Notched impact strength ASTM D256 (J/m)	110	650	750	850	700	700
Notched impact strength ASTM D256 at −40°C (J/m)	25	160	320	450	225	225
Impact strength at 23°C (kJ/m^2)	2	28	45	70	40	40
Thermal properties						
HDT A (1.8 MPa) (°C)	57	95	50	95	120	120
Thermal conductivity (W/m.K)	0.2	0.2	0.2	0.2	0.2	0.2
Coefficient of thermal expansion (10^{-5}/°C)	7	10	9	13	8	8
Electrical properties						
Volume resistivity (ohm.cm)	10^{14}	10^{16}	10^{14}	10^{16}	10^{14}	10^{16}
Dielectric constant	3	3	3	3		
Loss factor (10^{-4})	15	1000	22	1000		
Dielectric strength (kV/mm)	14	18	18	24		
Fire behaviour						
Oxygen index (%)	20	25				
UL94 fire rating	HB	V2	HB	HB	HB	HB

Glass fibre reinforced alloys	10% GF		30% GF		30% GF High ductility	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.3	1.3	1.44	1.44	1.51	1.51
Shrinkage (%)	1.1	1.7	0.3	0.8	0.3	1.3
Absorption of water (%)	0.11	0.11	0.09	0.09	0.1	0.1
Mechanical properties						
Shore hardness, D	80	85	80	85	80	85
Rockwell hardness, R	113	113	109	109	110	110
Rockwell hardness, M	30	50	30	50	30	50
Tensile strength (MPa)	62	62	89	89	80	80
Elongation at break (%)			3	3	6	6
Tensile modulus (GPa)			7	7	7.5	7.5
Flexural modulus (GPa)	2.7	2.7	5.2	5.2	5.9	5.9
Notched impact strength ASTM D256 (J/m)	190	190	170	170	165	165
Notched impact strength ASTM D256 at −40°C (J/m)	110	110	100	100	150	150
Impact strength at 23°C (kJ/m^2)			16	16		
Thermal properties						
HDT A (1.8 MPa) (°C)	120	120	150	150	165	165
Thermal conductivity (W/m.K)	0.2	0.2	0.2	0.2	0.2	0.2
Coefficient of thermal expansion (10^{-5}/°C)	5	6	2	3	1	2
Electrical properties						
Volume resistivity (ohm.cm)	10^{14}	10^{16}	10^{14}	10^{16}	10^{14}	10^{16}
Dielectric constant	3	4	3	4	3	4
Loss factor (10^{-4})	20	100	30	200	30	200
Dielectric strength (kV/mm)	19	19	21	21	20	20
Fire behaviour						
Oxygen index (%)	20	20	19	19	21	21
UL94 fire rating	HB	V2	HB	HB	HB	HB

Table 4.101 (Continued)

Summary of some general assessments concerning the chemical behaviour at room temperature of polyester and polycarbonate, which are not necessarily representative of polyester/PC alloys or of all grades of polyester and PC. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	Polyester	PC
Light	UV protection is needed	UV protection is needed
Weak acids	Good to limited behaviour	Good to limited behaviour
Strong acids	Unsatisfactory	Good to unsatisfactory behaviour according to the concentration
Bases	Good to unsatisfactory behaviour according to the nature and concentration	Good to unsatisfactory behaviour according to the nature and concentration
Solvents	Chemical resistance is generally good to limited at room temperature versus dilute bases and weak acids, oils, greases, aliphatic hydrocarbons, certain alcohols Limited to unsatisfactory resistance to aromatic and halogenated hydrocarbons Polyesters are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols	Good to limited resistance against oils, greases, aliphatic hydrocarbons, certain alcohols Unsatisfactory against aldehydes, esters, ethers, ketones, aromatic hydrocarbons, chlorinated solvents, amines, certain alcohols, phenols . . .

	PBT 30% GF		PBT/ASA alloys 30% GF		PBT/ASA alloys 10% GF	
Miscellaneous properties						
Density (g/cm^3)	1.5	1.6	1.45	1.47	1.3	1.34
Shrinkage (%)	0.2	1	0.3	0.7	0.1	0.9
Absorption of water (%)	0.1	0.1	0.2	0.4	0.2	0.4
Mechanical properties						
Shore hardness, D	95	>95				
Rockwell hardness, M	90	95				
Stress at yield (MPa)	135	140	125	135		
Strain at yield (%)	2	3	2	3		
Tensile strength (MPa)	135	140	125	138	75	75
Elongation at break (%)	2	3			3	3
Tensile modulus (GPa)	9	11.5	9	10	4	5
Flexural modulus (GPa)	9	11.5	8	9		
Notched impact strength ASTM D256 (J/m)	50	90	85	85	50	60
Thermal properties						
HDT B (0.46 MPa) (°C)	215	250	204	220	190	200
HDT A (1.8 MPa) (°C)	195	225	175	190	105	130
Continuous use temperature (°C)	100	140				
Melting temperature (°C)	220	265				
Thermal conductivity (W/m.K)	0.24	0.24				
Specific heat (cal/g/°C)	0.28	0.28				
Coefficient of thermal expansion (10^{-5}/°C)	2	5	3	3	5	6
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{15}	10^{16}	10^{15}	10^{16}
Dielectric constant	3	4	3	4	3	4
Loss factor (10^{-4})	20	120	30	180	30	205
Dielectric strength (kV/mm)	50	50				
Fire behaviour						
Oxygen index (%)	19	20				
UL94 fire rating	HB	HB	HB	HB	HB	HB

Drawbacks

The general drawbacks are a certain sensitivity to heat, UV, light and weathering, requiring efficient protection for outdoor exposure (stabilized grades are marketed); ecological problems because of the halogen presence; toxicity and corrosivity of fumes in the event of fire; cost (though justified by the performances); creep when the temperature rises; more difficult to process than ABS.

Application examples

- Consumer goods
    - lawn and garden applications . . .
    - business equipment housings, computer and printer components, cash register bases . . .
    - domestic appliance housings . . .
    - recreational products . . .
- Electricity & electronics
    - boxes . . .
    - communication components . . .
- Miscellaneous
    - fireproofed parts and goods . . .
    - pipes and fittings for plumbing . . .

Trade name examples: Novaloy . . .

Table 4.102 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.102 Property examples of ABS/PVC alloys compared to ABS and PVC

	ABS		ABS/PVC alloys		PVC	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.00	1.15	1.13	1.3	1.35	1.5
Shrinkage (%)	0.4	0.9	0.3	0.6	0.1	0.6
Absorption of water (%)	0.1	0.8	0.2	0.2	0.04	0.4
Mechanical properties						
Shore hardness, D	75	85	73	73	65	90
Rockwell hardness, M	10	50			<10	70
Stress at yield (MPa)	20	64	30	46	35	55
Strain at yield (%)			8	8		
Tensile strength (MPa)	30	60	43	50	35	60
Elongation at break (%)	2	100	20	20	2	80
Tensile modulus (GPa)	1	3	2.2	2.6	2.4	4
Flexural strength (MPa)			55	77	69	103
Flexural modulus (GPa)	1	3	2.2	2.8	2.1	3.5
Notched impact strength ASTM D256 (J/m)	100	500	100	400	20	110
Thermal properties						
HDT B (0.46 MPa) (°C)	90	125	75	75	57	80
HDT A (1.8 MPa) (°C)	80	120	70	94	54	75
Continuous use temperature (°C)	65	110	60	70	50	80
Minimum service temperature (°C)	−40	−20			−10	0
Thermal conductivity (W/m.K)	0.2	0.4			0.16	0.16
Specific heat (cal/g/°C)	0.3	0.4			0.2	0.3
Coefficient of thermal expansion (10^{-5}/°C)	6	13	5	9	5	18

Table 4.102 (Continued)

	ABS		ABS/PVC alloys		PVC	
	Min.	Max.	Min.	Max.	Min.	Max.
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}	10^{15}	10^{15}	10^{15}	10^{16}
Dielectric constant	2.4	5	3	3	3	4
Loss factor (10^{-4})	20	350	400	400	25	250
Dielectric strength (kV/mm)	12	20	23	23	10	50
Arc resistance (s)	45	85			60	80
Fire behaviour						
Oxygen index	18	19	28	31	35	45
UL94 fire rating	HB	HB	V1	V0	V0	V0

Summary of some general assessments concerning chemical behaviour at room temperature of ABS and PVC, which are not necessarily representative of ABS/PVC alloys or of all grades of ABS and PVC. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	ABS	PVC
Light	UV protection is needed	UV protection is needed
Weak acids	Good behaviour	Good behaviour
Strong acids	Limited to unsatisfactory behaviour according to the nature and concentration	Good to unsatisfactory behaviour according to the nature and concentration
Bases	Good to limited behaviour according to the nature and concentration	Good behaviour
Solvents	Good to limited resistance against vegetable oils, saturated aliphatic hydrocarbons, polyglycols, and various foodstuffs	Good behaviour with aliphatic hydrocarbons Variable resistance to oils, greases, alcohols
	Unsatisfactory against aldehydes, esters, ethers, ketones, aromatic and certain aliphatic hydrocarbons, chlorinated solvents, aromatic amines, polyglycol ethers . . .	Attacked by aromatic hydrocarbons, chlorinated solvents, esters, ethers and ketones

4.29.7 Polysulfone-based alloys

Polysulfones (PSU) and polyphenylsulfones (PPSU) can be modified by alloying with ABS, PBT, PC or proprietary polymers. The main sought-after characteristics are lower cost and easier processing, combined with a good balance of mechanical, thermal and chemical properties.

Advantages

Polysulfones are appreciated for: good mechanical and electrical properties; rigidity; good creep behaviour; fatigue endurance; fair shrinkage and moisture uptake; the broad range of service temperatures (−100°C up to +150/200°C); optical and microwave transparency; fire resistance; suitability for food contact and sterilization.

PSU/PC alloys offer a combination of: high heat deflection temperature; steam and hot-water resistance; ability to be autoclaved; electrical properties; and dimensional stability. Suitable grades can be classified V0 in the UL94 fire rating and can be used for food and drinking water contact.

PSU/ABS can be electroplated to a bright metal finish, suited for many functional plated plumbing parts.

Glass fibre reinforced PSU/PBT alloys offer good electrical properties combined with high heat deflection temperatures and a V0 classification in the UL94 fire rating.

PPSU alloys have the best hydrolytic stability, thermal stability and oxidation resistance. This resin is resistant to mineral acids and alkalis, while ketones, chlorinated hydrocarbons and aromatic hydrocarbons may cause stress cracking.

Drawbacks

Polysulfones are handicapped by their light and UV sensitivity, requiring efficient protection for outdoor exposure; sensitivity to environmental stress cracking and attack by chemicals such as aromatic hydrocarbons, chlorinated solvents and ketones; the cost, justified by the performances; a sometimes insufficient fire resistance, but special grades are marketed.

Trade name examples: Acudel, Mindel . . .

Table 4.103 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.103 Property examples of PSU and PPSU alloys compared to PSU, PPSU, PC, ABS and PBT

	PSU		PSU/PC alloys		PC	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.24	1.29	1.23	1.23	1.2	1.2
Shrinkage (%)	0.6	0.7	0.7	0.7	0.5	0.7
Absorption of water (%)	0.2	1.1	0.2	0.2	0.1	0.2
Mechanical properties						
Shore hardness, D	90	90			85	95
Rockwell hardness, R	>120	>120			114	>120
Rockwell hardness, M	69	70			50	85
Stress at yield (MPa)	72	83	65	65	50	65
Strain at yield (%)			5	6	7	7
Tensile strength (MPa)	63	80	57	57	55	77
Elongation at break (%)	40	100	100	100	100	150
Tensile modulus (GPa)	2.1	2.7	2.4	2.4	2.1	2.5
Flexural modulus (GPa)	2.3	2.9	2.6	2.6	2.1	2.5
Notched impact strength, ASTM D256 (J/m)	53	70	85	85	650	950
Modulus retention at 180°C (%)	66	66				
Thermal properties						
HDT B (0.46 MPa) (°C)	181	181			130	145
HDT A (1.8 MPa) (°C)	174	205	149	149	125	140
Continuous use temperature (°C)	150	150			90	125
Steam sterilization (cycles)			100	100		
Brittle point (°C)	−100	−100			−25	−25
Thermal conductivity (W/m.K)	0.26	0.26			0.2	0.2
Specific heat (cal/g/°C)	0.27	0.27			0.3	0.3
Coefficient of thermal expansion (10^{-5}/°C)	3	6	10	10	6	7
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{17}	10^{16}	10^{16}	10^{15}	10^{16}
Dielectric constant	3.1	3.2	3	3	3	3
Loss factor (10^{-4})	11	50	30	30	7	100
Dielectric strength (kV/mm)	20	30	20	20	15	30
Arc resistance (s)	60	60	130	130	10	120
Fire behaviour						
Oxygen index (%)	30	38			24	25
UL94 fire rating	V1	V0	V0	V0	V2	V2

Table 4.103 (Continued)

Summary of some general assessments concerning chemical behaviour at room temperature of polysulfones and PC, which are not necessarily representative of polysulfone-based alloys or of all grades of polysulfone and PC. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	Polysulfone	PC
Light	UV stabilization is needed	UV protection is needed
Weak acids	Good behaviour	Good to limited behaviour
Strong acids	Unsatisfactory behaviour with concentrated acids	Good to unsatisfactory behaviour according to the concentration
Bases	Good to limited behaviour	Good to unsatisfactory behaviour according to the nature and concentration
Solvents	Polysulfones resist acids at medium concentrations, alcohols, aliphatic hydrocarbons, greases, oils, gasoline, chlorine water	Good to limited resistance against oils, greases, aliphatic hydrocarbons, certain alcohols
	They are attacked by aromatic hydrocarbons, chlorinated solvents, ketones, esters, phenols, aldehydes, amines	Unsatisfactory against aldehydes, esters, ethers, ketones, aromatic hydrocarbons, chlorinated solvents, amines, certain alcohols, phenols . . .

	PSU		PSU/ABS alloys		ABS	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.24	1.29	1.13	1.13	1.00	1.15
Shrinkage (%)	0.6	0.7	0.6	0.7	0.4	0.9
Absorption of water (%)	0.2	1.1	0.25	0.25	0.1	0.8
Mechanical properties						
Shore hardness, D	90	90			75	85
Rockwell hardness, R	>120	>120				
Rockwell hardness, M	69	70			<10	50
Stress at yield (MPa)	72	83	50	50	20	64
Strain at yield (%)			4	4		
Tensile strength (MPa)	63	80	43	43	30	60
Elongation at break (%)	40	100	25	25	2	100
Tensile modulus (GPa)	2.1	2.7	2.1	2.1	1	3
Flexural modulus (GPa)	2.3	2.9	2.1	2.2	1	3
Notched impact strength, ASTM D256 (J/m)	53	70	320	320	100	500
Thermal properties						
HDT B (0.46 MPa) (°C)	181	181			90	125
HDT A (1.8 MPa) (°C)	174	205	149	149	80	120
Continuous use temperature (°C)	150	150			65	110
Glass transition temperature (°C)	187	190			95	115
Brittle point (°C)	−100	−100			−40	−20
Thermal conductivity (W/m.K)	0.26	0.26			0.20	0.40
Specific heat (cal/g/°C)	0.27	0.27			0.30	0.40
Coefficient of thermal expansion (10^{-5}/°C)	3	6	6	7	6	13
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{17}			10^{16}	10^{16}
Dielectric constant	3.1	3.2			2.4	5
Loss factor (10^{-4})	11	50			20	350
Dielectric strength (kV/mm)	20	30			12	20
Arc resistance (s)	60	60			45	85
Fire behaviour						
Oxygen index (%)	30	38			18	19
UL94 fire rating	V1	V0			HB	HB

(*Continued*)

Table 4.103 (Continued)

Summary of some general assessments concerning chemical behaviour at room temperature of polysulfones and ABS, which are not necessarily representative of polysulfone-based alloys or of all grades of polysulfone and ABS. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	Polysulfone	ABS
Light	UV protection is needed	UV protection is needed
Weak acids	Good behaviour	Good behaviour
Strong acids	Unsatisfactory behaviour with concentrated acids	Limited to unsatisfactory behaviour according to the nature and concentration
Bases	Good to limited behaviour	Good to limited behaviour according to the nature and concentration
Solvents	Polysulfones resist acids at medium concentrations, alcohols, aliphatic hydrocarbons, greases, oils, gasoline, chlorine water They are attacked by aromatic hydrocarbons, chlorinated solvents, ketones, esters, phenols, aldehydes, amines	Good to limited resistance against vegetable oils, saturated aliphatic hydrocarbons, polyglycols and various foodstuffs Unsatisfactory against aldehydes, esters, ethers, ketones, aromatic and certain aliphatic hydrocarbons, chlorinated solvents, aromatic amines, polyglycol ethers . . .

	PSU 30% GF		PSU/PBT GF		PBT 30% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.4	1.5	1.47	1.52	1.5	1.6
Shrinkage (%)	0.1	0.6	0.25	0.6	0.2	1
Absorption of water (%)	0.3	0.4	0.1	0.1	0.1	0.1
Mechanical properties						
Shore hardness, D	95	>95			95	>95
Rockwell hardness, R	115	120				
Rockwell hardness, M	87	100	80	80	90	95
Stress at yield (MPa)	100	125			135	140
Strain at yield (%)	2	3			2	3
Tensile strength (MPa)	100	125	103	122	135	140
Elongation at break (%)	2	3	2	3	2	3
Tensile modulus (GPa)	9	10			9	11.5
Flexural modulus (GPa)	7	8.5	6.2	9.4	9	11.5
Notched impact strength, ASTM D256 (J/m)	55	80	53	96	50	90
Thermal properties						
HDT B (0.46 MPa) (°C)	180	190			215	250
HDT A (1.8 MPa) (°C)	175	185	166	166	195	225
Continuous use temperature (°C)	150	150	140	150	100	140
Glass transition temperature (°C)	187	190				
Thermal conductivity (W/m.K)			0.22	0.22	0.24	0.24
Specific heat (cal/g/°C)					0.28	0.28
Coefficient of thermal expansion (10^{-5}/°C)	2	3	2	3	2	5
Electrical properties						
Volume resistivity (ohm.cm)			10^{16}	10^{17}	10^{16}	10^{16}
Dielectric constant			3	4	3	4
Loss factor (10^{-4})			20	90	20	120
Dielectric strength (kV/mm)			20	30	50	50
Arc resistance (s)			125	125		
Fire behaviour						
Oxygen index (%)			35	35	19	20
UL94 fire rating	V1	V0	V0	V0	HB	HB

Table 4.103 (Continued)

Summary of some general assessments concerning chemical behaviour at room temperature of polysulfones and polyester, which are not necessarily representative of polysulfone-based alloys or of all grades of polysulfone and polyester. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	Polysulfone	Polyester
Light	UV protection is needed	UV protection is needed
Weak acids	Good behaviour	Good to limited behaviour
Strong acids	Unsatisfactory behaviour with concentrated acids	Unsatisfactory
Bases	Good to limited behaviour	Good to unsatisfactory behaviour according to the nature and concentration
Solvents	Polysulfones resist acids at medium concentrations, alcohols, aliphatic hydrocarbons, greases, oils, gasoline, chlorine water	Chemical resistance is generally good to limited at room temperature versus dilute bases and weak acids, oils, greases, aliphatic hydrocarbons, and certain alcohols
	They are attacked by aromatic hydrocarbons, chlorinated solvents, ketones, esters, phenols, aldehydes, amines	Limited to unsatisfactory resistance to aromatic and halogenated hydrocarbons Polyesters are attacked by organic and mineral acids, oxidizing agents, concentrated bases, phenols

	PPSU		PPSU alloy HI		PPSU alloy	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.29	1.3	1.28	1.28	1.28	1.28
Shrinkage (%)	0.7	0.7	0.7	0.7	0.7	0.7
Absorption of water (%)	0.37	0.4				
Mechanical properties						
Shore hardness, D	85	90				
Rockwell hardness, R	110	122				
Rockwell hardness, M	50	75				
Strain at yield (%)	7	8	7	8	6	7
Tensile strength (MPa)	70	80	70	70	77	77
Elongation at break (%)	60	120	50	100	50	50
Tensile modulus (GPa)	2.3	2.4	2.3	2.4	2.7	2.7
Flexural modulus (GPa)	2.4	2.5	2.5	2.6	2.7	2.8
Notched impact strength, ASTM D256 (J/m)	365	700	267	267	105	105
Thermal properties						
HDT A (1.8 MPa) (°C)	200	208	190	207	197	197
Steam sterilization (cycles)	>1000	>1000				
Glass transition temperature (°C)	220	220				
Thermal conductivity (W/m.K)	0.3	0.3				
Coefficient of thermal expansion (10^{-5}/°C)	1.7	6				
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}			10^{16}	10^{16}
Dielectric constant	3.4	3.5			3.4	3.4
Loss factor (10^{-4})	6	76			80	80
Dielectric strength (kV/mm)	14	18			18	19
Fire behaviour						
Oxygen index (%)	38	38				
UL94 fire rating	V1	V0				

4.29.8 Polyphenylene sulfide-elastomer alloys

Advantages

Polyphenylene sulfides are appreciated for: good mechanical and electrical properties; rigidity; good creep behaviour; fatigue endurance; low shrinkage and moisture uptake; broad range of service temperatures (−196°C up to +200/240°C); weathering resistance; good chemical resistance; fire resistance; suitability for food contact.

Alloying with elastomers improves impact behaviour and processing.

Drawbacks

Polyphenylene sulfides are handicapped by their sensitivity to notched impact, requiring special cares when designing; and the cost, though justified by the performances.

Alloying with elastomers slightly lowers heat deflection temperatures.

Trade name examples: Xtel . . .

Table 4.104 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.104 Property examples of PPS-elastomer alloys

	PPS 20–40% GF		PPS/elastomer alloys		PPS/elastomer alloys	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.5	1.7	1.55	1.55	1.65	1.65
Shrinkage (%)	0.2	0.5	0.3	0.6	0.3	0.5
Absorption of water (%)	0.02	0.05				
Mechanical properties						
Shore hardness, D	90	>95				
Rockwell hardness, M	80	104				
Stress at yield (MPa)	130	150				
Strain at yield (%)	1	4				
Tensile strength (MPa)	130	150	200	215	175	180
Elongation at break (%)	1	4	1.9	2.1	1.6	1.7
Tensile modulus (GPa)	6	14				
Flexural modulus (GPa)	6	15	11	12	12	12
Notched impact strength, ASTM D256 (J/m)	35	100	90	90	80	90
Thermal properties						
HDT B (0.46 MPa) (°C)	270	280				
HDT A (1.8 MPa) (°C)	250	270	245	245	240	240
Continuous use temperature (°C)	200	220				
Thermal conductivity (W/m.K)	0.3	0.3				
Coefficient of thermal expansion (10^{-5}/°C)	1	4	2	6	2	6
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}	10^{16}				
Dielectric constant	3.8	4	3.8	4	3.8	4
Loss factor (10^{-4})	13	100	150	200	100	200
Dielectric strength (kV/mm)	17	31	24	24	22	22
Arc resistance (s)	34	85	100	100	100	100
Fire behaviour						
Oxygen index (%)	25	32	47	47	32	
UL94 rating	HB	V0	V0	V0	V0	V0

Table 4.104 (Continued)

Summary of some general assessments concerning chemical behaviour of PPS at room temperature, which are not necessarily representative of PPS/elastomer alloys or of all grades of PPS. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

Light	Good behaviour
Weak acids	Good behaviour
Strong acids	Fair behaviour except with oxidizing acids
Weak bases	Limited behaviour
Strong bases	Limited behaviour
Solvents	At room temperature, polyphenylene sulfide generally resists most alcohols, aliphatic and aromatic hydrocarbons, greases, oils, gasoline, ketones, esters, ethers, glycols Behaviour with halogenated solvents, bases, oxidizing acids, amines, aromatic oxygenated solvents can be limited When the temperature rises, polyphenylene sulfide can be attacked by hot strong acids and bases, chlorinated solvents, oxidizing agents, halogens, amines

4.29.9 Polyetherimide/polycarbonate alloys (PEI/PC)

Polyetherimide/polycarbonate alloys offer properties, processability and prices intermediate between those of polyetherimide and polycarbonate.

Polyetherimide is appreciated for: good mechanical and electrical properties; high service temperatures; rigidity; good creep behaviour; fatigue endurance; low shrinkage and moisture uptake; inherent flame retardancy and low smoke emission in the event of fire; transparency to visible light, infrared and microwaves; inherent resistance to UV and weathering; good resistance to hydrolysis and steam sterilization; high-energy radiation resistance; possibility of food contact.

Advantages

PEI/PC alloys, including glass-filled grades, may provide a cost-competitive alternative to glass-filled PEI with a better processability, provided the designer accepts the decrease in performances.

Drawbacks

Polyetherimides are handicapped by the cost, which is justified by the performances; a high density; a sometimes insufficient chemical resistance; the limited number of grades and sources.

The PEI/PC alloys, including glass-filled grades, have lower performances but may enlarge the choice of grades with lower costs.

Trade name examples: Ultem ATX . . .

Targeted applications are electronics, telecommunications and automotive components.

Table 4.105 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

4.29.10 Other alloys

There are numerous other alloys, some being experimental, certain being of specific use and other in-house blends. Some cases are quoted, without claiming to be exhaustive.

Table 4.105 Property examples of PEI/PC alloys compared to PEI and PC

Filler	PEI		PEI/PC alloy	PEI/PC alloy 10% GF	PC	
	Min.	Max.			Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.27	1.3	1.27	1.33	1.2	1.2
Shrinkage (%)	0.7	0.8	0.5–0.7	0.5–0.7	0.5	0.7
Absorption of water (%)	0.2	0.3	0.25	0.25	0.1	0.2
Mechanical properties						
Shore hardness, D	95	>95			85	95
Rockwell hardness, R	>120	>120			114	>120
Rockwell hardness, M	109	112			50	85
Stress at yield (MPa)	100	110	101	105	50	65
Strain at yield (%)	7	7	3	3	7	7
Tensile strength (MPa)	90	100			55	77
Elongation at break (%)	60	60			100	150
Tensile modulus (GPa)	3	3	3.3	3.9	2.1	2.5
Flexural modulus (GPa)	3	3.3	3.3	3.8	2.1	2.5
Modulus retention at 100°C (%)	85	90				
Modulus retention at 150°C (%)	65	70				
Notched impact strength, ASTM D256 (J/m)	50	60	75	60	650	950
Thermal properties						
HDT B (0.46 MPa) (°C)	195	210			130	145
HDT A (1.8 MPa) (°C)	190	200	182	193	125	140
Continuous use temperature (°C)	170	180			90	125
Glass transition temperature (°C)	215	215			150	150
Thermal conductivity (W/m.K)	0.22	0.22			0.2	0.2
Coefficient of thermal expansion (10^{-5}/°C)	5	6			6	7
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{17}			10^{15}	10^{16}
Dielectric constant	3.1	3.2			3	3
Loss factor (10^{-4})	13	25			7	100
Dielectric strength (kV/mm)	28	33			15	30
Arc resistance (s)	128	128			10	120
Fire behaviour						
Oxygen index (%)	47	47			24	25
UL94 rating	V0	V0			V2	V2

Summary of some general assessments concerning chemical behaviour at room temperature of PEI and PC, which are not necessarily representative of PEI/PC alloys or of all grades of PEI and PC. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	PEI	PC
Light	UV and hydrolysis resistant	UV protection is needed
Weak acids	Good behaviour	Good to limited behaviour
Strong acids	Good behaviour with dilute acids	Good to unsatisfactory behaviour according to the concentration
Bases	Good behaviour limited to pH <9	Good to unsatisfactory behaviour according to the nature and concentration
Solvents	PEI resists mineral acids, dilute bases (pH < 9), freons, oils, greases, gasoline, most fuels, certain hydrocarbons and fully halogenated hydrocarbons, most cooking oils and greases, most detergents and disinfectants	Good to limited resistance against oils, greases, aliphatic hydrocarbons, certain alcohols
	They are attacked by certain hydrocarbons, partially chlorinated solvents, ketones	Unsatisfactory against aldehydes, esters, ethers, ketones, aromatic hydrocarbons, chlorinated solvents, amines, certain alcohols, phenols . . .

PPE/PP alloys

PPE particles are dispersed into a matrix of polypropylene via a patented alloying technology resulting in a material benefiting from:

- the low-temperature toughness, creep resistance, aesthetics, hydrolytic and thermal resistance of the PPE
- the chemical resistance, lower cost and density of the PP matrix.

Suitable grades can withstand multiple heating cycles to 125°C in high-pressure environments.

Trade name examples: Noryl PPX . . .

Table 4.106 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

PC/AES (polycarbonate/acrylonitrile-ethylene-styrene) alloys

PC/AES grades are modified to reach a good balance of impact resistance, particularly at low temperature, and weather resistance. Performances are comparable with those of PC/ABS alloys.

Table 4.106 Property examples of PPE/PP alloys compared to PPE and PP

	PPE		Unfilled PPE/PP alloys		PP	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.04	1.1	0.97	0.99	0.90	0.91
Shrinkage (%)	0.5	0.8			1	3
Absorption of water (%)	0.06	0.12			0.01	0.10
Mechanical properties						
Shore hardness, D	85	90			70	83
Rockwell hardness, M	50	70			<10	40
Stress at yield (MPa)	45	65			35	40
Strain at yield (%)	2	7				
Tensile strength (MPa)	45	60	30	34	20	40
Elongation at break (%)	45	60	110	195	150	600
Tensile modulus (GPa)	2.1	2.8	1.5	1.7	1	1.6
Flexural modulus (GPa)	2.1	2.8	1.4	1.7	1	1.6
Notched impact strength ASTM D256 (J/m)	130	300	250	390	20	500
Thermal properties						
HDT B (0.46 MPa) (°C)	110	138	108	113	82	120
HDT A (1.8 MPa) (°C)	90	130			50	60
Continuous use temperature (°C)	80	110			110	130
Brittle point (°C)	−50	−40			−20	−10
Thermal conductivity (W/m.K)	0.16	0.22			0.15	0.21
Specific heat (cal/g/°C)	0.32	0.32			0.46	0.46
Coefficient of thermal expansion (10^{-5}/°C)	3	7	9	12	6	17
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}			10^{16}	10^{18}
Dielectric constant	2.7	2.7			2.3	2.3
Loss factor (10^{-4})	4	9			3	5
Dielectric strength (kV/mm)	20	22			20	28
Arc resistance (s)	53	80			135	180
Fire behaviour						
Oxygen index (%)	18	19			17	18
UL94 fire rating	HB	HB			HB	HB

(*Continued*)

Table 4.106 (Continued)

	PPE 30% GF		PPE/PP alloy 30–40% GF		PP 30–40% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.26	1.28	1.19	1.3	1.1	1.23
Shrinkage (%)	0.1	0.4			0.1	1
Absorption of water (%)	0.06	0.1			0.01	0.02
Mechanical properties						
Shore hardness, D	85	90			85	88
Rockwell hardness, M	50	60			40	50
Stress at yield (MPa)	100	130			42	70
Strain at yield (%)	3	3			2	3
Tensile strength (MPa)	100	130	80	100	42	70
Elongation at break (%)	3	3	2	4	2	3
Tensile modulus (GPa)	7	9	6	10	4	10
Flexural modulus (GPa)	7	9	5	9	4	7
Notched impact strength ASTM D256 (J/m)	90	130	140	150	45	160
Thermal properties						
HDT B (0.46 MPa) (°C)	138	154	155	158	140	155
HDT A (1.8 MPa) (°C)	134	144			125	140
Continuous use temperature (°C)	80	110			110	130
Glass transition temperature (°C)	100	150			−20	−10
Melting temperature (°C)					160	173
Minimum service temperature (°C)					−30	−5
Thermal conductivity (W/m.K)	0.28	0.28			0.3	0.3
Coefficient of thermal expansion (10^{-5}/°C)	1.5	2.5	1.6	2	2	3
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}			10^{16}	10^{17}
Dielectric constant	2.9	2.9			2.6	2.6
Loss factor (10^{-4})	10	15			10	20
Dielectric strength (kV/mm)	22	22			30	45
Arc resistance (s)					60	75
Fire behaviour						
Oxygen index (%)					17	18
UL94 fire rating	HB	HB			HB	HB

Summary of some general assessments concerning chemical behaviour at room temperature of polyphenylene-ether and polypropylene, which are not necessarily representative of PPE/PP alloys or of all grades of PPE and PP. These general indications should be verified by consultation with the producer of the selected alloys and by tests under operating conditions.

	PPE	PP
Light	UV protection is needed	UV protection is needed
Weak acids	Good behaviour	Good behaviour
Strong acids	Good to limited behaviour	Good behaviour except oxidizing acids
Weak bases	Good behaviour	Good behaviour
Strong bases	Good to limited behaviour	Good behaviour
Solvents	Chemical resistance is generally good to limited at room temperature versus oils, greases, aliphatic hydrocarbons, alcohols Poor resistance versus ketones, esters, ethers, aromatic and halogenated hydrocarbons, hot oxidizing agents, amines, phenols	Good behaviour up to 60°C except aromatics and chlorinated solvents, certain oxidizing chemicals

Trade name examples: Bayblend DP . . .

Table 4.107 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.107 Property examples of a PC/AES alloy compared to PC/ABS alloys and PC

	PC		PC/ABS		PC/AES	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.2	1.2	1.12	1.16	1.1	1.1
Shrinkage (%)	0.5	0.7	0.5	0.7	0.5	0.8
Absorption of water (%)	0.1	0.2	0.15	0.3		
Mechanical properties						
Shore hardness, D	85	95	80	85		
Rockwell hardness, R	114	>120	110	112		
Rockwell hardness, M	50	85	30	50		
Stress at yield (MPa)	50	65	47	60	46	46
Strain at yield (%)	7	7	3	8	4	4
Tensile strength (MPa)	55	77	45	55	42	42
Elongation at break (%)	100	150	>50	125	>50	>50
Tensile modulus (GPa)	2.1	2.5	2	2.5	1.9	2
Flexural modulus (GPa)	2.1	2.5	2	2.5		
Notched impact strength ASTM D256 (J/m)	650	950	500	650	450	450
Notched impact strength ASTM D256 at −30°C (J/m)					200	200
Notched impact strength ASTM D256 at −40°C (J/m)			400	450		
Impact strength at 23°C (kJ/m^2)			48	80		
Impact strength at −20°C (kJ/m^2)			42	46		
Thermal properties						
HDT B (0.46 MPa) (°C)	130	145			116	116
HDT A (1.8 MPa) (°C)	125	140	100	132	98	98
Continuous use temperature (°C)	90	125				
Brittle point (°C)	−25	−25				
Thermal conductivity (W/m.K)	0.2	0.2				
Specific heat (cal/g/°C)	0.3	0.3				
Coefficient of thermal expansion (10^{-5}/°C)	6	7	8	8	9	10
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{16}	10^{16}	10^{16}	10^{16}
Dielectric constant	3	3			3	3
Loss factor (10^{-4})	7	100	35	35	30	75
Dielectric strength (kV/mm)	15	30	24	24	35	35
Fire behaviour						
Oxygen index (%)	24	25	22	24		
UL94 fire rating	V2	V2	HB	HB	HB	HB

PC/SAN (polycarbonate/styrene-acrylonitrile copolymer) alloys

PC/SAN alloys are blends of polycarbonate (PC), styrene-acrylonitrile copolymer (SAN) and a special rubber system. The enhanced resistance to thermal ageing allows applications such as instrument panel support for the Ford Focus C-MAX, support structures for centre consoles, armrests and cup holders.

Trade name examples: Bayblend KU 2-1522 . . .

Table 4.108 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.108 Property examples of 10% GF reinforced PC/SAN alloy compared to unfilled PC and 10% glass fibre reinforced SAN

	PC unfilled		PC/SAN alloy 10% GF		SAN 10% GF	
	Min.	Max.	Min.	Max.	Min.	Max.
Miscellaneous properties						
Density (g/cm^3)	1.2	1.2	1.22	1.22	1.15	1.16
Shrinkage (%)	0.5	0.7	0.3	0.5	0.2	0.4
Absorption of water (%)	0.1	0.2			0.10	0.30
Mechanical properties						
Shore hardness, D	85	95			90	95
Rockwell hardness, R	114	>120			>120	>120
Rockwell hardness, M	50	85			89	91
Stress at yield (MPa)	50	65	70	70	90	100
Strain at yield (%)	7	7	3	3		
Tensile strength (MPa)	55	77	68	68		
Elongation at break (%)	100	150	3	3	1	3
Tensile modulus (GPa)	2.1	2.5	4.2	4.2		
Flexural modulus (GPa)	2.1	2.5			5	6
Notched impact strength ASTM D256 (J/m)	650	950	100	100	40	50
Notched impact strength ASTM D256 at −30°C (J/m)			60	60		
Thermal properties						
HDT B (0.46 MPa) (°C)	130	145	134	134		
HDT A (1.8 MPa) (°C)	125	140	121	121	100	105
Continuous use temperature (°C)	90	125			85	95
Brittle point (°C)	−25	−25			20	20
Thermal conductivity (W/m.K)	0.2	0.2				
Specific heat (cal/g/°C)	0.3	0.3				
Coefficient of thermal expansion (10^{-5}/°C)	6	7	4	8		
Electrical properties						
Volume resistivity (ohm.cm)	10^{15}	10^{16}	10^{16}	10^{16}		
Dielectric constant	3	3	3	3.3		
Loss factor (10^{-4})	7	100	30	100		
Dielectric strength (kV/mm)	15	30	40	40		
Fire behaviour						
Oxygen index (%)	24	25			18	19
UL94 fire rating	V2	V2	HB	HB	HB	HB

PE/COC – LLDPE/cyclic olefin copolymer

PE/COC benefits from:

- stiffness and strength of COC
- price and processability of linear low-density polyethylene.

The tracks of zippers for commercial sliced meat and animal cracker closures are made of this type of blend.

Table 4.109 compares property examples of COC and LLDPE, which are not necessarily representative of PE/COC alloys or of all grades of PE and COC. These general indications should be verified by consultation with the producer of the selected alloys and by tests under sample conditions.

Trade name examples: proprietary alloys . . .

Table 4.109 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.109 Cyclic olefin copolymers and LLDPE: examples of properties

Grades	COC	LLDPE
Miscellaneous properties		
Density (g/cm^3)	1.01	0.915–0.950
Shrinkage (%)	0.4–0.7	2–2.5
Absorption of water (%)	<0.01	0.005–0.010
Mechanical properties		
Shore hardness, D	78	55–56
Rockwell hardness, M	20	<10
Tensile strength (MPa)	42–63	25–45
Elongation at break (%)	20–140	300–900
Tensile modulus (GPa)	2–2.2	0.266–0.525
Flexural strength (MPa)	55–97	
Flexural modulus (GPa)	1.8–2.1	0.280–0.735
Notched impact strength ASTM D256 (J/m)	18–80	54 to NB
Thermal properties		
HDT A (1.8 MPa) (°C)	68–145	<40
Continuous use temperature (°C)	90–110	90–110
Glass transition temperature (°C)	70–162	–110
Coefficient of thermal expansion (10^{-5}/°C)	7	>9
Electrical properties		
Volume resistivity (ohm.cm)	$>10^{16}$	$>10^{16}$
Dielectric constant	2.3	2.3
Loss factor (10^{-4})	2	
Dielectric strength (kV/mm)	40 to >70	
Fire behaviour		
UL94 fire rating	HB	HB

4.30 Thermoplastic elastomers (TPE)

Between thermoplastics, characterized by easy processing but low elasticity, and elastomers, with their outstanding elastic properties but with more-complex processing (see Figure 4.131(a), relatively new materials appeared in the 1960s: the thermoplastic elastomers or TPEs.

The consumption of TPEs is still limited but progressing, with relatively high growth rates, though these differ greatly from one TPE family to another and from one country to another.

The TPEs consist of rigid phases and flexible phases, conferring on them an elasticity similar to that of reticulated traditional elastomers, as long as the temperature does not rise too much.

The two phases can be obtained in two main ways:

- Copolymerization of rigid and flexible sequences in the same molecule, for example:
  - styrene – butadiene – styrene for SBS
  - polyester (or polyether) – isocyanate for TPU
  - polyether – amide for PEBA
- Blending of a soft rubber, possibly partially vulcanized, dispersed in a rigid thermoplastic matrix. For example, EPDM can be dispersed in a polypropylene matrix leading to:
  - a PP/EPDM alloy if EPDM is not crosslinked
  - a PP/EPDM-V alloy if EPDM is dynamically vulcanized.

These two methods can be combined and some TPEs are alloys or blends of a copolymer with soft and rigid sequences (SBS or SEBS, for example) and a thermoplastic, often a polyolefin.

Figure 4.131(a) displays schematic structures of thermoplastics and crosslinked rubbers, while Figure 4.131(b) displays two possible schematic structures of thermoplastic elastomers.

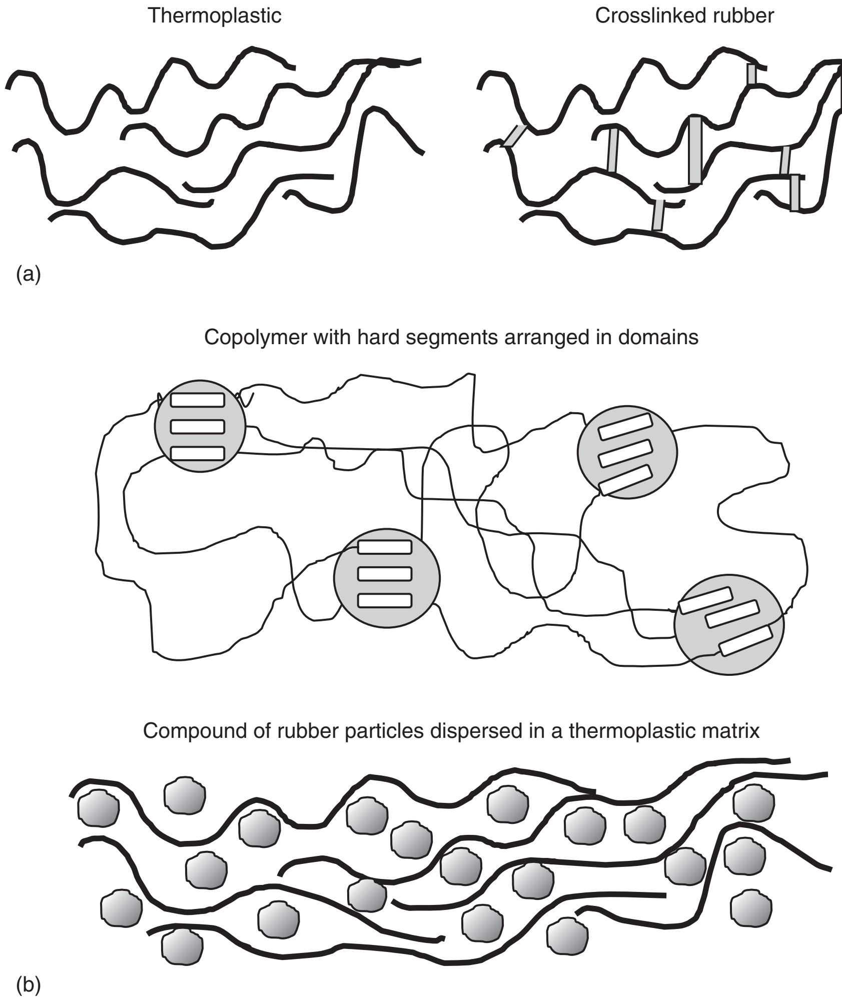


Figure 4.131. (a) Schematic structures of thermoplastics and crosslinked rubbers; (b) Schematic structure of TPEs

The jungle of acronyms

Among the numerous acronyms relating to thermoplastic elastomers, let us quote without claiming to be exhaustive:

TPE	ThermoPlastic Elastomer
TPR	ThermoPlastic Rubber
TPV	ThermoPlastic Vulcanizate
TPU	ThermoPlastic polyUrethane
TPS	ThermoPlastic Styrenic
TPO	ThermoPlastic Olefin
TPEE or COPE	ThermoPlastic Ester Elastomer or CO-PolyEster
SBC	Styrenic Block Copolymer
SBS	Styrene-Butadiene-Styrene
SEBS	Styrene Ethylene/Butylene Styrene

SEPS	Styrene Ethylene/Propylene Styrene
SIS	Styrene Isoprene Styrene
PP/EPDM-V	Vulcanized EPDM dispersed in polypropylene
PP/NBR-V	Vulcanized nitrile rubber dispersed in polypropylene
PP/IIR-V	Vulcanized butyl rubber dispersed in polypropylene
PP/EPDM	Unvulcanized EPDM blended with polypropylene or block copolymerized PP-EPDM (reactor TPO)
TPE/PVC	PVC-based TPE, alloys of PVC and rubber
PEBA	PolyEther Block Amide
MPR	Melt Processable Rubber
F-PVC	Flexible PVC

Advantages of TPEs

TPEs are generally appreciated for:

- their easier processing by elimination of the vulcanization step
- the possibility to use all the processing methods for thermoplastics, including welding
- the possibility of easier recycling of wastes
- often, the possibility of co-processing with other thermoplastics
- their low-temperature behaviour
- good impact strength
- good fatigue resistance
- good electrical properties
- fair tear and abrasion resistance
- the coloration possibilities.

Drawbacks

TPEs are generally handicapped by:

- the limited elasticity
- the loss of elasticity when the temperature rises, with the risks of creep and relaxation
- the price.

When one wants to replace crosslinked elastomers by TPEs, it is necessary to survey the problem with a fresh eye and to redesign the subset where the part is used and redraw it to reduce the strains and integrate a maximum of functions to reduce the end-cost.

TPEs can be gathered into families:

- TPS or styrenics, gathering together SBS, SEBS . . .
- TPOs, comprising TPEs with a polyolefin matrix and an unvulcanized rubber. They can be produced by blending or by block copolymerization of polypropylene and EPDM (reactor TPOs). Sometimes TPVs are included in TPOs.
- TPVs, comprising TPEs with a thermoplastic matrix (often polypropylene) and a dynamically vulcanized rubber (often EPDM).
- MPR or melt processable rubber; mainly Alcryn.

Figure 4.132 schematically displays the various families of TPEs.

For a selected family of TPEs, the characteristics depend on the hardness. Generally, tensile strength and chemical resistance increase with hardness and elongation at break decreases.

Figure 4.133 displays examples of tensile strength versus Shore D hardness for three families of TPEs.

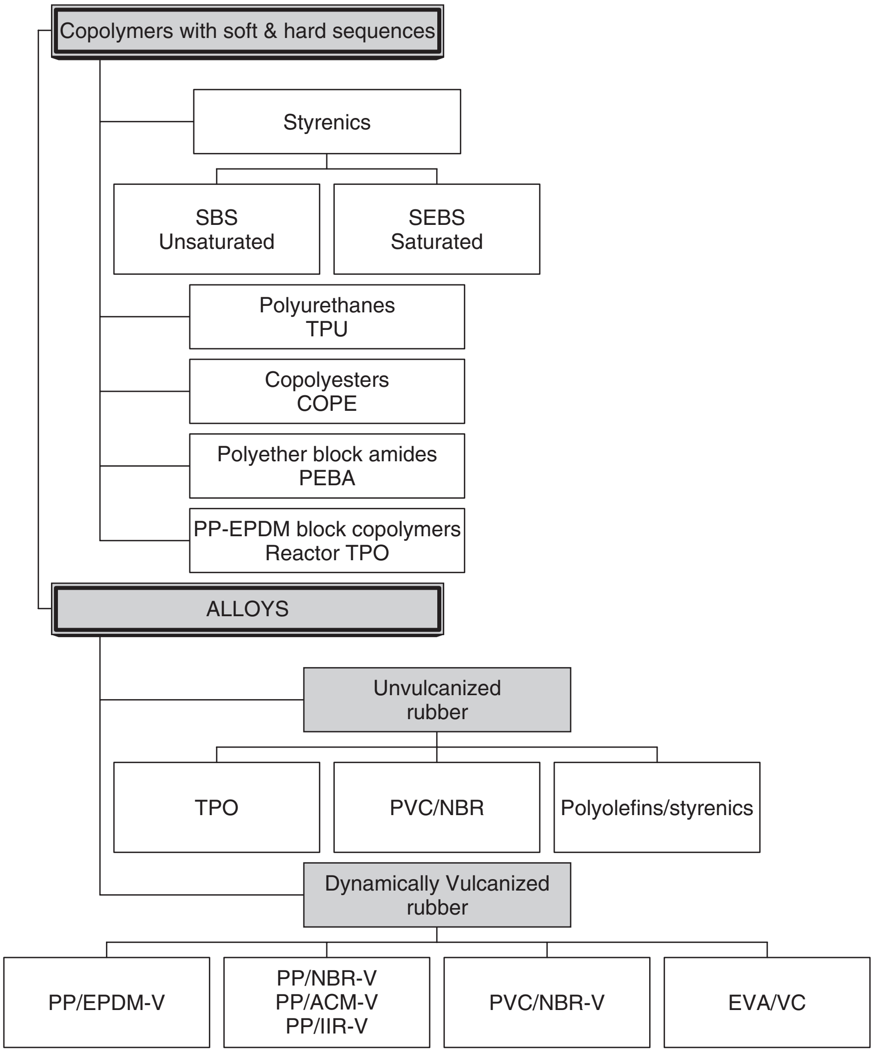


Figure 4.132. Various families of TPEs

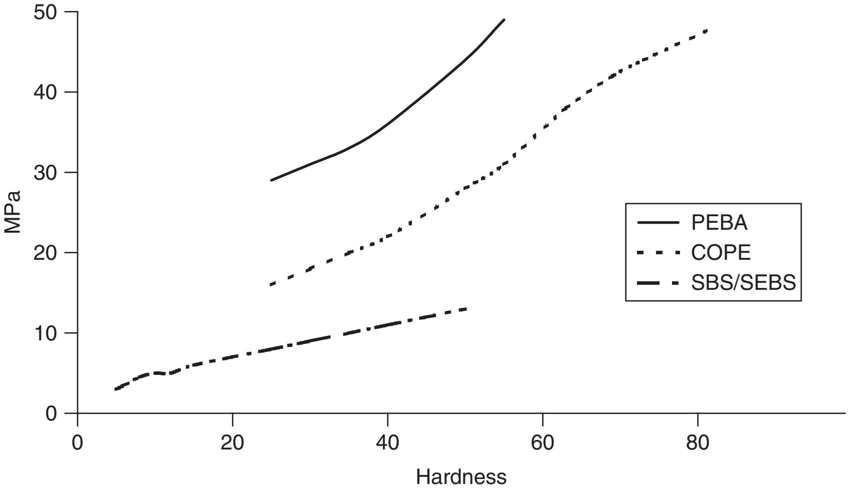


Figure 4.133. Examples of tensile strength (MPa) versus hardness (Sh D)

Figure 4.134 displays examples of swelling (%) versus Shore A hardness after immersion of a TPV in ASTM oils.

These results are examples only and they cannot be generalized or used for designing.

Table 4.110 displays examples of engineering property ranges for some TPEs. For each family, the upper line relates to the minimum of the examined property and the lower line

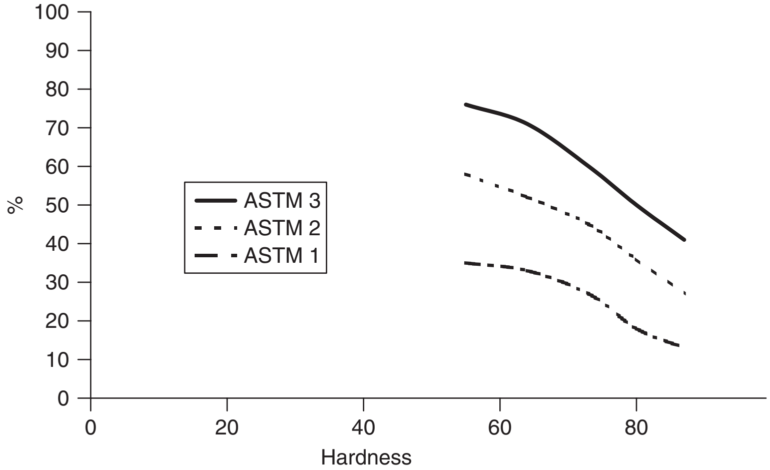


Figure 4.134. Examples of swelling (%) versus hardness (Sh A) after immersion in ASTM oils

Table 4.110 Schematic comparison of engineering properties of some TPEs

	Hardness	Compression set	Abrasion	Service temperature		Price
	Shore A or D	Rating 1 to 5	Rating 1 to 5	High	Low	Rating 1 to 5
				(°C)	(°C)	
SBS/SIS	25A	1	3	50	−50	5
	51D	2	3	75	−60	5
SEBS	10A	1	2	80	−40	3
	60D	2	2	120	−50	4
TPO	55A	1	3	60	−30	5
	50D	1	3	120	−60	5
PP/EPDM-V	35A	2	3	100	−30	4
	54D	4	3	135	−60	4
PP/NBR-V	70A	2	3	90	−30	3
	45D	4	3	120	−40	3
PP/IIR-V	45A	2	3	100	−30	3
	85A	4	3	130	−60	3
MPR	47A	2	3	80	−30	
	80A	3	3	120	−90	
TPE/PVC	50A	1	3	60	−30	4
	90A	3	3	100	−60	5
TPU	62A	2	5	80	−30	3
	75D	3	5	120	−70	4
COPE	80A	2	5	110	−40	2
	82D	3	5	135	−100	2
PEBA	75A	2	3	85	−40	1
	70D	4	4	130	−60	1

1: material is generally unsatisfactory for this property; 5: material is excellent.

to the maximum. The maximum (or minimum) hardness value is not linked to the maximum (or minimum) of the other properties. Compression set, abrasion resistance and price are rated from 1 to 5, with 5 always attributed to the most attractive materials: high abrasion resistance, low compression set and cost. These data cannot be used for designing, computing or to make economic predictions.

Table 4.111 displays examples of ageing and chemical property ranges for some TPEs. These comparisons are very schematic and cannot be used for designing. Ozone resistance is a specific property of rubbers used in numerous specifications. The rating system is the same as previously: 5 is always attributed to the most attractive materials. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.111 Schematic comparison of ageing resistance and chemical behaviour of some TPEs

	Hardness	Ozone resistance	Hydrolysis resistance	Oxidation resistance	Mineral oil resistance
	Shore A or D	Rating 1 to 5	Rating 1 to 5	Rating 1 to 5	Rating 1 to 5
SBS/SIS	25A	2	4	2	1
	51D	2	5	2	2
SEBS	10A	5	4	5	1
	60D	5	5	5	2
TPO	55A	5	4	3	1
	50D	5	5	4	2
PP/EPDM-V	35A	5	4	3	3
	54D	5	5	4	3
PP/NBR-V	70A	4	4	3	4
	45D	5	5	3	4
PP/IIR-V	45A	5	4	3	3
	85A	5	5	4	3
MPR	47A	5	4	3	4
	80A	5	5	3	4
TPE/PVC	50A		2		3
	90A		4		
TPU	62A	5	2	2	2
	75D	5	3	2	4
COPE	80A	5	2	3	3
	82D	5	3	3	4
PEBA	75A	5	2	2	2
	70D	5	3	2	4

1: material is generally unsatisfactory for this property; 5: material is excellent

Consumption and applications of TPEs

Global demand for thermoplastic elastomers (TPEs) is estimated at 2 million tonnes in 2005 and is forecast to increase by 6% per year. TPEs as a whole represent roughly 10% of elastomers or 1% of plastics. Consequently, economic statistics are rare and we can only make some assumptions concerning the consumption of each family:

Styrenics	40%
TPOs, including TPVs	35%
TPUs	10%
Copolyesters	8%
PEBAs	1%
Others, including PVC based	6%

Different data may be quoted depending on the country, source and distribution between the various families.

SBS applications are generally in footwear, adhesives, bitumen modification, low-specification seals and soft-touch grips.

SEBS are used for more-demanding applications because of a higher heat resistance and an improved chemical resistance.

TPO applications are in automotive bumpers and dashboards because of their higher toughness than conventional polypropylene copolymers.

TPV applications are mainly in automotive seals and pipe seals where a good compression set and heat resistance are required.

TPU applications are in soling materials, ski boots, industrial belting, and in wire & cable needing good tear strength, abrasion resistance and flex fatigue endurance.

TPEE or COPE applications are in the automotive sector for blow-moulded boots and bellows, wires and cables, industrial hoses needing a higher rigidity, good heat resistance, good fatigue endurance and tear strength.

MPR competes with crosslinked nitrile rubber for demanding applications (in the automotive sector, for example) needing oil and grease resistance, noise dampening, stress relaxation similar to vulcanized rubber, good bonding to PVC, PC, ABS.

PEBA is used in cable jacketing and aeronautics for its heat behaviour and good resistance versus certain chemicals.

Specific ISO standards concerning TPEs

ISO 34-1:2004 Rubber, vulcanized or thermoplastic – Determination of tear strength – Part 1: Trouser, angle and crescent test pieces

ISO 34-2:1996 Rubber, vulcanized or thermoplastic – Determination of tear strength – Part 2: Small (Delft) test pieces

ISO 36:1999 Rubber, vulcanized or thermoplastic – Determination of adhesion to textile fabric

ISO 37:1994 Rubber, vulcanized or thermoplastic – Determination of tensile stress-strain properties

ISO 48:1994 Rubber, vulcanized or thermoplastic – Determination of hardness (hardness between 10 IRHD and 100 IRHD)

ISO 132:1999 Rubber, vulcanized or thermoplastic – Determination of flex cracking and crack growth (De Mattia)

ISO 188:1998 Rubber, vulcanized or thermoplastic – Accelerated ageing and heat resistance tests

ISO 813:1997 Rubber, vulcanized or thermoplastic – Determination of adhesion to a rigid substrate – 90 degree peel method

ISO 815:1991 Rubber, vulcanized or thermoplastic – Determination of compression set at ambient, elevated or low temperatures

ISO 1431-1:2004 Rubber, vulcanized or thermoplastic – Resistance to ozone cracking – Part 1: Static and dynamic strain testing

ISO 1431-3:2000 Rubber, vulcanized or thermoplastic – Resistance to ozone cracking – Part 3: Reference and alternative methods for determining the ozone concentration in laboratory test chambers

ISO 1432:1988 Rubber, vulcanized or thermoplastic – Determination of low temperature stiffening (Gehman test)

ISO 1827:1991 Rubber, vulcanized or thermoplastic – Determination of modulus in shear or adhesion to rigid plates – Quadruple shear method

ISO 1853:1998 Conducting and dissipative rubbers, vulcanized or thermoplastic – Measurement of resistivity

ISO 2285:2001 Rubber, vulcanized or thermoplastic – Determination of tension set under constant elongation, and of tension set, elongation and creep under constant tensile load

ISO 2782:1995 Rubber, vulcanized or thermoplastic – Determination of permeability to gases

ISO 3384:1999 Rubber, vulcanized or thermoplastic – Determination of stress relaxation in compression at ambient and at elevated temperatures

ISO 3865:1997 Rubber, vulcanized or thermoplastic – Methods of test for staining in contact with organic material

ISO 3934:2002 Rubber, vulcanized and thermoplastic – Preformed gaskets used in buildings – Classification, specifications and test methods

ISO 4649:2002 Rubber, vulcanized or thermoplastic – Determination of abrasion resistance using a rotating cylindrical drum device

ISO 4664-1:2005 Rubber, vulcanized or thermoplastic – Determination of dynamic properties – Part 1: General guidance

ISO 4665:1998 Rubber, vulcanized and thermoplastic – Resistance to weathering

ISO 6179:1998 Rubber, vulcanized or thermoplastic – Rubber sheets and rubber-coated fabrics – Determination of transmission rate of volatile liquids (gravimetric technique)

ISO 6505:1997 Rubber, vulcanized or thermoplastic – Determination of tendency to adhere to and to corrode metals

ISO 6914:2004 Rubber, vulcanized or thermoplastic – Determination of ageing characteristics by measurement of stress relaxation

ISO 7619-1:2004 Rubber, vulcanized or thermoplastic – Determination of indentation hardness – Part 1: Durometer method (Shore hardness)

ISO 7619-2:2004 Rubber, vulcanized or thermoplastic – Determination of indentation hardness – Part 2: IRHD pocket meter method

ISO 7743:2004 Rubber, vulcanized or thermoplastic – Determination of compression stress-strain properties

ISO 11346:2004 Rubber, vulcanized or thermoplastic – Estimation of life-time and maximum temperature of use

ISO 18064:2003 Thermoplastic elastomers – Nomenclature and abbreviated terms

ISO 23794:2003 Rubber, vulcanized or thermoplastic – Abrasion testing – Guidance

ISO/WD 10350-3 Plastics – Acquisition and presentation of comparable single-point data – Part 3: Thermoplastic elastomer materials

ISO 23711:2003 Elastomeric seals – Requirements for materials for pipe joint seals used in water and drainage applications – Thermoplastic elastomers

ISO 14910-1:1997 Plastics – Thermoplastic polyester/ester and polyether/ester elastomers for moulding and extrusion – Part 1: Designation system and basis for specifications

ISO 14910-2:1997 Plastics – Thermoplastic polyester/ester and polyether/ester elastomers for moulding and extrusion – Part 2: Preparation of test specimens and determination of properties

In the following we will discuss:

- styrenics
  - styrene butadiene styrene (SBS)
  - styrene ethylenebutylene styrene (SEBS)

- TPOs, mainly PP/EPDM produced by blending of a polypropylene matrix and a dispersed unvulcanized EPDM or by copolymerization of polypropylene and sequences of EPDM
- TPVs
  - PP/EPDM-V, dynamically vulcanized EPDM and polypropylene
  - PP/NBR-V, dynamically vulcanized NBR and polypropylene
  - PP/IIR-V, dynamically vulcanized butyl rubber and polypropylene
  - MPR (Melt Processable Rubber), a blend of vinylidene chloride and crosslinked EVA, sometimes referred to as EVA/VC
- TPU, thermoplastic polyurethanes
- TPEE (or COPE), copolyesters
- TPE/PVC or PVC-based TPE: often blends of PVC and NBR.

4.30.1 Thermoplastic styrenics TPS (SBS, SEBS, SIS, SEPS. . .)

These materials have two-phase structures based on hard segments of polystyrene and soft segments of butadiene for SBS, or isoprene for SIS, etc.

The properties, of which hardness is often used for the denomination of the grades, strongly vary as functions of:

- the nature of the flexible segments
- the morphology of the macromolecular chains (linear, star . . .)
- the length of segments
- the ratio of rigid and flexible segments
- the blending with other polymers . . .

Of course, TPS are formulated with fillers, oils and other additives like other thermoplastics.

Generally, SBS is preferred for the manufacture of footwear and other similar parts, and the modification of bitumen and asphalt.

SIS is preferred for the production of pressure-sensitive adhesives.

SEBS is obtained by hydrogenation of certain TPS block copolymers. The saturated structure of the soft segments enhances oxidation, chemical and thermal resistances.

SBS and SEBS have many common features but mainly differ in ageing resistance and chemical behaviour:

- on the one hand, SBS, rich in fragile double bonds, is more sensitive to oxidizing agents including ozone, heat, UV and weathering
- on the other hand, SEBS has a better resistance to ageing and weathering, a better retention of properties when the temperature rises above the glass transition point of polystyrene, a more limited behaviour at low temperatures, a higher rigidity and lower elongations at break, and a higher viscosity in solution. Hydrogenated TPS are also more expensive.

TPS are marketed in a multitude of versions:

- basic polymers containing only fundamental additives.
- formulated compounds containing fillers, oils, protective additives . . . for the manufacture of parts or goods.
- alloys with other polymers, formulated with ingredients, for the manufacture of parts or products.

Advantages

TPS are appreciated for their broad range of hardnesses, down to very low values (25 Shore A for SBS); low price; fatigue endurance to repeated flexions and impacts; abrasion resistance of suitable grades; low-temperature behaviour (particularly for SBS); low density; ease of waste recycling; broad possibilities of formulation and colouring; soft touch; overmoulding on polyolefins, EVA or polystyrene for suitable grades . . .

SEBS is chosen for a better oxidation, ageing and weathering resistance; a broader rigidity range; and better retention of properties when the temperatures rise above the glass transition of polystyrene.

Drawbacks

TPS are handicapped by risks of creep, relaxation and permanent set, the more so as the temperature rises (high compression set at 70°C for certain grades); swelling in mineral oils and oily products; limited ageing resistance for SBS; limited thermal behaviour (50°C maximum for certain SBS).

SEBS has a more-limited behaviour at low temperatures, a higher cost and a higher viscosity in solution.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- injection, extrusion, blown films, blow-moulding, thermoforming, calendering, spinning in a molten state . . .
- UV and/or heat stabilized, oil extended, low temperature, soft touch, transparent, sterilizable, food contact, for heavy soundproofing parts, high purity for medical or pharmaceutical applications, very low hardness, conductive, additives for modification of other polymers . . .
- for footwear, electrical applications, insulation of wires and electric cables, food industry, adhesives, bitumen modification . . .

Costs

The costs, as for all plastics, fluctuate highly with the crude oil price. SBS are generally among the cheapest TPEs. SEBS are more expensive.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering.

Consumption and applications

(See Chapter 2 for further information.)

The share of the TPS in the TPEs is estimated at approximately 40%. If applications such as polymer modifiers and bitumen additives are excluded, the percentage goes down to approximately the same order of magnitude as that of the TPOs.

The world market for:

- TPS can be roughly estimated at 800 000 tonnes per year
- hydrogenated styrene elastomers could be approximately 100 000 tonnes per year.

These data are only assumptions and other predictions may be quoted elsewhere.

TPS are used in the footwear, automotive, construction, hygiene, packaging, sports and leisure, consumer durable and disposable sectors for various moulded and extruded technical goods, soft-touch overmoulding, etc., SEBS satisfying more stringent specifications than SBS particularly versus heat and weathering.

Example applications are:

- airbag covers, armrests, upholstery . . .
- rack and pinion boots . . .
- automotive weather-stripping . . .
- air-duct covers and hoses . . .
- insulation of electric wires . . .
- window seals . . .
- gasketing, tap washers, toilet buffers . . .
- workbench feet, end caps, appliance feet and pads . . .
- impermeable liners, protective sheets . . .
- toys . . .
- films, PVC replacement films . . .
- adhesives, sealants, coatings . . .
- bitumen modification, roads, roofing, paving, impact-resistant shingles . . .
- polymer modification . . .

Elasticity

Elasticity depends on:

- the basic TPS – SBS, SEBS . . .
- the formulation
- the temperature.

Figure 4.135 displays examples of compression set for SBS and SEBS grades after 22 h at 20°C, conditions that are far from severe. Note:

- the broad dispersion of results for a given hardness
- the compression set increase (or decrease of elasticity) as the hardness increases
- the high compression set values for certain grades under very mild conditions.

At higher temperatures, compression set increases fast, for example:

- 18% up to 50% for low hardness SEBS after 22 h at 70°C
- 20% up to more than 75% for SEBS after 22 h at 120°C.

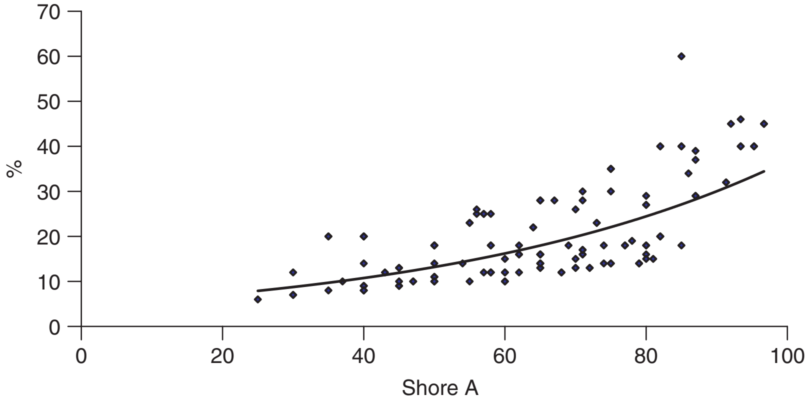


Figure 4.135. SBS & SEBS: compression set (%) after 22 h at 20°C versus Shore A hardness

Low-temperature behaviour

The glass transition temperature of the elastomeric phase is:

- −80°C for basic SBS
- −42°C for basic SEBS

which forecasts low service temperatures of −60°C and −40°C, respectively, for compounds.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at:

- 50–70°C for SBS compounds
- up to 100°C for SEBS.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

Half-lives based on tensile strength or elongation at break are estimated at:

- For given grades of SBS:
  - greater than 5 years at 40°C
  - 3 to more than 5 years at 55°C
  - less than 1 year up to more than 5 years at 70°C
  - less than 1 year at 85°C.
- For given grades of SEBS:
  - greater than 5 years at 70°C
  - 4 to more than 5 years at 85°C
  - Up to 5 years at 100°C.

These results relate to some grades only and cannot be generalized.

Optical properties

Some grades are transparent.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties vary widely according to the grades but are, in general, of a sufficient level for the typical applications. For given compounds, tensile strength can be as low as 1 or 2 MPa. The abrasion resistance of the appropriate grades allows their use in soling. The tear strengths, very variable for the same hardness range, are generally of a modest level. Certain grades have a very high flexibility with hardness going down to 10 Shore A.

Dimensional stability

Alterations by moisture exposure are low.

For a 75 Shore A SEBS, the water absorption after immersion for 168 h in water at 70°C is weak (1.1%).

These results relate to some grades only and cannot be generalized.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular or reinforcement orientation.

Dynamic fatigue

TPS are used in applications involving repeated deformations, even at low temperature, such as shoe soles, for example.

Weathering

SBS, as well as all elastomers rich in double bonds, are not suited to exposure to light, UV or ozone, whereas SEBS show good behaviour.

Chemicals

Chemical resistance depends on:

- the presence or absence of double bonds, SEBS being more resistant than SBS.
- the hardness for a selected family.

Resistance to moisture and hydrolysis is good if the temperature is in accordance with the heat resistance of the considered grade.

Suitably formulated compounds are usable in contact with food.

TPS, being hydrocarbons, are sensitive to oils and other hydrocarbons. SEBS can have a better oil resistance than SBS. For example, after 70 h in ASTM3 oil at 100°C, the weight change is approximately 90%.

Generally, the chemical behaviour is:

- satisfactory with water, acetone, ethylene oxide, formaldehyde, dilute hydrochloric, sulfuric, phosphoric and some organic acids
- limited to satisfactory in dilute nitric and acetic acids, bases, chlorine water, chromic acid
- limited in ethylene glycol, butanol, ethanol, vegetable oils, fatty acids
- limited to unsatisfactory in chlorinated solvents, aliphatic and aromatic hydrocarbons, oils, dry chlorine, concentrated nitric acid, butyl acetate, cyclohexanone, ethers, phenols.

Table 4.112 displays some general assessments of the behaviour of given grades after prolonged immersion in a range of chemicals at the specified temperatures. The results are not necessarily representative of all the SBS. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Fire resistance

SBS and SEBS burn easily. Fireproofing agents can reduce the aptitude for combustion.

Electrical properties

SBS and SEBS are insulating and are used for low-tension wire and cable jacketing.

Special grades are antistatic or conductive.

Table 4.112 SBS: examples of chemical behaviour

Chemical	Concentration (%)	Temperature	Estimated behaviour
Acetic anhydride	Unknown	20	l
Acetone	100	20	S
Acetyl chloride	100	20	l
Air	100	70	S
Air	100	100	l
Air	100	150	n
Air	100	200	n
Ammonia gas	100	20	S
Ammonium carbonate	Unknown	20	S
Ammonium sulfate	50	20	S
Amyl acetate	100	20	n
Amyl acetate	100	60	n
Amyl alcohol	100	20	n
Amyl alcohol	100	50	n
Aniline	100	20	l
Aniline	100	100	n
Aqueous ammonia	10	20	S to l
Benzaldehyde	100	20	n
Benzaldehyde	100	100	n
Benzene	100	20	n
Benzene	100	60	n
Benzene	100	100	n
Benzoic acid	Unknown	20	n
Benzyl alcohol	100	20	n
Boric acid	10	100	n
Bromine	Unknown	20	S
Butane liquid	100	20	n
Butanol	100	20	l
Butanol	100	100	n
Butter	100	100	n
Butyl acetate	100	20	n
Butyl acetate	100	60	n
Butyric acid	100	20	l
Carbon dioxide	Unknown	20	S
Carbon sulfide	100	20	n
Carbon sulfide	100	60	n
Carbon tetrachloride	100	20	l
Chloroacetic acid	Unknown	20	l
Chlorine (dry gas)	100	20	S to n
Chlorobenzene	100	20	n
Chlorobenzene	100	50	n
Chlorobromomethane	100	20	n
Chloroform	100	20	n
Chlorosulfonic acid	Unknown	20	l
Chromic acid	Unknown	20	l
Cresol	100	20	n
Cresol	Unknown	70	n
Cyclohexane	100	20	n
Cyclohexanone	100	20	n
Cyclohexanone	100	50	n
Diacetone alcohol	100	20	S
Diethylether	100	20	n
Diethylether	100	60	n
Dimethylformamide	100	20	S

Table 4.112 (Continued)

Chemical	Concentration (%)	Temperature	Estimated behaviour
Ethanol	Unknown	20	l
Ethylchloride	100	20	l
Ethylene dichloride	100	20	l
Ethyleneglycol	Unknown	20	l
Ethyleneglycol	Unknown	93	n
Fluosilicic acid	Unknown	20	S
Formaldehyde	Unknown	20	S
Formic acid	Unknown	20	S
Freon	100	20	l
Glucose	Unknown	20	S
Hydrobromic acid	Unknown	20	l
Hydrochloric acid	36	20	S
Hydrochloric acid	Unknown	20	S
Hydrocyanic acid	20	20	S
Hydrofluoric acid	Unknown	20	S to l
Hydrogen peroxide	30	20	S
Hydrogen peroxide	90	20	l
Hydrogen sulfide	Unknown	20	l
Iron(III) chloride	Unknown	20	S
Kerosene	100	20	n
Lactic acid	Unknown	20	S
Lactic acid	4	20	l
Lead acetate	Unknown	20	S
Linseed oil	100	20	n
Linseed oil	100	60	n
Magnesium chloride	Unknown	20	S
Malic acid	Unknown	20	l
Methyl chloride	100	20	l
Milk	100	20	S
Mineral oil	100	20	l
Naphtha	Unknown	20	n
Naphtha	Unknown	50	n
Natural gas	100	20	n
Nitric acid	10	20	l
Nitric acid	65	20	l
Nitric acid	100	20	n to l
Nitrobenzene	100	20	n
Nitrobenzene	100	50	n
Nitrobenzene	100	60	n
Oleic acid	Unknown	20	l
Oxalic acid	Unknown	20	l
Petrol	100	20	n
Phenol	Unknown	20	n
Phenol	Unknown	93	n
Phosphoric acid	Unknown	20	S
Potassium hydroxide	45	20	l
Potassium hydroxide	5	20	S
Pyridine	Unknown	20	l
Sea water	100	20	S
Silicone oil	100	20	S
Silver nitrate	Unknown	20	S
Soap	Solution	20	S
Sodium bicarbonate	Unknown	20	S
Sodium borate	Unknown	20	S

(*Continued*)

Table 4.112 (Continued)

Chemical	Concentration (%)	Temperature	Estimated behaviour
Sodium carbonate	10	20	S
Sodium chloride	10	20	S
Sodium hydroxide	10	20	S
Sodium hydroxide	55	20	S
Sodium hypochlorite	10	20	S
Sodium hypochlorite	Unknown	20	l
Sodium nitrate	Solution	20	S
Stearic acid	Unknown	20	S
Styrene	100	20	n
Sulfur dioxide	Unknown	20	l
Sulfuric acid	10	20	S
Sulfuric acid	20	20	S
Sulfuric acid	60	20	l
Tannic acid	Unknown	20	S
Tartric acid	10	20	S
Toluene	100	20	n
Toluene	100	60	n
Trichloroacetic acid	Unknown	20	l
Trichloroethylene	100	20	n
Trichloroethylene	100	60	n
Trichloroethylene	100	93	n
Turpentine oil	100	20	n
Vegetable oil	100	20	l
Water	100	20	S
Wine	Unknown	20	S
Xylene	100	20	n
Xylene	100	50	n
Zinc chloride	Unknown	20	S

S: satisfactory; l: limited; n: not satisfactory

Joining, decoration

Welding and joining with adhesives are possible.

All precautions must be taken concerning health and safety according to local laws and regulations.

The transparency of TPS allows a large variety of pure colours by addition of masterbatches.

Trade name examples

Asaflex, Asaprene, Bergaflex, C-Flex, Dynaflex, Elastamax, Elexar, Epofriend, Europrene Sol T, Evoprene D, Evoprene G, Finaclear, Finaflex, Finaprene, Garaflex G, Gomex, Kraton, Kraton D, Kraton G, Lacbloc, Monprene, Multiflex, Quintac, Sconablend, Septon, Solprene, Stereon, Styroflex, Taipol, Tefabloc, Tekron, Terlac, Thermolast K, Tufprene, Tuftec, Vector, Vitaprene.

Property tables

Table 4.113 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.113 TPS: examples of properties

	Basic SBS			Basic SEBS		
Hardness (Shore)	30A	38A	72A	75A	75A	75A
Density (g/cm^3)	0.92	0.93	0.94	0.91	0.91	0.92
Tensile strength (MPa)	28	28	33	32	35	24
Elongation at break (%)	1300	1200	880	500	500	700
Stress at 300% (MPa)	0.9	1.8	2.9	4.9	5.6	6.3
Glass transition temperature (°C)	−80	−80	−80	−42	−42	−42
	SBS compounds for footwear					
Hardness (Shore)	46A	70A	72A	72A	80A	89A
Density (g/cm^3)	0.94	0.94	0.94	0.94	0.94	0.94
Tensile strength (MPa)	12	33	33	23	18	14
Elongation at break (%)	1100	880	880	1000	920	830
Stress at 300% (MPa)	1.9	2.9	2.9	2	2	3.9
Abrasion loss (DIN) (mm^3)	100			160	150	190
Glass transition temperature (°C)	−80	−80	−80	−80	−80	−80
	Compounds with low & medium hardness					
	SBS-based			SEBS-based		
Hardness (Shore)	25A	40A	70A	20A	40A	70A
Density (g/cm^3)	1.2	1.1–1.7	0.9–1.2	0.9–1	0.9–1.2	0.9–1.2
Tensile strength (MPa)	2.5	2–6	4–7	1–2	2–8	4–10
Elongation at break (%)	450	600–900	300–700	300–650	400–900	350–700
Stress at 300% (MPa)			3			
Tear strength (N/mm)	11	15–18	32–40	6–13	15–28	29–48
Compression set, 22 h at 20°C (%)	<20	9–20	13–17	6	8–14	13–15
Compression set, 72 h at 20°C (%)						17–18
Compression set, 22 h at 70°C (%)				38	18–50	26–53
Compression set, 22 h at 100°C (%)					32–70	45–75
Low service temperature (°C)	−60	−60	−60	−40	−40	−40
Continuous use temperature (°C)	50–70	50–70	50–70	80–100	80–100	80–100
	Compounds with high hardness					
	SBS-based			SEBS-based		
Hardness (Shore)	25D	40D	60D	25D	40D	60D
Density (g/cm^3)	1–1.2	1–1.1	1.2–1.3	1.1	1.2	1.2
Tensile strength (MPa)	5–9	9–11	14–17	8–12	9–14	18
Elongation at break (%)	300–700	400–500	400–500	600–650	400–550	450–600
Stress at 300% (MPa)	5					
Tear strength (N/mm)	35–50	40–50	50	46–58	40–55	48–50
Compression set, 22 h at 20°C (%)	14–20			19		
Compression set, 22 h at 70°C (%)				55–80		
Low service temperature (°C)	−60	−60	−60	−40	−40	−40
Continuous use temperature (°C)	50–70	50–70	70	80–100	80–100	80–100
	TPS					
Electrical properties						
Volume resistivity (ohm.cm)	10^{16}					
Dielectric constant	2.4					
Dielectric strength (kV/mm)	26					
Fire behaviour						
Oxygen index (%)	18					
UL94 rating	HB					

(*Continued*)

Table 4.113 (Continued)

General assessments concerning the chemical behaviour at room temperature of SBS, which are not representative of SEBS or of all grades of SBS, should be verified by consultation with the producer of the selected grades and by tests under operating conditions.
Chemical resistance depends on:
- the presence or absence of double bonds, SEBS being more resistant than SBS
- the hardness for a given family.

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	SBS resistance is unsatisfactory but SEBS is better
Weak acids	Satisfactory to limited according to the acid
Strong acids	Limited to unsatisfactory according to the acid and its concentration
Bases	Satisfactory to limited behaviour according to the base and it concentration
Solvents	Generally, behaviour at room temperature is: Satisfactory with water, acetone, ethylene oxide, formaldehyde, diluted hydrochloric, sulfuric, phosphoric and some organic acids Limited to satisfactory in diluted nitric and acetic acid, bases, chlorine water, chromic acid Limited in ethylene glycol, butanol, ethanol, vegetable oils, fatty acids Limited to unsatisfactory in chlorinated solvents, aliphatic and aromatic hydrocarbons, dry chlorine, oils, concentrated nitric acid, butyl acetate, cyclohexanone, ethers, phenols
Food contact	Possible for special grades

4.30.2 Thermoplastic olefinics TPO (PP/EPDM. . .)

These materials are:

- generally, blends of unvulcanized EPDM and polypropylene
- more rarely, two-phase structures based on hard segments of polypropylene and soft segments of EPDM.

The properties, of which hardness is often used for the denomination of the grades, strongly vary as functions of:

- the nature of the polypropylene
- the nature of the EPDM
- the type of production process, blend or co-polymerization
- the ratio of polypropylene and EPDM.

Of course, TPOs can be formulated with fillers, plasticizers and other additives like other thermoplastics.

TPOs are at the boundary between thermoplastics, to which they are linked by some sources, and TPEs, with a high thermoplastic character and a weak elastic behaviour. Sold by the same producer, the cost of a TPO is approximately 60–65% of that for an equivalent TPV.

Advantages

TPOs are appreciated for their broad range of hardnesses, going down to 60 Shore A without plasticizers; low density, good property/price ratio; weather resistance; low-temperature behaviour; ease of waste recycling, broad possibilities of formulation and colouring; soft touch; compatibility with the polyolefins (overmoulding, co-injection, co-extrusion, welding) for suitable grades . . .

Drawbacks

TPOs are handicapped by a weak elasticity and a marked plastic behaviour even at ambient temperature; risks of creep, relaxation and permanent set, the more so the higher the temperature rises (high compression set at 70°C for certain grades); swelling in mineral oils and oily products; limited thermal behaviour.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- injection, extrusion, blown films, blow-moulding, thermoforming, calendering, high flow, ultra-high flow, low-pressure moulding . . .
- UV and/or heat stabilized; improved colour and gloss retention; cold-temperature ductility and flexibility; soft touch; food contact; low hardness; conductive; high stiffness; high-impact; ultra-high impact; high modulus; colourable; scratch resistant; paint performance; electrostatic painting . . .
- for automotive fascias, automotive interiors, packaging, roofing . . .

Costs

The costs, as for all plastics, fluctuate highly with the crude oil price. TPOs are generally among the cheapest TPEs.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering.

Consumption and applications

(See Chapter 2 for further information.)

The share of the TPOs, including TPVs, in the TPEs is estimated at approximately 35%.

TPOs are used in the automotive, construction, packaging, sports and leisure, consumer durable and disposable goods, electricity, food and medical sectors for various moulded and extruded technical goods, soft-touch overmoulding . . .

Example applications are:

- automotive soft skins for interior and instrument panels, claddings, lower B pillars skins, soft-touch overmoulding . . .
- interior door panels, scuff plates . . .
- airbag covers, armrests, upholstery . . .
- automotive fascias, front-ends, mudguards . . .
- TPO skins for low-pressure injection moulding . . .
- insulation of electric wires, connectors . . .
- workbench feet, appliance feet, supports and pads . . .
- returnable packaging, totes and bins . . .
- handles, soft-touch overmoulding . . .
- profiles, tubes, pipes, sheathing . . .
- toys . . .
- films, PVC replacement films . . .
- roofing . . .

Elasticity

Elasticity depends on:

- the nature of the polypropylene
- the nature of the EPDM
- the type of production process, blend or co-polymerization
- the ratio of polypropylene and EPDM
- the formulation
- the actual temperature.

Figure 4.136 displays examples of compression sets after 22 h at 70°C, which are not severe conditions, for TPO grades with hardnesses in the Shore A and D scales. Note the high set levels for all the tested samples.

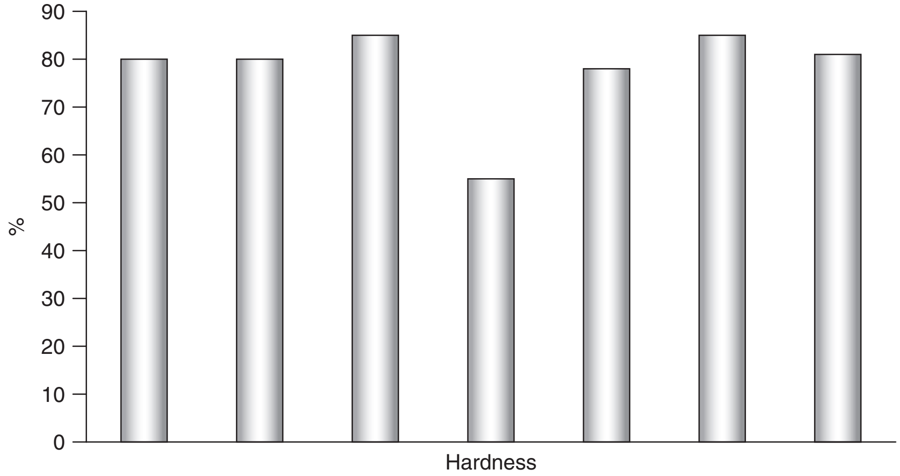


Figure 4.136. TPOs: compression set (%) after 22 h at 70°C versus increasing hardness

Low-temperature behaviour

The brittle points generally range from −60°C for the most-flexible grades up to −40°C for the most-rigid grades.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at 70°C up to 105°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

The flexural modulus varies rapidly with the temperature and, at 70°C, retention is as low as 25% or 30%.

HDT B (0.46 MPa) is, for example, 57°C for a 35 Shore D grade.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

For a grade of 85 Shore A, property retentions after 500 h at 120°C are:

- 65% for the elongation at break
- 73% for the tensile strength.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties vary widely depending on the grades but are generally of a fair level for the typical applications.

Dimensional stability

Alterations by moisture exposure are low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, and the direction of testing with regard to the molecular or reinforcement orientation.

Weathering

TPO resists hydrolysis well but is naturally sensitive to light and UV. It must be protected by addition of anti-UV and other protective agents and possibly by a few percent of an appropriate carbon black.

Chemicals

Chemical resistance depends on the hardness and the EPDM/PP ratio.

Being hydrocarbons, polypropylene and EPDM are sensitive to oils and other hydrocarbons. TPOs rich in polypropylene are more resistant.

TPOs absorb little water and are not very sensitive to it. Moreover, hydrolysis-resistant grades are marketed.

Suitable grades are usable in contact with food and are used for food packaging.

Chemical resistance is generally good but TPOs are attacked by the oxidizing acids, chlorinated solvents, certain oxidants, aromatic hydrocarbons, certain aliphatic hydrocarbons.

Copper, manganese and cobalt are oxidation catalysts and must be avoided, in particular for inserts.

Resistance can be limited to certain aldehydes, ketones, esters, ethers, amines.

Table 4.114 displays some general assessments concerning the behaviour after prolonged immersion in various chemicals at room temperature of given grades of polypropylene and EPDM, which are not necessarily representative of all the PPs and EPDMs. Moreover, the chemical behaviour of a compound can be different from those of its ingredients. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Fire resistance

TPOs burn inherently easily. Fireproofing agents can reduce the aptitude for combustion.

Table 4.114 Examples of chemical behaviour of polypropylene and EPDM

Chemical	Concentration (%)	Estimated behaviours	
		Polypropylene	EPDM
Acetic acid	10	S	S
Acetic aldehyde	100	S	S to l
Acetic anhydride	100	S	l
Acetone	100	S	S
Acetophenone	100	l	S
Acetyl chloride	100	l	n
Aluminium chloride	Solution	S	S
Ammonia gas	100	S	S
Ammonia liquid	100	S	S
Ammonium sulfate	50	S	S
Amyl acetate	100	l	l
Amyl alcohol	100	S	l
Aniline	100	S	S
ASTM1 oil	100	S	n
ASTM3 oil	100	l	n
Benzaldehyde	100	l	S
Benzene	100	l	n
Benzyl alcohol	100	S	S
Benzylchloride	100	l	n
Butanol	100	S	S
Butyl acetate	100	l	l
Butylphenol	100	S	n
Carbon sulfide	100	l	n
Carbon tetrachloride	100	l to n	n
Castor oil	100	S	l
Cellosolve	100	S	l
Cellosolve acetate	100	S	S
Chlorine (dry gas)	100	n	n
Chlorobenzene	100	l	n
Chloroform	100	l	n
Chlorosulfonic acid	100	n	n
Citric acid	10	S	S
Cresol	100	S	n
Cyclohexane	100	l	n
Cyclohexanol	100	S	n
Cyclohexanone	100	l	l
Decaline	100	n	n
Dibutylphthalate	100	S	S
Diethylamine	100	S	n
Diethyleneglycol	100	S	S
Diethylether	100	l	l
Dimethylamine	100	S	l
Dimethylformamide	100	S	l
Dimethylhydrazine	100	S	l
Dioxan	100	l	l
Ethylchloride	100	n	l
Fluorine	100	n	l
Formaldehyde	37	S	S
Formic acid	85	S	S
Freon 113	100	S	l
Freon 115	100	S	S
Freon 12	100	S	l
Freon 13b1	100	S	S
Freon 21	100	S	l
Freon 22	100	S	S
Freon 32	100	S	S
Furfural	100	S	l

Table 4.114 (Continued)

Chemical	Concentration (%)	Estimated behaviours	
		Polypropylene	EPDM
Glycerol	100	S	S
Glycollic acid	33	S	S
Hexane	100	l	n
Hydrazine	100	S	S
Hydrobromic acid	48	S	S
Hydrofluoric acid	40	l	S
Hydrogen	100	S	S
Hydrogen peroxide	30	S	S
Isobutanol	100	S	S
Isooctane (Fuel A)	100	l	n
Isopropanol	100	S	S
Lactic acid	90	S	S
Lead acetate	10	S	S
Linseed oil	100	S	S
Liquid paraffin	100	l	n
Methanol	100	S	S
Methylacetate	100	S	l
Methylbutylketone	100	l	l
Methylethylketone	100	S	S
Milk	100	S	S
Mineral oil	100	S	n
Nitric acid	10	S	S
Nitric acid	65	S	n
Nitric acid	100	n	n
Nitrobenzene	100	S	S
Perchloroethylene	100	l	n
Petroleum	100	S	n
Phosphoric acid	85	S	S
Picric acid	Solution	S	S
Potassium permanganate	20	S	S
Propanol	100	S	S
Propylene oxide	100	S	l
Sea water	100	S	S
Silicone oil	100	S	S
Sodium hydroxide	10	S	S
Sodium hydroxide	55	S	S
Sodium nitrate	Solution	S	S
Soya oil	100	S	l
Sulfur dioxide (dry)	100	S	S
Sulfuric acid	10	S	S
Sulfuric acid	70	S	S
Sulfuric acid	98	l	n
Sulfurous acid	Solution	S	S
Tetrachloroethane	100	l	n
Tetrahydrofuran	100	l	n
Thionyl chloride	100	n	n
Toluene	100	l	n
Transformer oil	100	S	n
Trichloroethylene	100	n	n
Turpentine oil	100	n	n
Water	100	S	S
White spirit	100	S	n
Xylene	100	n	n

S: satisfactory; l: limited; n: not satisfactory

Electrical properties

TPOs are insulating and are used for low-tension wire and cable covering.

Special grades are antistatic or conductive.

Joining, decoration

Welding and joining with adhesives are possible.

All precautions must be taken concerning health and safety according to local laws and regulations.

TPOs allow a large variety of colours.

Trade name examples

Hifax, Inspire, Marlex, Milastomer, Ultraply, Vistaflex . . .

Property tables

Table 4.115 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.115 TPO: examples of properties

	Compounds with Shore A hardness			
Hardness (Shore)	60A	65A	70A	75A
Density (g/cm^3)	0.9	0.9–1	1	1
Tensile strength (MPa)	13–15	4–10	8–9	6
Elongation at break (%)	700–850	450–750	600–750	600–650
Stress at 100% (MPa)	1.6	1.6–2.2	2.5–3	3.5
Tear strength (N/mm)	34	33	33	31
Tensile modulus (GPa)	0.008			0.07–0.1
Compression set, 22 h at 20°C (%)	30	35–40	45–50	54–64
Compression set, 168 h at 20°C (%)		70		
Compression set, 22 h at 70°C (%)		80		80–85
Low service temperature (°C)	−60	−50 to −60	−50	−50
Continuous use temperature (°C)	70–105	70–105	70–105	70–105
	Compounds with Shore D hardness			
Hardness (Shore)	30D	35D	45D	47D
Density (g/cm^3)	1–1.1	0.9–1	0.9	0.9
Tensile strength (MPa)	4–6	7–14	13	12
Elongation at break (%)	600–700	600–750	600–650	600
Stress at 100% (MPa)	4.1	4–6		7
Tear strength (N/mm)	49	59–90	70–80	95
Strain at yield (%)		29		
Tensile modulus (GPa)	0.1	0.2–0.3	0.5–0.6	0.2
HDT B (0.46 MPa) (°C)		57		
HDT A (1.8 MPa) (°C)			43	
Compression set, 22 h at 20°C (%)	38	53		57
Compression set, 22 h at 70°C (%)	55–78	85		81
Low service temperature (°C)	−50	−40 to −50	−40 to −50	−45
Continuous use temperature (°C)	70–105	70–105	70–105	70–105

Table 4.115 (Continued)

	Compounds with Rockwell R hardness			
Rockwell R hardness	74	87	89	93
Miscellaneous properties				
Density (g/cm^3)	1.06	1	1	0.99
Mechanical properties				
Shore hardness, D	72	75	76	77
Rockwell hardness, R	74	87	89	93
Rockwell hardness, M	<20	<20	<20	<20
Stress at yield (MPa)	25	27	20	28
Flexural modulus (GPa)	2.3	2.3	1.7	2.2
Notched impact strength, ASTM D256 (J/m)	NB	53	60	53
Notched impact strength at −30°C (J/m)	45	21	16	21
Thermal properties				
HDT B (0.46 MPa) (°C)	120	132	107	121
HDT A (1.8 MPa) (°C)	65	72	57	

The following general assessments concerning the chemical behaviour at room temperature of TPOs, which are not representative of all grades of TPOs, should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Chemical resistance depends on the composition of TPOs and their hardness.

General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers or/and black colour are needed
Weak acids	Good behaviour
Strong acids	Good behaviour except for very high concentrations and oxidizing acids
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Good behaviour except aromatic hydrocarbons, chlorinated solvents, certain aliphatic hydrocarbons, some oxidizing agents Resistance can be limited to certain aldehydes, ketones, esters, ethers, amines
Food contact	Possible for special grades

4.30.3 Thermoplastic vulcanizates, TPV (PP/EPDM-V, PP/NBR-V, PP/IIR-V . . .)

These materials are blends of a vulcanized rubber, often EPDM, dispersed in a thermoplastic matrix, often polypropylene:

- the most common are PP/EPDM-V, a dynamically vulcanized EPDM dispersed in a polypropylene
- rarer are PP/NBR-V, a dynamically vulcanized nitrile rubber dispersed in a polypropylene and
- PP/IIR-V, a dynamically vulcanized butyl rubber dispersed in a polypropylene
- other TPVs are made, for example, of a speciality rubber dispersed in a polypropylene or polyamide matrix.

The properties, among which hardness is often used for the denomination of the grades, are strongly dependent on:

- The nature of the matrix
- The nature of the rubber
- The type of curing system
- The crosslinking density
- The type of production process, notably the size of the rubber particles
- The ratio of matrix and rubber.

Of course, TPVs can be formulated with fillers, plasticizers and other additives like other thermoplastics.

TPVs are more elastic than TPOs but they are also more expensive. Sold by the same producer, the cost of a TPV can be 50% higher or more than an equivalent TPO.

- PP/EPDM-V is the general-purpose family of TPVs.
- PP/NBR-V is used for its better behaviour with hydrocarbons and oils.
- PP/IIR-V is used for its gas impermeability and possibly its damping properties.

4.30.3.1 PP/EPDM-V

PP/EPDM-Vs are marketed in two series, one for technical applications and the other for general-purpose and economical applications. Differences concern technical performances and cost.

Advantages

PP/EPDM-Vs are appreciated for their better elasticity and lower compression set than TPOs, combined with: a broad hardness range of 35 Shore A up to 50 Shore D; low density; good property/price ratio; ozone and heat behaviour; weather resistance, especially for black compounds; low-temperature behaviour; ease of waste recycling; broad possibilities of formulation and colouring; soft touch; compatibility with polyolefins (overmoulding, co-injection, co-extrusion, welding) for suitable grades; overmoulding on ABS, polycarbonate and polystyrene for acceptable grades . . .

Drawbacks

PP/EPDM-Vs are handicapped by a lower elasticity than conventional rubbers, the more so as the hardness increases; certain risks of creep, relaxation and permanent set, the more so the higher the temperature; some swelling in mineral oils and oily products; inherent flammability, but FR grades are marketed; limited thermal behaviour; higher cost than TPOs.

Special grades

They can be classified according to the type of processing, specific properties or targeted applications:

- injection, extrusion, blown films, blow-moulding, thermoforming, calendering, foaming, high flow, ultra-high flow . . .
- fully, highly or moderately crosslinked; lower cost; UV and/or heat stabilized; improved colour and gloss retention; cold-temperature ductility and flexibility; soft touch; food contact; FDA or NSF compliant; improved surface appearance for cosmetic parts; fireproofed; low compression set and creep; reduced oil swelling; improved chemical resistance; low hardness; high-impact; high modulus; colourable; scratch resistant . . .
- for automotive weatherseals, automotive interior applications, packaging, roofing . . .

Costs

As for all plastics, the costs fluctuate greatly with the crude oil price. PP/EPDM-Vs are more expensive than TPOs and SBS.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering, foaming.

Consumption and applications

(See Chapter 2 for further information.)

PP/EPDM-V targets specific applications and has lower consumption than TPOs.

PP/EPDM-Vs are used in the appliance, automotive, construction, consumer goods, packaging, electrical & electronics (E&E), industrial, food and medical sectors for various moulded and extruded technical goods, soft-touch overmoulding, grips . . .

Examples

- Appliances, kitchen, household
    - grips, handles for irons, flatware, vacuum cleaners, steam extractors, handheld vacuums, and other floor care items, coloured utensil grips . . .
    - feet, pads for small appliances, dishwasher sump boots . . .
    - foamed seals for coolers, integrated seals . . .
    - bumpers or edge accessories for vacuum cleaners, steam extractors, handheld vacuums
    - strain reliefs, cord holders . . .
    - motor and vibration mounts . . .
    - wheel treads . . .
    - grips, handles, feet, pads for office supply, personal care, sports and leisure, tools and garden devices . . .
    - toys . . . .
- Automotive
    - under the hood: tubes and connectors, plugs, bumpers, grommets for steering, air induction systems, fuel line systems . . .
    - interior: grips, knobs, mats, plugs, bumpers, grommets . . .
    - under the chassis: suspension parts, belly pans, plugs, grommets . . .
    - control cables . . .
    - Exterior: bumpers, spoilers, trims, lighting seals, mirror gaskets, dynamic and static weatherseals . . .
- Construction
    - geomembranes . . .
    - roofing . . .
    - residential and non-residential glazing, window and door weatherseals . . .
    - expansion joints, water-stops . . .
- Consumer goods, electronics applications
    - grips, buttons, bumpers, seals, feet, gaskets, spacers for computers, printers, copiers, scanners and fax machines, telecommunications, audio & video . . .
    - microphone boom on headset . . .
    - scroll wheel on Logitech mouse . . .
    - printer rollers . . .
    - scanner lids . . .
    - shockproof, water-resistant shields and other parts of webcams, cameras, personal digital assistants . . .
- Consumer packaging
    - cosmetics and toiletries . . .
    - food & beverage: caps for dairy products, fruit juices, sports drinks, beers, wines and food . . .
    - pharmaceutical packaging closures, seals and liners . . .
    - kitchen and household food storage, lids and seals, cookware, housewares and closures . . .
    - airtight boxes with integrated TPV seal (bi-injection moulding of PP and PP/EPDM-V).

- E&E
  - moulded electrical accessories, electrical connectors, shields, electrical connections . . .
  - power transmission and distribution systems . . .
  - wire and cable jacketing (halogen-free FR) . . .
  - telecommunication splice seals . . .
- Medical
  - syringe plunger tips, epidural syringe plungers . . .
  - seals, gaskets and diaphragms, blood filter seals overmoulded on a PC base . . .
  - medical equipment components, homeopathic drug dispensers . . .
  - medical tubing . . .
  - endoscopic camera holders, epidural needle fixation devices . . .
  - medical clogs . . .
- Miscellaneous
  - industrial sheet goods . . .
  - coated fabrics . . .
  - pipe seals . . .
  - caster wheels . . .

Elasticity

Elasticity depends on:

- the nature of the polypropylene
- the nature of the EPDM
- the type of curing system
- the ratio of polypropylene and EPDM
- the formulation
- the actual temperature.

Figure 4.137 displays examples of compression sets after 22 h at 70°C, which is not a severe condition, for PP/EPDM-V grades with hardnesses in the Shore A and D scales. Note:

- the lower set levels compared to those of TPS and TPOs
- the increase in compression set when the hardness increases, notably towards the Shore D scale (Shore A higher than 90).

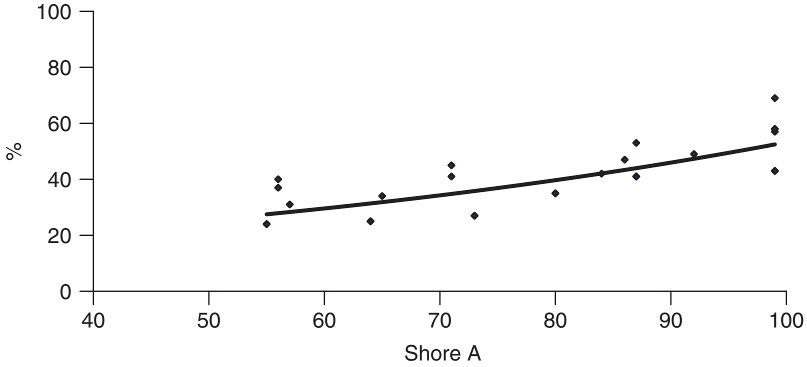


Figure 4.137. PP/EPDM-V: compression set (%) after 22 h at 70°C versus Shore A hardness

Low-temperature behaviour

The brittle points generally range from −62°C for the most-flexible grades up to −35°C for the most-rigid grades.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at 100°C up to 120°C, possibly 135°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

The modulus changes quickly with the temperature and, at 100°C, retention can be as low as 10% for hard grades but can reach 45% for a 65 Shore A grade.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

For two grades of different hardness, property retentions after 1000 h at 125°C are:

- 88% for the elongation at break
- 93% and 117% for the tensile strength.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties vary widely according to the grades but are generally of a fair level for the typical applications. Designers must pay careful attention to the tensile strength, which ranges from 3 MPa to 30 MPa depending on the hardness and the TPV family.

Dimensional stability

Alterations by moisture exposure are low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation.

Weathering

PP/EPDM-V resists hydrolysis well but is naturally sensitive to light and UV. It must be protected by addition of anti-UV and other protective agents and possibly by a few percent of an appropriate carbon black.

Chemicals

The chemical resistance depends on the hardness, the EPDM/PP ratio and the curing system.

Polypropylene and EPDM, being hydrocarbons, are sensitive to oils and other hydrocarbons. Grades rich in polypropylene are generally more resistant to chemicals.

PP/EPDM-V absorbs little water and is not very sensitive to it. Moreover, hydrolysis-resistant grades are marketed and used, for example, in washing machines.

Suitable grades are usable in contact with food and are used for food packaging.

Chemical resistance is generally good but PP/EPDM-Vs are attacked by chlorinated solvents, certain oxidants, aromatic hydrocarbons, certain aliphatic hydrocarbons.

Resistance can be limited to certain polar solvents.

Table 4.116 displays some examples concerning the swelling (%) after immersion in various chemicals for a number of days up to 1 year. Negative figures correspond to a decrease in the sample volume. These results relate to some grades only and cannot be generalized.

Table 4.116 PP/EPDM-V: examples of swelling (%) after immersion for some days up to 1 year

Chemical	Concentration (%)	Temperature (°C)	Time (days)	Swelling (%)
Acetic acid	100	23	7	1–5
Acetic acid	Unknown	23	7	6–9
Acrylonitrile	Unknown	23	7	−6 to 1
Aniline	100	23	7	1
Antifreeze	50	125	7	2–7
ASTM1 oil	100	100	3	9–60
ASTM1 oil	100	100	7	5–40
Automatic transmission fluid	100	125	7	31–72
Beer	100	23	7	1
Brake fluid	100	23	7	−2 to 1
Brake fluid	100	100	7	−29 to −2
Bromobenzene	100	23	7	32–116
Butyl acetate	100	23	7	−12 to 2
Calcium chloride & bromide	32	150	7	0–1
Coca cola	100	23	7	0–1
Coffee	100	23	7	0–1
Coke light	100	23	7	0–1
Cyclohexane	100	23	7	29–87
Diethylether	100	23	7	−3 to 13
Dimethylformamide	100	23	7	0–4
Dioctylphthalate	100	23	7	−9 to 0
Dioxan	100	23	7	−23 to 4
Ethanol	95	23	7	−2 to 2
Freon 11	100	5	7	24–107
Fuel B	100	23	7	18–113
Fuel C	100	23	7	17–69
Glycerol	100	23	7	0–1
Grease (lithium)	100	23	7	2–44
Hexane	100	23	7	3–36
Hydrochloric acid	10	23	7	−1 to 1
Isooctane (Fuel A)	100	23	7	7–37
Mayonnaise	100	23	7	1
Methylethylketone	100	23	7	−23 to 1
Milk	100	23	7	0–1
Nitrobenzene	100	23	7	−9 to 17
Orange juice	100	23	7	0–1
Piperidine	Unknown	23	7	11–51
Potassium hydroxide	10	23	7	−2 to 1
Propanol	100	23	7	−16 to −1
Pydraul 312	100	125	7	14–22
Pyridine	Unknown	23	7	−16 to 2
Sea water	100	23	7	−30 to 0
Sodium chloride	15	23	7	0–1
Sodium hydroxide	50	23	7	0
Sprite	100	23	7	0–1
Sulfuric acid	98	23	7	0–5
Sunvis 706 fluid	100	125	7	27–58
Tomato ketchup	100	23	7	0–1
Transmission fluid	100	125	7	39–73
Trichloroethylene	100	23	7	56–195
Turpentine oil	100	23	7	20–84
Ucon 50HB5100	100	125	7	−22 to −11
Ucon CC732	100	125	7	2–11
Vegetable oil	100	23	7	−7 to 0
Vinegar	100	23	7	0–1
Washing powder	2.5	23	7	0
Water	100	23	30	0

Table 4.116 (Continued)

Chemical	Concentration (%)	Temperature (°C)	Time (days)	Swelling (%)
Water	100	23	60	0–1
Water	100	23	90	1–2
Water	100	23	180	1–3
Water	100	23	365	1–4
Water	100	70	30	2–7
Water	100	70	60	3–8
Water	100	70	90	4–9
Water	100	70	180	4–11
Water	100	70	365	5–15
Water	100	83	30	3–7
Water	100	83	60	4–10
Water	100	83	90	4–12
Water	100	83	180	5–14
Water	100	83	365	6–19
Water	100	100	7	2–6
Wine	100	23	7	0–1
Xylene	100	23	7	14–57
Zinc chloride	10	23	7	0

Furthermore, swelling alone is not sufficient to estimate the chemical resistance. Complementary tests are needed. These indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Fire resistance

PP/EPDM-V inherently burns easily. Fireproofing agents can reduce the aptitude for combustion to reach a UL94 V0 rating.

Electrical properties

PP/EPDM-Vs are insulating and are used for low-tension wire and cable covering.

Joining, decoration

Welding and joining with adhesives are possible.

All precautions must be taken concerning health and safety according to local laws and regulations.

PP/EPDM-V allows a wide variety of colours.

Trade name examples

Santoprene, Sarlink, Vyram . . .

Property tables

Table 4.117 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

4.30.3.2 PP/NBR-V

PP/NBR-V is marketed for its hydrocarbon resistance, which competes with conventional nitrile rubber.

Advantages

PP/NBR-V is appreciated for its resistance to hydrocarbons, oils and greases combined with a fair compression set, a broad hardness range, low density, good property/price ratio,

Table 4.117 PP/EPDM-V: examples of properties

	Compounds with Shore A hardness			
Hardness (Shore)	35A	55A	75A	85A
Density (g/cm^3)	0.9–1	0.9–1	1	1
Tensile strength (MPa)	3–4	3–5	6–8	7–16
Elongation at break (%)	400–500	350–500	400–600	300–600
Stress at 100% (MPa)	1	1.6–3	3–4	4–7
Tear strength (N/mm)	12	7–20	12–35	15–49
Tensile modulus (GPa)			0.02–0.03	0.1
Compression set, 22 h at 20°C (%)		23–26	23	29–37
Compression set, 168 h at 20°C (%)	15	15–26	28	
Compression set, 22 h at 70°C (%)		22	27–37	40–50
Low service temperature (°C)	−60	−60 to −62	−60 to −63	−60
Continuous use temperature (°C)	100–120	100–120	100–120	100–120
	Compounds with Shore D hardness			
Hardness (Shore)	35D	40D	45D	50D
Density (g/cm^3)	0.9–1	0.9–1	0.9–1	0.9–1
Tensile strength (MPa)	12–13	17–19	15	22–28
Elongation at break (%)	450	550–600	750	600
Stress at 100% (MPa)	8–10	9–11	11	10–16
Tear strength (N/mm)	20–75	40–65	86	80–90
Tensile modulus (GPa)	0.1	0.14	0.27	0.35
Compression set, 22 h at 20°C (%)		32		40
Compression set, 22 h at 70°C (%)	49	43–57	40	58–69
Low service temperature (°C)	−60	−55	−40	−32 to −34
Continuous use temperature (°C)	100–120	100–120	100–120	100–120

The following general assessments concerning the chemical behaviour at room temperature of PP/EPDM-Vs, which are not representative of all grades of PP/EPDM-Vs, should be verified by consultation with the producer of the selected grades and by tests under operating conditions.
Chemical resistance depends on the composition of TPVs and their hardness.
General chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers or/and black coloration are needed
Weak acids	Good behaviour
Strong acids	Good behaviour except for very high concentrations and oxidizing acids
Weak bases	Good behaviour
Strong bases	Good behaviour
Solvents	Good behaviour except aromatic hydrocarbons, chlorinated solvents, certain aliphatic hydrocarbons, some oxidizing agents Resistance can be limited to certain polar solvents
Food contact	Possible for special grades

low-temperature behaviour, fair ageing resistance, accuracy of moulding, ease of waste recycling, and co-processing with polyolefins, EVA and some other TPVs for suitable grades.

Drawbacks

PP-NBR-V is handicapped by a lower elasticity than conventional nitrile rubbers, the more so as the hardness increases; certain risks of creep, relaxation and permanent set, the more so the higher the temperature; the cost; inherent flammability, but FR grades are marketed; a limited thermal behaviour; the lack of sources.

Costs

The costs, as for all plastics, fluctuate highly with the crude oil price. PP/NBR-Vs are more expensive than PP/EPDM-V.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering.

Consumption and applications

(See Chapter 2 for further information.)

PP/NBR-V targets automotive and similar applications relating to hydrocarbon and oil contact. Consumption is inferior to that of PP/EPDM-V.

Examples:

- Automotive: under the hood:
  - ○ tubes and connectors for air induction systems . . .
  - ○ bellows . . .
  - ○ seals for gas oil filters, carburettors, brake fluid tanks . . .
  - ○ mounts for damping noise and vibration, shock absorbers . . .
- Industry
  - ○ seals, tubes, pipes, profiles for oil contact . . .
  - ○ mounts for damping noise and vibration, shock absorbers . . .

Elasticity

Elasticity depends on:

- the nature of the polypropylene
- the nature of the NBR
- the type of curing system
- the ratio of polypropylene and NBR
- the formulation
- the actual temperature.

Figure 4.138 displays examples of compression sets after 22 h at 100°C, which are rather harsh conditions, for PP/NBR-V grades with hardnesses on the Shore A scale. Note:

- the fair set levels taking the temperature into account
- the increase in compression set when hardness increases.

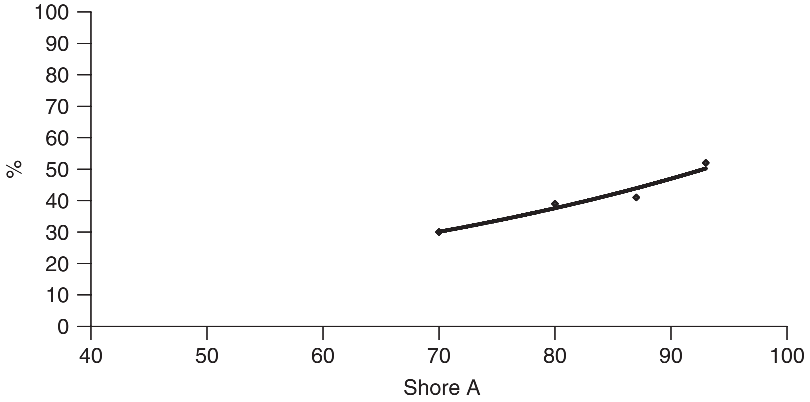


Figure 4.138. PP/NBR-V: compression set (%) after 22 h at 100°C versus Shore A hardness

Low-temperature behaviour

The brittle points generally range from −40°C for the most-flexible grades up to −30°C for the most-rigid grades.

Between the ambient temperature and −25°C, the 100% modulus of an 80 Shore A grade is multiplied by 2.3.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at 100°C up to 125°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

The short-term tear strength retention at 100°C can vary from 28% up to 54% according to the tested grades.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

For a tested grade, property retentions after 1000 h at 100°C are:

- 84% for the elongation at break.
- 147% for the tensile strength.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties vary widely according to the grades but are generally of a fair level for the typical applications. Designers must pay careful attention to the tensile strength, which ranges from 6 MPa to 15 MPa depending on the hardness.

Dimensional stability

Alterations by moisture exposure are fair.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation.

Weathering

PP/NBR-V resists hydrolysis well but is naturally sensitive to light and UV. It must be protected by addition of anti-UV and other protective agents and possibly by a few percent of an appropriate carbon black.

Chemicals

Chemical resistance depends on the hardness, the NBR/PP ratio and the curing system.

Vulcanized NBR being resistant to hydrocarbons, PP/NBR-V is more resistant to oils and greases than PP/EPDM-V.

PP/NBR-V absorbs little water and is not very sensitive to it.

Table 4.118 displays some examples concerning the swelling (%) after immersion in various chemicals for 7 days. Negative figures correspond to a decrease in the sample volume. These results relate to some grades only and cannot be generalized. Furthermore, swelling alone is not sufficient to estimate the chemical resistance. Complementary tests are needed.

Table 4.118 PP/NBR-V: examples of swelling (%) after immersion for 7 days

Chemical	Concentration (%)	Temperature (°C)	Time (days)	Swelling (%)	
				PP/EPDM-V	PP/NBR-V
Hydrolysis resistance					
Water	100	100	7	2–6	5–15
Sodium hydroxide	50	23	7	0	
Sodium hydroxide	50	100	7		0
Hydrochloric acid	10	23	7	−1 to 1	5–11
Oil resistance					
ASTM3 oil	100	100	3	25–71	3–14
Fuel C	100	23	7	17–69	18–21
Petrol (10% ethanol)	100	23	7		21–25

These indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Compared to PP/EPDM-V, note:

- the more limited swelling of PP/NBR-V in oils, the more so as the PP/EPDM-V grades showing lower swelling are the hardest, which are not common for PP/NBR-V
- the slightly higher sensitivity of PP/NBR-V to hydrolysis.

Fire resistance

PP/NBR-V burns inherently easily and is compliant with a UL94 HB rating.

Electrical properties

PP/NBR-V are insulating and are used for low-tension wire and cable covering exposed to oils.

Joining, decoration

Welding and joining with adhesives are possible.

All precautions must be taken concerning health and safety according to local laws and regulations.

Trade name examples

Geolast . . .

Property tables

Table 4.119 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.119 PP/NBR-V: examples of properties

Hardness (Shore)	72A	82A	90A	46D
Density (g/cm^3)	1	1	1	1
Tensile strength (MPa)	6	8	11	15
Elongation at break (%)	260	290	330	365
Stress at 100% (MPa)	3.3	4–5	6–7	11–12
Tear strength (N/mm)	26	33	52	79
Compression set, 22 h at 20°C (%)	26	29	39	46
Compression set, 22 h at 100°C (%)	28	31	41	52
Low service temperature (°C)	−40	−40	−38	−35
Tensile strength retention after 7 days at 150°C (%)	73	60	67	79
Continuous use temperature (°C)	100–125	100–125	100–125	100–125

4.30.3.3 PP/IIR-V

PP/IIR-V is marketed to compete with conventional butyl rubber thanks to its low gas permeability, compliance with the pharmacopoeia and, secondarily, its damping properties.

Advantages

PP/IIR-V is appreciated for its low gas permeability combined with compliance with the pharmacopoeia, fair compression sets, the rubber-like hardness range, low density, low-temperature behaviour, fair ageing resistance, sterilization resistance, damping properties, ease of waste recycling . . .

Drawbacks

PP-IIR-V is handicapped by a lower elasticity than conventional rubbers, the more so as the hardness increases; certain risks of creep, relaxation and permanent set, the more so the higher the temperature; the cost; inherent flammability; the lack of sources.

Costs

The costs, as for all plastics, fluctuate highly with the crude oil price. PP/IIR-V is more expensive than PP/EPDM-V.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering.

Consumption and applications

(See Chapter 2 for further information.)

PP/IIR-V targets specific applications relating to low gas permeability, pharmacopoeia compliance, and/or damping properties. Consumption is inferior to that of PP/EPDM-V.

PP/IIR-V is used in medical, industrial and consumer goods requiring low permeability to moisture, air and oxygen, competing with butyl rubber.

Elasticity

Elasticity depends on:

- the nature of the polypropylene
- the nature of the IIR
- the type of curing system
- the ratio of polypropylene and IIR
- the formulation
- the actual temperature.

Compression sets after 22 h at 70°C are of the order of 18–35% for 45–65 Shore A grades.

Low-temperature behaviour

The brittle points are generally in the range from −60°C up to −30°C.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at 90°C up to 130°C, according to the applied conditions.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

For two tested grades, property retentions after 1000 h at 125°C are:

- 67–96% for the elongation at break
- 64–110% for the tensile strength.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties vary widely according to the grades but are generally of a fair level for the typical applications. Designers must pay careful attention to the tensile strength, which ranges from 3 MPa to 12 MPa according to the hardness.

Dimensional stability

Alterations by moisture exposure are low.

Chemicals

Chemical resistance depends on the hardness, the IIR/PP ratio, and the curing system.

Chemical behaviour is generally satisfactory with water, detergents, acids, bases, alcohols and amines but is limited to unsatisfactory versus aliphatic and aromatic hydrocarbons, chlorinated solvents, oils, fuels, and unleaded petrol.

Fire resistance

PP/IIR-V burns inherently easily and is compliant with a UL94 HB rating.

Electrical properties

PP/IIR-Vs are insulating.

Joining, decoration

Welding and joining with adhesives are possible.

All precautions must be taken concerning health and safety according to local laws and regulations.

Trade name examples

Trefsin . . .

Property tables

Table 4.120 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.120 PP/IIR-V: examples of properties

	Compounds with Shore A hardness			
Hardness (Shore)	45A	60A	75A	85A
Density (g/cm^3)	1	1	1	1
Tensile strength (MPa)	3	6	5–9	7–12
Elongation at break (%)	260	470	260–440	280–460
Stress at 100% (MPa)	1.1	1.9	2.5–5	3.8–6.5
Tear strength (N/mm)		23	28	38
Compression set, 22 h at 20°C (%)		20	30	60
Compression set, 22 h at 70°C (%)	18	30		
Continuous use temperature (°C)	90–130	90–130	90–130	90–130

4.30.4 TPE/PVC

PVC-based TPEs (TPE/PVC) are marketed in two series:

- general-purpose grades with high compression sets for economical applications
- improved compression set, more-expensive grades for more-technical applications.

There is a broad range of products:

- unvulcanized rubber, often NBR, dispersed in a conventional PVC. These grades are often in-house formulations and are not taken into account in TPE statistics
- unvulcanized rubber dispersed in a high molecular weight PVC
- dynamically vulcanized rubber dispersed in a high molecular weight PVC.

TPE/PVCs are positioned between soft PVC and general-purpose crosslinked rubbers.

They are currently handicapped by the ecological problems concerned with chlorine and possibly with some plasticizers.

Advantages

TPE/PVCs are appreciated for their cost compared to TPVs, SEBS and general-purpose cured rubbers such as EPDMs and polychloroprenes; possibilities of in-house formulation; rubber-like hardnesses; weathering resistance for suitably proofed grades; fair abrasion, scuff and mar resistance; fair aliphatic hydrocarbon behaviour; fair flex fatigue resistance; ease of waste recycling, broad possibilities of formulation and colouring; transparent grades; soft touch; electric insulation; possibility of co-extrusion with flexible or rigid PVC for suitable grades; easy welding and joining; fireproofing . . .

Drawbacks

TPE/PVCs are handicapped by the ecological problems involved with chlorine and possibly with some plasticizers; a lower elasticity than conventional rubbers, the more so as the hardness increases; certain risks of creep, relaxation and permanent set, the more so the higher the temperature rises; higher cost than TPOs; aromatic and chlorinated hydrocarbon behaviour; limited thermal behaviour; density; fume toxicity and corrosivity in the event of fire; tool corrosion risks.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- injection, extrusion, blown films, blow-moulding, thermoforming, calendering, foaming, high flow, ultra-high flow . . .
- crosslinked; UHMW; lower cost; UV and/or heat stabilized; improved colour and gloss retention; cold-temperature ductility and flexibility; soft touch; food contact; matt surface; plasticizer-free for contact with organic glazing; fireproofed; low compression set and creep; reduced oil swelling; improved chemical resistance; transparent; colourable . . .
- for automotive applications, weatherseals, foamed goods, wire coating . . .

Costs

The costs, as for all plastics, fluctuate highly with the crude oil price. Most common TPE/PVCs are cheaper than SEBS, TPVs and general-purpose cured rubbers such as EPDMs and polychloroprenes but are more expensive than TPOs and SBS.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering, foaming.

Consumption and applications

(See Chapter 2 for further information.)

TPE/PVC targets general-purpose applications mainly in the automotive sector but also in construction, industrial, consumer goods, packaging, electrical & electronics applications for various moulded and extruded technical goods, soft-touch overmoulding, grips . . .

Examples

- Automotive
    - interior: skins, grips, knobs, mats, plugs, bumpers . . .
    - steering wheels, gear-shift knobs . . .
    - gear-shift boots . . .
    - console box lids . . .
    - window encapsulations . . .
    - wire harness grommets . . .
    - exterior: trims, seals, weatherseals . . .
    - tubes for windscreen washers . . .
    - pipe covering . . .
- Construction
    - residential and non-residential glazing, window and door weatherseals . . .
    - roofing . . .
    - flooring . . .
- E&E
    - moulded electrical accessories, electrical connectors . . .
    - wire and cable jacketing . . .
- Appliances, kitchen, household, consumer goods
    - grips, handles . . .
    - feet, pads for small appliances . . .
    - seals, integrated seals . . .
    - motor and vibration mounts . . .
    - toys . . . .
- Industrial
    - grips, handles, overmoulding . . .
    - feet, pads, mounts . . .
    - seals, integrated seals . . .
    - shoe soles . . .
- Miscellaneous
    - leather-like goods . . .
    - shock-proofing casings . . .

Elasticity

Elasticity depends on:

- the nature of the PVC
- the nature of the rubber
- the type of curing system
- the ratio of PVC and rubber
- the formulation
- the actual temperature.

Figure 4.139 displays examples of compression sets after 22 h at 70°C, which are not severe conditions, for TPE/PVC grades with hardnesses in the Shore A scale. Note:
- the broad scattering of compression sets
- the high average level of the data.

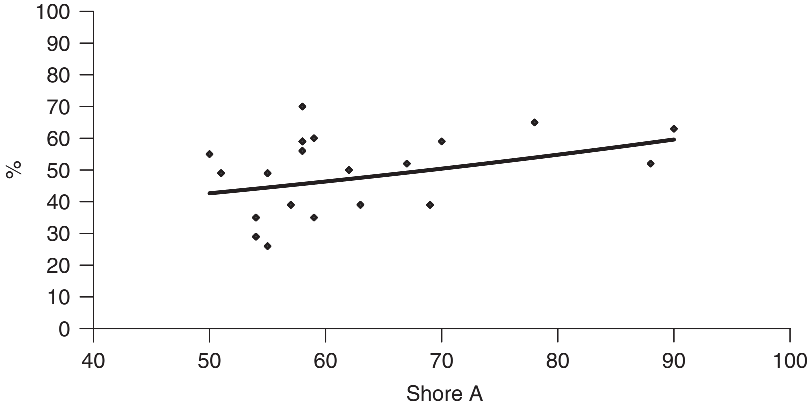


Figure 4.139. TPE/PVC: compression set (%) after 22 h at 70°C versus Shore A hardness

Low-temperature behaviour

The brittle points generally range from −45°C up to −30°C, with a few grades ranging from −62°C up to −40°C.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at 85°C up to 105°C, possibly more for an exceptional grade.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

The hardness decay when the temperature rises is inferior to that of PVC but superior to that of conventional rubbers.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

For ten tested grades of different hardnesses, half-lives based on elongation at break vary from 55 days up to more than 900 days at 85°C. Half-lives based on tensile strength are very much longer, greater than 1800 days at the same temperature.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties vary widely according to the grades but are generally of a fair level for the typical applications. Designers must pay careful attention to the tensile strength, which ranges from 6 MPa to 20 MPa depending on the hardness and the TPE family.

Dimensional stability

Alterations by moisture exposure are low.

Weathering

TPE/PVC resists hydrolysis well and is naturally sensitive to light and UV, but special grades are marketed with a sufficient weathering resistance to allow exterior applications in the automotive industry and construction.

Chemicals

Chemical resistance depends on:

- the nature of the PVC, notably its molecular weight
- the nature of the rubber
- the possible curing of the rubber phase
- the ratio of PVC and rubber
- the formulation
- the actual temperature.

TPE/PVC is generally not very sensitive to hydrolysis, acids and bases.

Resistance to aliphatic hydrocarbons at ambient temperature is generally sufficient for numerous applications but can be unsatisfactory for applications specifically requiring resistance.

TPE/PVCs can be attacked by chlorinated solvents, aromatic hydrocarbons, certain aliphatic hydrocarbons, ketones . . .

Suitable grades are usable in contact with food.

Fire resistance

PVC is inherently resistant to fire but rubbers are not. Consequently, the fire behaviour depends on the PVC/rubber ratio, the formulation and the use of fireproofing agents. Some TPE/PVC grades reach a UL94 V0 rating. In the event of fire, beware of the fume toxicity and corrosivity.

Electrical properties

TPE/PVCs are insulating and are used for low-tension wire and cable covering.

Joining, decoration

Welding and joining with adhesives are possible.

All precautions must be taken concerning health and safety according to local laws and regulations.

TPE/PVC allow a large variety of colours.

Trade name examples

Flexalloy, Garaflex, Marvylex, Sunfrost, Sunprene, Vaycron . . .

Property tables

Table 4.121 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

4.30.5 Thermoplastic polyurethanes (TPU)

Polyurethanes are obtained by the reaction between polyols and isocyanates. They are of diverse chemical natures and applications. Most are thermosets (see *Thermosets and Composites*, M. Biron, Elsevier Ltd (2004); ISBN: 1856174115) but others are thermoplastics (TPU), ranging from elastomer flexibility to polyethylene rigidity.

Table 4.121 TPE/PVC: examples of properties

	Compounds with Shore A hardness			
Hardness (Shore)	50A	60A	70A	90A
Density (g/cm^3)	1.1–1.2	1.1–1.2	1.1–1.2	1.1–1.2
Tensile strength (MPa)	6–11	10–14	10–17	15–19
Elongation at break (%)	250–500	350–500	300–500	20–200
Stress at 100% (MPa)		3–4	3–5	
Compression set, 22 h at 70°C (%)	29–49	22–60	27–65	
Low service temperature (°C)	−62	−40	−45 to −30	
Continuous use temperature (°C)	85–105	85–105	85–105	85–105

The following general assessments concerning the chemical behaviour at room temperature of TPE/PVCs, which are not representative of all grades of TPE/PVCs, should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Chemical resistance depends on the composition of the TPE/PVCs and general chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers are needed
Acids	Generally fair behaviour
Bases	Generally fair behaviour
Solvents	Good to limited behaviour with aliphatic hydrocarbons at ambient temperature Unsatisfactory behaviour with chlorinated solvents, aromatic hydrocarbons, ketones . . .
Food contact	Possible for special grades

The thermoplastic polyurethanes consist of rigid isocyanate sequences and flexible polyester or polyether sequences. The properties, of which hardness is often used for the denomination of the grades, vary broadly as functions of:

- the nature of the flexible segments: polyesters, polyethers, polycarbonates, polycaprolactones . . .
- the nature of the rigid segments
- the length of the flexible segments
- the flexible/rigid segment ratio.

Generally, compared with polyethers, the polyesters present:

- the best hydrocarbon behaviour
- a greater sensitivity to water and hydrolysis
- a more-limited resistance to ageing, with some exceptions.

TPUs can be reinforced with glass fibres.

Unless otherwise specified we will not make a distinction between the various subfamilies.

Thermoset polyurethanes are not treated here.

Advantages

TPUs are appreciated for their high mechanical performances; tenacity; excellent abrasion and tear resistances; broad range of moduli and hardnesses going down to 60 Shore A; attractive price/property ratios; good oil, fuel and aliphatic hydrocarbon behaviours; fair ozone resistance; fair thermal resistance for suitable grades; good flex fatigue resistance; ease of waste recycling; broad possibilities of colouring; transparent grades; soft-touch grades; electric insulation; good low-temperature behaviour; compatibility with PC, ABS, flexible or rigid PVC for suitable grades.

Drawbacks

TPUs are handicapped by a lower elasticity than conventional rubbers, the more so the higher the hardness; certain risks of creep, relaxation and permanent set, the more so the higher the temperature; higher cost than TPOs; risks of hydrolysis especially for the polyester types; UV exposure yellowing; incompatibility between certain polyester and polyether grades; aromatic and chlorinated hydrocarbon behaviour; limited thermal behaviour; density; inherent flammability, but FR grades are marketed; risks of fume toxicity in the event of fire.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- injection, extrusion, blown films, blow-moulding, thermoforming, calendering, high flow, ultra-high flow . . .
- UV, hydrolysis and/or heat stabilized; lower cost; improved colour and gloss retention; cold-temperature ductility and flexibility; soft touch; food contact; fireproofed; low compression set and creep; reduced oil swelling; improved chemical resistance; better resistance to microorganisms; transparent; colourable; glass fibre reinforced; antistatic grades . . .
- for automotive, wire coating, films, adhesives . . .

Costs

As for all plastics, the costs fluctuate highly with the crude oil price. TPUs are more expensive than TPOs and SBS.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering.

Consumption and applications

(See Chapter 2 for further information.)

TPUs target general-purpose and technical applications in various sectors such as automotive, construction, industrial, consumer goods, packaging, electrical & electronics applications for various moulded and extruded technical goods, soft-touch overmoulding, grips . . .

Examples

- Automotive
  - side mouldings . . .
  - constant velocity boots . . .
  - lumbar supports . . .
  - mounts . . .
- Sporting goods
  - in-line skates . . .
  - ski boots . . .
  - swim fins . . .
  - goggles . . .
  - sports shoe soles . . .
- Construction
  - architectural glass lamination . . .

- E&E
  - ○ moulded electrical accessories, electrical connectors . . .
  - ○ wire and cable jacketing . . .
- Industry
  - ○ gaskets and seals, hydraulic seals . . .
  - ○ hoses and tubing, hydraulic hoses, fire hose liners, flexible tubing . . .
  - ○ films and sheets . . .
  - ○ motor and vibration mounts . . .
  - ○ caster wheels . . .
  - ○ drive belts . . .
  - ○ conveyor belts . . .
  - ○ food processing equipment . . .
  - ○ mining screens . . .
- Coated fabrics
  - ○ inflatable rafts . . .
  - ○ life vests . . .
  - ○ protective clothing . . .
  - ○ weatherproof clothing . . .
- Miscellaneous
  - ○ shock-proofing casings . . .
  - ○ cattle tags . . .
  - ○ toys . . .
  - ○ magnetic media . . .
  - ○ medical tubing . . .
  - ○ biomedical apparatus components . . .
  - ○ alloys with polycarbonate, ABS or others

Elasticity

Elasticity depends on:

- the nature of the polyurethane and the molecular weight
- the ratio of soft and hard segments
- the formulation
- the actual temperature.

Figure 4.140 displays examples of compression sets after 22 h at 70°C, which are not severe conditions, for TPU grades with hardnesses in the Shore A and D scales (Shore A superior to 90). Note:

- the broad scattering of compression sets
- the high average level of the data.

Low-temperature behaviour

The brittle points are generally in the range from −70°C up to −65°C, with a few grades with higher temperatures, −50°C for example. Low service temperatures are often about −40°C.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at 80°C with possible short periods at 120°C. A slow thermal degradation can start at 240°C with emission of fumes, requiring efficient ventilation of workstations.

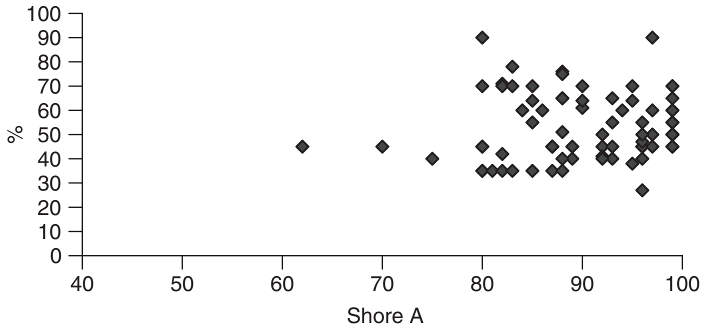


Figure 4.140. TPU: compression set (%) after 22 h at 70°C versus Shore A hardness

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

For three tested grades of different hardnesses, half-lives based on elongation at break vary from 500 days up to more than 2000 days at 85°C. Half-lives based on tensile strength are not so good –300 days up to 1100 days at the same temperature.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties are generally of a good to excellent level including abrasion, tear resistance and tensile strength.

Weathering

TPUs are naturally sensitive to light, UV and hydrolysis but special grades are marketed. Specific grades target applications in tropical climates.

Chemicals

Generally, compared with polyethers, the polyesters present:

- the best hydrocarbon behaviour
- a greater sensitivity to water and hydrolysis
- a more-limited resistance to ageing, with some exceptions

The chemical resistance also depends on the molecular weight and the hardness.

The behaviour with pure or salt water at ambient temperature is generally good, without significant deterioration of the mechanical properties over several years. However, when the temperature rises the properties decrease, particularly above 60°C.

Concentrated acids and bases quickly attack the polyurethanes and contact must be avoided.

Dilute acids and bases have a moderate effect at ambient temperature, which develops to a greater or lesser degree with the temperature. Prolonged contact must be avoided.

Table 4.122 displays some results concerning general assessments of behaviour after prolonged immersion in water and aqueous solutions at the specified temperatures for given grades, which are not necessarily representative of all the TPUs. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Table 4.122 TPU: examples of general assessments after prolonged immersion in water and aqueous solutions at 20 and 60°C

Chemical	Concentration (%)	Temperature (°C)	Estimated behaviour	
			Polyesters TPU-AU	Polyethers TPU-EU
Acetic acid	3	20	l	S
Acetic acid	3	60	n	l
Battery acid	Unknown	20	n	S
Battery acid	Unknown	60	n	l
Boric acid	3	20	l	S
Boric acid	3	60	l	l
Butyric acid	3	20	l	S
Butyric acid	3	60	n	l
Citric acid	3	20	l	S
Citric acid	3	60	n	l
Formic acid	3	20	l	S
Formic acid	3	60	n	l
Hydrochloric acid	3	20	n	S
Hydrochloric acid	3	60	n	l
Hydrogen peroxide	35	20	l	l
Lactic acid	3	20	l	S
Lactic acid	3	60	n	l
Lauric acid	3	20	l	S
Lauric acid	3	60	n	l
Nitric acid	3	20	n	n
Nitric acid	3	60	n	n
Oleic acid	3	20	l	S
Oleic acid	3	60	n	l
Phenol solution	3	20	l	S
Phenol solution	3	60	l	l
Phosphoric acid	3	20	l	S
Phosphoric acid	3	60	n	l
Propionic acid	3	20	l	S
Propionic acid	3	60	n	l
Sea water	100	20	S	S
Sea water	100	60	l	S
Sodium bisulfate	3	20	l	S
Sodium bisulfate	3	60	l	l
Sodium hypochlorite	3	20	l	l
Sodium hypochlorite	0.5	20	l	S
Sodium hypochlorite	3	60	n	l
Sodium hypochlorite	0.5	60	l	l
Sodium nitrate	3	20	l	S
Sodium nitrate	3	60	l	l
Stearic acid	3	20	l	S
Stearic acid	3	60	n	l
Sulfuric acid	3	20	n	S
Sulfuric acid	3	60	n	l
Water	100	20	S	S
Water	100	60	l	S

S: satisfactory; l: limited; n: not satisfactory

Note:

- the better behaviour of polyethers (TPU-EU)
- the harshness of dilute acids at concentrations as low as 3%.

TPUs generally show good resistance to conventional oils, greases, gas oil and fuels without alcohol; however, certain additives in high-performance oils can be incompatible with the TPUs.

Fuels containing alcohol or rich in aromatic hydrocarbons can cause degradation or unacceptable swelling. Chlorinated solvents cause significant swelling.

TPU can be attacked by chlorinated solvents, aromatic hydrocarbons, ketones . . . Highly polar solvents such as THF can dissolve TPUs.

Suitable grades are usable in contact with food.

Fire resistance

TPUs burn inherently easily and are compliant with a UL94 HB rating. FR grades can reach a UL94 V0 rating. In the event of fire, beware the fume toxicity.

Electrical properties

TPUs are insulating and are used for low-tension wire and cable covering.

Joining, decoration

Welding and joining with adhesives are possible.

All precautions must be taken concerning health and safety according to local laws and regulations.

TPU allows a large variety of colours.

Trade name examples

Avalon, Desmopan, Elastollan, Estane, Irogran, Isoplast, Laricol, Laripur, Pearlcoat, Pearlthane, Pellethane, Texin . . .

Property tables

Table 4.123 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.123 TPU: examples of properties

	Compounds with Shore A hardness			
Hardness (Shore)	62A	70A	80A	90A
Density (g/cm^3)	1.15	1.2	1.2	1.2
Tensile strength (MPa)	30	22–40	28–50	30–55
Elongation at break (%)	850	750–830	560–730	450–650
Tensile modulus (GPa)				0.02–0.03
Stress at 100% (MPa)	2	2.5–4	3.5–5	6–7
Stress at 300% (MPa)		5–7	8	6–7
Tear strength (N/mm)	30	40	53–65	45–85
Abrasion loss (mm^3)	35	30–35	30–62	30–70
Compression set, 22 h at 70°C (%)	45	45	35–90	35–75
Brittle point (°C)			−70	−70
Continuous use temperature (°C)	85	85	85	85

(*Continued*)

Table 4.123 (Continued)

	Compounds with Shore D hardness			
Hardness (Shore)	50D	60D	70D	75D
Density (g/cm^3)	1.2	1.2	1.2	1.2
Tensile strength (MPa)	30–52	35–55	40–55	40–50
Elongation at break (%)	400–550	350–500	350–400	250–350
Tensile modulus (GPa)	0.15	0.16–0.33	0.5–0.6	0.65–0.73
Stress at 100% (MPa)	9–17	16–20	23	30
Stress at 300% (MPa)	15–18	27		
Tear strength (N/mm)	40–150	40–170	170–220	250
Abrasion loss (mm^3)	20–90	20–50	30–40	20–30
Compression set, 22 h at 70°C (%)	27–65	45–60	65	60
Brittle point (°C)	−70 to −65	−70 to −65	−70 to −65	−70 to −65
Continuous use temperature (°C)	85	85	85	85
	Glass fibre reinforced TPUs			
Glass fibre (%)	10	20	25	50
Hardness (Shore)	50D	60–73D	70D	85D
Density (g/cm^3)	1.3	1.4	1.4	1.7
Tensile strength (MPa)	30	50–80	70	150
Elongation at break (%)	65	10–40	15	4–5
Tensile modulus (GPa)	0.35	1–3	2–3	12–13
Notched impact strength, Charpy 23°C (kJ/m^2)	NB	30–NB	35	14
Notched impact strength, Charpy −30°C (kJ/m^2)	30	10–20	12	8
HDT B (0.46 MPa) (°C)	125	120–155	170	175
HDT A (1.8 MPa) (°C)	65	90–120	130	130
Coefficient of thermal expansion (10^{-5}/°C)	2.8	2	1.5	1.2
	Electrical property examples			
Shore A	62A	80A	93A	
Shore D			41D	75D
Volume resistivity (ohm.cm)	10^8–10^9	10^{10}	10^{10}	10^{13}
Dielectric constant	8	7	6	5
Loss factor (10^{-4})	300	500–2200	500	300–500
Dielectric strength (kV/mm)	15	35	45	50

The following general assessments concerning the chemical behaviour at room temperature of TPUs, which are not representative of all grades of TPUs, should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Chemical resistance depends on the composition of TPUs and general chemical properties are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers are needed
Acids	Generally unsatisfactory behaviour
Bases	Generally unsatisfactory behaviour
Solvents	Good behaviour with conventional oils, greases, gas oil, fuels without alcohol but certain additives in high-performance oils can be incompatible with the TPUs Fuels containing alcohol or rich in aromatic hydrocarbons can cause degradation or unacceptable swelling Behaviour is generally unsatisfactory with chlorinated solvents, aromatic hydrocarbons, ketones, highly polar solvents such as THF . . .
Food contact	Possible for special grades

4.30.6 Melt processable rubber (MPR)

These materials are based on a partially crosslinked, chlorinated olefin interpolymer alloy.

MPRs are marketed in several series according to cost, performance and processability.

Hardnesses are in the Shore A scale.

Advantages

MPRs are appreciated for their resistance to oils; hardnesses in the range of conventional rubbers; good weather resistance for black compounds and UV-stabilized grades; good ozone behaviour; fair abrasion and tear resistance; transparent versions; coextrusion with flexible or rigid PVC; possibility of colouring; property/price ratio; low-temperature behaviour; ease of waste recycling; soft touch; damping properties; adherence to ABS, PC/ABS, ASA, SAN, PC, PBT, PC/ASA, metals for suitable grades . . .

Drawbacks

MPRs are handicapped by a lower elasticity than conventional rubbers, the more so the higher the hardness; certain risks of creep, relaxation and permanent set, the more so the higher the temperature; sometimes limited flex fatigue resistance; ecological problems involved with halogens; tool corrosion risks; lack of sources; cost.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- injection, extrusion, blown films, blow-moulding, thermoforming, calendering, foaming . . .
- lower cost; UV and/or heat stabilized; cold-temperature ductility and flexibility; soft touch; food contact; FDA or NSF compliant; fireproofed; reduced compression set and creep; improved chemical resistance; low hardness; translucent; transparent; colourable . . .
- for automotive weatherseals, electrical, packaging applications . . .

Costs

As for all plastics, the costs fluctuate highly with the crude oil price. MPRs are more expensive than TPOs and SBS.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering, foaming.

Consumption and applications

(See Chapter 2 for further information.)

MPRs target specific applications and have lower consumption than TPOs.

They are used in the appliance, automotive, construction, consumer goods, packaging, electrical & electronics, industrial, food and medical sectors for various moulded and extruded technical goods, soft-touch overmoulding, grips . . .

Examples:

- Injection and blow-moulded parts, seals and gaskets resisting oils, handles of motorbikes, cable guides . . .
- Extruded goods, tubes, hoses, pipes, profiles . . .
- Wire and electric cables for industry and robotics . . .

- Damping mounts for noises and vibrations . . .
- Window and door weatherstripping . . .
- Coated fabrics, films and sheet goods . . .
- Soft handles and grips . . .

Elasticity

Figure 4.141 displays examples of compression sets after 22 h at 100°C, which are rather harsh conditions, for MPR grades with hardnesses in the Shore A scale. Note the rather high set levels.

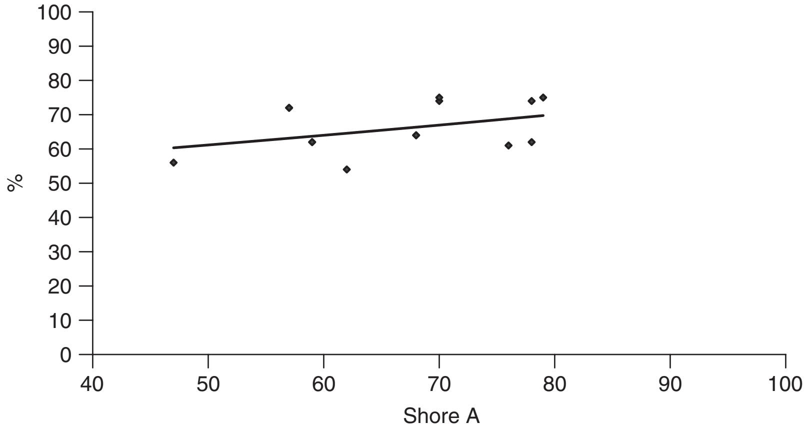


Figure 4.141. MPR: compression set (%) after 22 h at 100°C versus Shore A hardness

Low-temperature behaviour

The brittle points generally range from −90°C up to −30°C. Clash-Berg stiffness temperatures are higher, from −50°C up to −17°C.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The continuous use temperature in an unstressed state is estimated at 107°C, possibly 120°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

The modulus changes rapidly with temperature and, at 100°C, retention can be in the 32–38% range for two tested grades.

For long-term heat ageing, property retention depends on the property and grades considered, notably the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

For several grades, mechanical properties are not significantly affected by ageing at 125°C for 7 days.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties vary widely according to the grades but are generally of a fair level for the typical applications. Tensile strength ranges from 7 MPa up to 13 MPa according to the grade. Elongation at break varies between 210% and 470%.

Dimensional stability

Alterations by moisture exposure are low.

Poisson's ratio

Poisson's ratio depends on numerous parameters concerning the grade used and its processing, the temperature, the possible reinforcements, the direction of testing with regard to the molecular or reinforcement orientation. For three grades, values of 0.44 up to 0.49 are quoted.

Weathering

UV-protected MPRs are marketed to resist long outdoor exposures, especially with black coloration.

Chemicals

Generally, MPRs resist water and oils reasonably well.

Table 4.124 shows some examples of swelling after 7 days of immersion in water, oils and fuel. These examples cannot be generalized and the data cannot be used for design purposes.

Table 4.124 MPRs: examples of swelling (%) after immersion for 7 days

Chemical	Concentration (%)	Temperature (°C)	Time (days)	Swelling (%)
ASTM1 oil	100	100	7	−39 to −6
ASTM3 oil	100	100	7	12–32
Fuel B	100	23	7	11–36
Water	100	100	7	5–15

Electrical properties

MPRs are insulating and are used for low-tension wire and cable covering.

Examples of electrical properties:

- resistivity: 1.4–2.3 × 10^8
- permittivity: 9–11
- dielectric strength: 5–12 kV/mm.

Trade name examples

Alcryn.

Property tables

Table 4.125 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

4.30.7 Thermoplastic polyester elastomers (TPEE or COPE)

Thermoplastic polyester elastomers (COPEs or TPEEs) are block copolymers of:

- a polyester and a polyether, more commonly
- two polyesters, more rarely.

Rigid segments can be, for example, a semicrystalline polybutylene terephthalate, and flexible sequences can be polyesters or polyethers – polyetherglycol, for example.

Table 4.125 MPRs: examples of properties

	General-purpose grades			
Hardness (Shore)	60A	70A	75A	80A
Density (g/cm^3)	1.2	1.2	1.35	1.25
Tensile strength (MPa)	10	12	10	13
Elongation at break (%)	300	270	360	210
Stress at 100% (MPa)	3.9	5.3	5.9	7.9
Compression set, 22 h at 20°C (%)	15	15	23	15
Compression set, 22 h at 100°C (%)	55	55	67	55
Brittle point (°C)	−51	−53	−30	−44
Continuous use temperature (°C)	107	107	107	107
	Compounds for injection moulding			
Hardness (Shore)	47A	59A	68A	78A
Density (g/cm^3)	1.06	1.1	1.14–1.2	1.2
Tensile strength (MPa)	7	8	9	12
Elongation at break (%)	420	420	320–400	320
Stress at 100% (MPa)	1.9	3	4–4.2	6.2
Compression set, 22 h at 20°C (%)	15	13	14–16	14
Compression set, 22 h at 100°C (%)	56	62	64	62
Brittle point (°C)	−91	−85	−85	−86
Continuous use temperature (°C)	107	107	107	107
	Compounds for extrusion			
Hardness (Shore)	57A	70A	78A	79A
Density (g/cm^3)	1.17	1.25	1.27	1.27
Tensile strength (MPa)	8	9	11	11
Elongation at break (%)	390–440	420–440	360	380
Stress at 100% (MPa)	2.6–2.9	3.9	5.1	5.9
Compression set, 22 h at 20°C (%)	16	20–21	25	24
Compression set, 22 h at 100°C (%)	72	74–75	74	75
Brittle point (°C)	−74 to −69	−62 to −60	−54	−58
Continuous use temperature (°C)	107	107	107	107

The properties, of which hardness is often used for the denomination of the grades, vary strongly as functions of the:

- nature of the flexible segments: polyesters or polyethers
- nature of the rigid segments
- molecular weight
- length of the flexible segments
- ratio of rigid to flexible segments.

The polyester-esters were especially developed for their combination of heat ageing and UV resistances but performances can be lower versus low temperatures and hydrolysis.

COPEs are in the Shore D hardness range.

They can be reinforced with glass fibres.

Unless otherwise specified we will not make a distinction between the various subfamilies.

Advantages

COPEs are appreciated for their high mechanical performances; tenacity; excellent abrasion and tear resistances; good flex fatigue resistance; high moduli; resistance to ozone, oils and oily products; low gas permeability; fair thermal resistance for suitable grades; ease of waste recycling; broad colouring possibilities; electric insulation; good low-temperature behaviour; overmoulding adhesion to ABS, PBT, PC and metals.

Drawbacks

COPEs are handicapped by a lower elasticity than conventional rubbers, the more so the greater the hardness; certain risks of creep, relaxation and permanent set, the more so the higher the temperature; high cost; risks of hydrolysis especially for the polyester-ester types; risks of UV degradation; lack of soft grades; density; inherent flammability, but FR grades are marketed.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- injection, extrusion, blown films, blow-moulding, thermoforming, calendering, high flow . . .
- UV, hydrolysis and/or heat stabilized; improved colour and gloss retention; cold-temperature ductility and flexibility; soft touch; food contact; fireproofed; improved chemical resistance; colourable; glass fibre reinforced; antistatic grades . . .
- for automotive, wire coating, films . . .

Costs

The costs, as for all plastics, fluctuate highly with the crude oil price. COPEs are more expensive than TPOs, SBS and TPVs.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering.

Consumption and applications

(See Chapter 2 for further information.)

COPEs target technical applications in various sectors such as automotive, electrical & electronics, industry, consumer goods, packaging and construction for various moulded and extruded technical goods, soft-touch overmoulding, grips . . .

Examples:

- Automotive
  - ○ constant velocity joint (CVJ) boots, rack and pinion bellows . . .
  - ○ air ducts . . .
  - ○ air bag covers, steering wheels . . .
  - ○ airbrake tubing . . .
  - ○ damping mounts for engine hoods . . .
- E&E
  - ○ moulded electrical accessories, electrical connectors . . .
  - ○ wire and cable jacketing . . .
  - ○ low noise gears . . .
  - ○ antenna covers . . .
  - ○ keypads . . .
- Consumer goods
  - ○ sunglasses: lens bridges, rear frames and arms . . .
  - ○ lens supports for CD-players . . .

  - headphones . . .
  - suitcase handles . . .
  - bedsprings . . .
  - liquid dispensers . . .
  - grips, pencil grips . . .
  - seals for perfume bottles . . .
- Sporting goods
  - front straps for ski boots . . .
  - goggles . . .
  - snowboard cover laminates . . .
  - shoe binding system components, tensioner ski bindings . . .
  - soling . . .
  - caterpillars for snowmobiles . . .
- Industry
  - seals, gaskets, packing . . .
  - hoses and tubing, flexible tubing, hose jackets, convoluted tubing, hydraulic hoses, pneumatic tubing . . .
  - tool handles and grips for pliers, screwdrivers . . .
  - profiles . . .
  - gears, sprockets, caster wheels . . .
  - bearings, plugs, pads, feet, damping mounts . . .
  - fuel tanks, oil-field parts . . .
  - films, sheets, thin and flexible membranes, diaphragms . . .
  - roller covering . . .
  - belting . . .
- Miscellaneous
  - breathable films for medical disposables, construction, packaging . . .
  - shock-proofing casings . . .
  - handcuff holders . . .
  - railway pads . . .

Elasticity

Elasticity depends on:

- the nature of the COPE
- the ratio of soft and hard segments
- the formulation
- the actual temperature.

Compression sets after 22 h at 70°C, which are not severe conditions, for some grades with hardnesses in the Shore D scale are in the 30–50% range.

Low-temperature behaviour

The brittle points generally range from −100°C up to −55°C. Notched impact strengths are often high without break at −30°C but some grades can break with Izod values of 20 J/m.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The continuous use temperatures in an unstressed state are generally estimated at 110°C up to 135°C for the polyester-ether grades. Polyester-esters are more resistant.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

For long-term heat ageing, property retention depends on the property and grades considered, the COPE type, and the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

For some examples, half-lives based on elongation at break and/or tensile strength are:

- 20 up to 35 days at 140°C for a polyester-ether
- 6 months at 120°C for a polyester-ether
- more than 3 years at 85°C for a polyester-ether
- 50 days at 175°C for a polyester-ester
- more than 4 months at 150°C for a polyester-ester.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties are generally of a good to excellent level including abrasion, tear resistance and tensile strength.

Weathering

COPEs are naturally sensitive to light, UV and hydrolysis but special weathering-resistant grades are marketed.

The polyester-esters are more UV-resistant but more sensitive to hydrolysis.

Chemicals

Generally:

- for homologous series, chemical resistance increases with hardness
- the polyester-esters can be more sensitive to hydrolysis.

The behaviour with water depends on the grade, stabilization and the temperature. Above 50°C, special stabilization is needed.

COPEs have good resistance to non-aromatic oils and greases, and aliphatic hydrocarbons. However, the additives in high-performance oils, and fuels containing alcohol or rich in aromatic hydrocarbons can cause degradation or excessive swelling.

Their behaviour is satisfactory to unsatisfactory with dilute acids and bases. Depending on the chemicals and concentrations, behaviour is limited with esters and ketones, ethyl acetate and methylethylketone.

The resistance is generally satisfactory with alcohols.

COPEs are attacked by aromatic hydrocarbons, chlorinated solvents, concentrated acids and bases, phenols.

Table 4.126 displays some results concerning general assessments of behaviour after prolonged immersion in chemicals at the specified temperatures for given grades, which are not necessarily representative of all the COPEs. These general indications should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Permeability

COPEs are polar and semicrystalline, which leads to a certain permeability to polar substances such as water and impermeability to non-polar substances such as hydrocarbons. For homologous series, the impermeability increases with hardness.

Fire resistance

COPEs inherently burn easily, have an oxygen index of 20–22 and are compliant with a UL94 HB rating. FR grades can reach a UL94 V0 rating.

Table 4.126 COPE: examples of general assessments after prolonged immersions

Chemical	Concentration (%)	Temperature (°C)	Estimated behaviour
Acetic acid	20	20	S
Acetic acid	30	20	S
Acetic acid	96	20	S to n
Acetone	Unknown	20	l
Acetylene	100	20	S
Ammonium chloride	Solution	20	S
Amyl acetate	100	20	l
Amyl alcohol	100	20	S
Aniline	100	20	n
ASTM1 oil	100	149	S
Beer	100	20	S
Borax	Solution	20	S
Boric acid	Solution	20	S
Calcium chloride	Solution	20	S
Calcium hypochlorite	5	20	S
Carbon dioxide	Unknown	20	S
Carbon monoxide	Unknown	20	S
Chlorosulfonic acid	Unknown	20	n
Citric acid	Solution	20	S
Copper chloride	Solution	20	S
Copper sulfate	Solution	20	S
Cotton oil	100	20	S
Cyclohexane	100	20	S
Dibutylphthalate	100	20	S
Diethylsebacate	Unknown	20	S
Dioctylphthalate	100	20	S
Ethylene oxide	Unknown	20	S
Ethyleneglycol	Unknown	20	S
Formaldehyde	40	20	l
Formic acid	Unknown	20	l
Freon 11	100	20	S
Freon 113	100	20	S
Freon 114	100	20	S
Freon 12	100	20	S
Fuel B (isooctane/toluene,70/30)	100	20	S
Fuel C (isooctane/toluene,50/50)	100	20	S
Fuel JP4	100	20	S
Glue	100	20	S
Glycerol	100	20	S
Hexane	100	20	S
Hydrazine	Unknown	20	n
Hydrochloric acid	20	20	l
Hydrochloric acid	37	20	n
Hydrogen sulfide	Unknown	20	S
Hydrogen	Unknown	20	S
Isooctane (Fuel A)	100	20	S
Isopropanol	100	20	S
Mercury	100	20	S
Methanol	Unknown	20	S
Methylene chloride	100	20	n
Mineral oil	100	20	S
Naphtha	100	20	S
Nitric acid	10	20	l
Nitric acid	30	20	n
Nitric acid	60	20	n

Table 4.126 (Continued)

Chemical	Concentration (%)	Temperature (°C)	Estimated behaviour
Nitric acid	70	20	n
Nitric acid	Fuming	20	n
Nitrobenzene	100	20	n
Oleic acid	Unknown	20	S
Palmitic acid	Unknown	20	S
Petrol	100	20	S
Phenol	Unknown	20	n
Potassium hydroxide	Solution	20	S
Pydraul 312	100	20	S
Sea water	100	20	S
Silicone grease	100	20	S
Skydrol 500B	100	20	S
Soap	Solution	20	S
Sodium chloride	Solution	20	S
Sodium hydroxide	20	20	S
Sodium hydroxide	46	20	l
Sodium hypochlorite	5	20	S
Sodium phosphate	Solution	20	S
Steam	100	100	l
Steam	100	110	n
Sulfuric acid	<50	20	S
Sulfuric acid	>50	20	n
Sulfuric acid	Oleum	20	n
Tannic acid	10	20	S
Triethanolamine	Unknown	20	n
Water	100	20	l
Zinc chloride	Solution	20	S

S: satisfactory; l: limited; n: not satisfactory

Electrical properties

COPEs are insulating and are used for low-tension wire and cable covering.

Joining, decoration

Welding and joining with adhesives are possible.

All precautions must be taken concerning health and safety according to local laws and regulations.

COPE allows a large variety of colours.

Trade name examples

Arnitel, Ecdel, Hytrel, Lomod, Pibiflex.

Property tables

Table 4.127 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

4.30.8 Polyether block amides (PEBA)

Polyether block amides (PEBA) are block copolymers of:

- a polyether for the soft segments
- a polyamide for the rigid segments.

Table 4.127 COPE: examples of properties

	Compounds with Shore D < 50			
Shore D hardness	27–30	35–38	40–43	46–50
Miscellaneous properties				
Density (g/cm^3)	1.1	1.1–1.2	1.1–1.2	1.15–1.4
Shrinkage (%)	0.4	0.6–1	0.8–1	1.5–1.7
Absorption of water (%)	0.8–0.95	0.6–7	0.6–7	0.4–2.5
Mechanical properties				
Tensile strength (MPa)	16–26	10–21	14–28	12–36
Elongation at break (%)	700–900	200–850	230–600	275–800
Flexural modulus (GPa)	0.03	0.03–0.06	0.05–0.1	0.09–0.17
Notched impact strength ASTM D256 (J/m) at 20°C	NB	NB	NB	NB
Notched impact strength at −30°C (J/m)	NB	NB	NB	NB
Compression set, 22 h at 20°C (%)		29–40	52	38
Thermal properties				
HDT B (0.46 MPa) (°C)	46	46–60	50–70	55–85
HDT A (1.8 MPa) (°C)				44–48
Brittle point (°C)	−105	−60	−66 to −105	−56 to −105
Coefficient of thermal expansion (10^{-5}/°C)		15–22	16	
Electrical properties				
Volume resistivity (ohm.cm)	10^{13}	10^{12}–10^{14}	10^{11}–10^{13}	10^{13}–10^{14}
Dielectric constant	4.4	4.1–5.6	4.2–5	4.2–4.4
Loss factor (10^{-4})	50–140	10–370	60–600	70–350
Dielectric strength (kV/mm)	16	17–20	16–17	16
Fire behaviour				
Oxygen index (%)	20	20	20–21	
UL94 fire rating	HB	HB	HB	V0 to HB

	Compounds with Shore D > 50			
Shore D hardness	56–60	61–63	68–75	80–82
Miscellaneous properties				
Density (g/cm^3)	1.2–1.3	1.2–1.25	1.24–1.28	1.27
Shrinkage (%)		1.5	1.6–2	2.2
Absorption of water (%)	0.2–2.5	0.23–0.6	0.16–0.85	0.2–0.3
Mechanical properties				
Tensile strength (MPa)	22–39	30–44	37–47	48–50
Elongation at break (%)	300–700	325–600	300–480	350
Tensile modulus (GPa)	0.27	0.37	0.9	
Flexural modulus (GPa)	0.19–0.25	0.3–0.4	0.47–0.78	0.9–1.2
Notched impact strength ASTM D256 (J/m) at 20°C	250 to NB	200 to NB	4–210	4–40
Notched impact strength at −30°C (J/m)	25–150	4–50	4–40	
Thermal properties				
HDT B (0.46 MPa) (°C)	50–120	85–130	115–154	140–156
HDT A (1.8 MPa) (°C)	44–46	48–51	50–52	55
Brittle point (°C)	−60 to −98	−70 to −98		−48 to −100
Coefficient of thermal expansion (10^{-5}/°C)	11	14	9–11	
Electrical properties				
Volume resistivity (ohm.cm)	10^{13}–10^{14}	10^{14}	10^{12}–10^{16}	
Dielectric constant	3.7–4	3.8	2.9–4	
Loss factor (10^{-4})	110–400	4–350	132–360	
Dielectric strength (kV/mm)	1–18		18	
Fire behaviour				
Oxygen index (%)	20–28	21	22	
UL94 fire rating	V2 to HB	HB	HB	HB

Table 4.127 (Continued)

The following general assessments concerning the chemical behaviour at room temperature of COPEs, which are not representative of all grades of COPEs, should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Chemical resistance depends on the composition and hardness of COPEs, and are subject to the compatibility of the fillers and reinforcements with the ambient conditions. If the fillers are well adapted, the chemical properties are the same for filled and neat polymers.

Light	UV stabilizers are needed
Weak acids	Satisfactory to limited behaviour according to the nature and concentration
Strong acids	Limited to unsatisfactory behaviour according to the nature and concentration
Weak bases	Limited behaviour
Strong bases	Unsatisfactory behaviour with concentrated bases
Solvents	COPEs resist non-aromatic oils and greases, and aliphatic hydrocarbons well. However, the additives in high-performance oils, fuels containing alcohol or rich in aromatic hydrocarbons can cause degradation or excessive swelling According to the chemicals and concentrations, behaviour is limited with esters and ketones, ethyl acetate and methylethylketone Resistance is generally satisfactory versus alcohols COPEs are attacked by aromatic hydrocarbons, chlorinated solvents, concentrated acids and bases, phenols
Food contact	Possible for special grades

NB: No break

The properties, including hardness, which is often used for the denomination of the grades, vary strongly as functions of the:

- nature of the flexible segments
- nature of the rigid segments
- molecular weight
- length of the flexible segments
- ratio of rigid to flexible segments.

PEBAs can be reinforced with glass fibres.

Advantages

PEBAs are appreciated for their high mechanical performances; tenacity; good abrasion resistance; good flex fatigue resistance; broad range of hardnesses including Shore D scale and upper Shore A scale values; good low-temperature behaviour; low density; fair thermal resistance for suitable grades; ease of waste recycling; broad possibilities of colouring; electric insulation; USP class VI clearance for suitable grades.

Drawbacks

PEBAs are handicapped by a lower elasticity than conventional rubbers, the more so the greater the hardness; certain risks of creep, relaxation and permanent set, the more so the higher the temperature; high cost; risks of hydrolysis; risks of UV degradation, but special grades are marketed; lack of soft grades; inherent flammability, but FR grades are marketed; sensitivity to certain chemicals.

Special grades

They can be classified according to the type of processing, specific properties, or targeted applications:

- injection, extrusion, blown films, blow-moulding, thermoforming, calendering, powdering, high flow . . .

- UV, hydrolysis and/or heat stabilized; improved colour and gloss retention; cold-temperature ductility and flexibility; soft touch; food contact; fireproofed; improved chemical resistance; colourable; glass fibre reinforced; antistatic grades; hydrophilic . . .
- for automotive, wire coating, films, medical applications . . .

Costs

The costs, as for all plastics, fluctuate highly with the crude oil price. PEBAs are more expensive than TPOs, SBS and TPVs.

Processing

All the molten-state methods are usable but the main ones are injection, extrusion, blow-moulding, thermoforming, calendering, electrostatic powdering.

Consumption and applications

(See Chapter 2 for further information.)

PEBAs target technical applications in various sectors such as medical, automotive, electrical & electronics, industry, consumer goods, and packaging for various moulded and extruded technical goods, soft-touch overmoulding, grips . . .

Examples:

- Automotive
  - air bag covers . . .
  - airbrake hose and tubing . . .
  - damping mounts . . .
  - screen wash tubes . . .
- E&E
  - wire and cable jacketing, electrical and communication cable jacketing, coil cables . . .
  - low noise gears . . .
- Sports and leisure
  - goggles, glasses frames
  - soling, outsoles for American football, soccer, rugby, baseball footwear . . .
  - snowshoe deckings, athletics shoes and equipment . . .
  - sport balls, golf balls . . .
  - ski parts, ski boot components . . .
  - athletic footwear components . . .
  - damping systems, vibration and shock absorption in sports equipment, damping of tennis rackets . . .
- Consumer goods
  - bedsprings . . .
  - liquid dispensers . . .
  - grips, pencil grips . . .
  - seals for perfume bottles . . .
- Industry
  - hoses and tubing, flexible tubing, hose jackets, convoluted tubing, hydraulic hoses, pneumatic tubing . . .
  - profiles . . .

  - gears, sprockets, caster wheels, low noise gear wheels . . .
  - bearings, plugs, pads, feet, damping mounts . . .
  - films, sheets, thin and flexible membranes, diaphragms . . .
  - belting, conveyor belts . . .
- Medical industry
  - delivery catheters . . .
  - medical instruments . . .
  - medical bandages . . .
  - surgical garments, sheeting, mattress covers . . .
- Films
  - breathable films for medical disposables, construction, packaging . . .
- Miscellaneous
  - photocopier, printer and telephone parts . . .
  - shock-proofing casings . . .

Elasticity

Elasticity depends on:

- the nature of the PEBA
- the ratio of soft and hard segments
- the formulation
- the actual temperature.

For five samples, rebound resiliency is in the range of 56–75%.

Low-temperature behaviour

The glass transition temperature of the polyether phase is about −60°C for a subfamily of PEBA, suggesting low service temperatures of this order if stiffening is not excessive.

These results relate to some grades only and cannot be generalized.

Thermal behaviour

The UL temperature indices of specific grades can be:

- 110°C for the electrical properties alone
- 85°C up to 95°C for the electrical and mechanical properties, excluding impact strength
- 85°C up to 95°C for the electrical and mechanical properties, including impact strength.

The continuous use temperatures in an unstressed state are sometimes estimated up to 130°C.

Service temperatures are lower under loading because of modulus decay, strain, creep, relaxation . . .

For long-term heat ageing, property retention depends on the property and grades considered, the nature of the PEBA, and the heat stabilizers used. Elongation at break is an especially heat-sensitive characteristic.

For some samples, half-lives based on elongation at break are:

- nearly 3 years at 80°C
- about 3 months at 110°C.

These results relate to some grades only and cannot be generalized.

Mechanical properties

The mechanical properties are generally of a good to excellent level including abrasion and tensile strength.

Weathering

PEBAs are naturally sensitive to light, UV and hydrolysis but special grades are marketed.

Half-lives corresponding to a 50% decay of elongation at break after Xenotest exposure are roughly:

- 5 months for UV-stabilized grades with 25 to 40 Shore D hardness
- 6 months for UV-stabilized grades with 55 to 70 Shore D hardness.

Chemicals

Chemical resistance varies widely with hardness and, generally, for homologous series, increases with it.

For example, the behaviour with water and hydrocarbons depends on the grade, stabilization, immersion time and the actual temperature. According to the sources and conditions, assessments vary from satisfactory to unsatisfactory.

Consequently, the behaviour should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

Permeability

For homologous series, the impermeability increases with hardness. Special grades have a high moisture permeability.

Fire resistance

PEBAs inherently burn easily and are compliant with a UL94 HB rating. FR grades are marketed.

Electrical properties

PEBAs are insulating and are used for low-tension wire and cable covering. Some grades are antistatic.

Joining, decoration

Welding and joining with adhesives are possible.

All precautions must be taken concerning health and safety according to local laws and regulations.

PEBAs allow a large variety of colours.

Trade name examples

Grilon, Pebax, Vestamid E.

Property tables

Table 4.128 relates to examples only and cannot be generalized. The data cannot be used for design purposes.

Table 4.128 PEBA: examples of properties

Shore hardness, D	25	35	40	45–47
Shore hardness, A	75	83		
Miscellaneous properties				
Density (g/cm^3)	1.01	1.01	1–1.14	1–1.03
Shrinkage (%)			0.6–1.3	0.6–1.5
Absorption of water (%)	1.2	1.2	1–1.2	
Mechanical properties				
Stress at yield (MPa)			7–8	
Strain at yield (%)			21–25	
Tensile strength (MPa)	29	34	17–36	23
Elongation at break (%)	715	710	200–530	50–200
Tensile modulus (GPa)			0.08	0.12–0.25
Flexural modulus (GPa)	0.016	0.02	0.075–0.1	
Notched impact strength ASTM D256 (J/m) at 20°C	NB	NB	NB	NB
Notched impact strength (J/m) at −30°C	NB	NB	NB	NB
Rebound resiliency (%)	75	70	62–64	
Thermal properties				
HDT B (0.46 MPa) (°C)	42	46	45–55	45–65
HDT A (1.8 MPa) (°C)				35–45
Coefficient of thermal expansion (10^{-5}/°C)	20	21	22	17–22
Electrical properties				
Volume resistivity (ohm.cm)			10^{11}	10^{8}–10^{11}
Dielectric constant			7.5	4–10
Loss factor (10^{-4})			700–1200	300–5750
Dielectric strength (kV/mm)			35	28–37
Fire behaviour				
UL94 fire rating	HB	HB	HB	HB

Shore hardness, D	50–55	60–66	68–72
Miscellaneous properties			
Density (g/cm^3)	1–1.1	1–1.1	1.01
Shrinkage (%)		0.6–1.4	
Absorption of water (%)	1–6	1.1–6	0.9–1.5
Mechanical properties			
Stress at yield (MPa)	11–15	15	24–34
Strain at yield (%)	20–27	15–31	15–19
Tensile strength (MPa)	20–51	51–57	52–62
Elongation at break (%)	200–550	200–430	200–400
Tensile modulus (GPa)	0.17–0.23	0.3–0.5	0.75
Flexural modulus (GPa)	0.16–0.21	0.3–0.4	0.39–0.73
Notched impact strength ASTM D256 (J/m) at 20°C	NB	NB	NB
Notched impact strength (J/m) at −30°C	22 to NB	8 to NB	5 to NB
Rebound resiliency (%)	54–58	49–56	
Thermal properties			
HDT B (0.46 MPa) (°C)	62–90	60–100	99–106
HDT A (1.8 MPa) (°C)	45	45–55	45
Coefficient of thermal expansion (10^{-5}/°C)	13–20	12–20	12–16
Electrical properties			
Volume resistivity (ohm.cm)	10^{3}–10^{11}	10^{9}–10^{13}	10^{11}
Dielectric constant	5–9.5	3–10	7.4–10
Loss factor (10^{-4})	150–1100	250–1750	760–1500
Dielectric strength (kV/mm)	32–38	28–39	30
Fire behaviour			
UL94 fire rating	HB	HB	HB

NB: No break

References

Technical guides, newsletters, websites

3M, Akzo Plastics, Allied Signal, Allrim, Amcel, Amoco, Arkema, Arco Chemical, Astar, Atochem, Bakelite GmbH, BASF, Bayer, BF Goodrich, BIP, Bisco, BP Chemicals, Bryte, Ceca, Celanese, Ciba, Cray Valley, Culver City Corp, Degussa, Devcon, Dow, DSM, Du Pont de Nemours, DuPont Dow, Dynamit Nobel, Eleco, Emerson & Cumming, EMS, Enichem, Epotecny, Eval, Exxon, Ferro, Ferruzzi, FiberCote, Framet Futura, GE Plastics, GE Silicones, Hexcel, Hoechst, Hüls, ICI, Irathane, Isomeca, Kommerling, Kuraray, La Bakélite, Loctite, Lohmann, Mecelec, Menzolit, Mitsui Chemicals, Monsanto, Montedison, Naphtachimie, Neste, Nief Plastic, Nippon Gohsei, Nippon Mitsubishi, Nonacor, Norflys, Orkem, Owens Corning, Perstop, Phillips Petroleum, PPG, PRW, Raschig, Recticel, Repsol, Rhodia, Rhône Poulenc, Rohm, Schulman, Scott Bader, Shell, Sika, Sintimid, SNIA Tecnopolimeri, SNPE, Solvay, Stratime, Symalit, Synres, Synthésia, T2L, Technochemie GmbH, Telenor, Thieme, Toray, Tramico, Tubize Plastics, Tubulam, Ube, Union Carbide, Uniroyal, Vetrotex, Vyncolit, Wacker, Wilson Fiberfil, YLA. . . .

Reviews

[1] *Plastics Additives & Compounding* (Elsevier Ltd)
[2] *Modern Plastics Encyclopaedia* (McGraw-Hill Publications)
[3] *Modern Plastics International* (Canon Communications LLC, Los Angeles, CA, USA)
[4] *Reinforced Plastics* (Elsevier Ltd)

Chapter 5

Thermoplastic processing

The thermoplastics are marketed in:

- pellets, powder or pasty forms, which leads to specific processing methods
- composite forms
- semi-manufactured products such as sheets, tubes, rods. . .

Thermoplasticity opens the door to many diversified processes:

- easy moulding, extrusion and calendering
- thermoforming
- welding
- assembly and boiler-making.

Some thermoplastics, polyethylenes principally, can be crosslinked.

Figure 5.1 proposes an arbitrary classification of some of these processes.

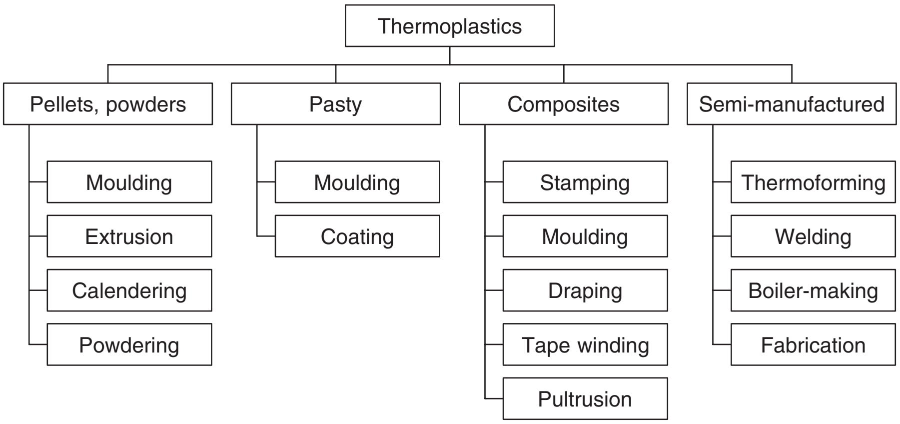


Figure 5.1. Thermoplastic processing methods

To give an idea of the importance of the various processing methods:

- the shares of the major processes employed for the most-used thermoplastic (polyethylene) are roughly:
  - ○ extrusion: 35%
  - ○ blow moulding: 35%
  - ○ injection moulding: 25%
  - ○ rotational moulding or rotomoulding: >1%
  - ○ others: 4%
- the share of thermoplastic composites (mainly PP) can be roughly estimated at a few percent of the total thermoplastic consumption
- the share of thermoplastic foams (mainly EPS but also PE, PP, PVC. . .) can be roughly estimated at a few percent of the total thermoplastic consumption
- for PVCs, the share of pastes (plastisols), excluding coatings, is roughly estimated at 2%. The other pastes are not listed in the economic statistics. The share of thermoplastic pastes can be roughly estimated at less than 1% of the total thermoplastic consumption.

5.1 Moulding thermoplastics

Injection and blow moulding are by far the most used of the moulding processes but compression is sometimes used for specific cases.

Rotomoulding is specifically used for polyethylene, plastisols and a few other powdered or pasty resins.

Slush moulding is broadly used for automotive dashboards.

Dipping and spraying onto formers are more rarely used for specific goods.

5.1.1 Injection moulding

5.1.1.1 Standard injection moulding

The softened or melted thermoplastic is forced into a mould cavity, and then cooled to solidify it and acquire its final performances. Apart from a coefficient of shrinkage and possibly warpage, the part has the shape of the cavity.

An injection-moulding machine (Figure 5.2) comprises three main parts:

- An extruder with a heating device for resin plasticizing or melting. The screw design and the temperatures depend on the injected material.

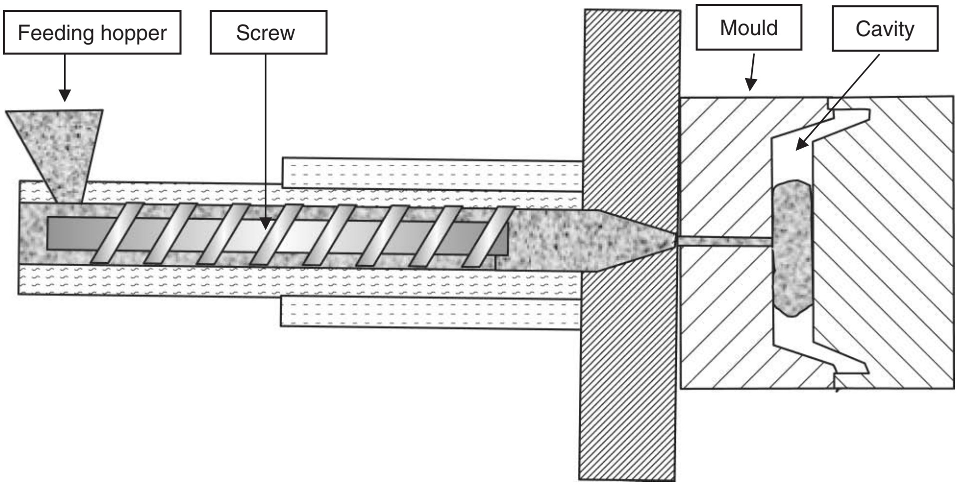


Figure 5.2. Principle of high-pressure injection moulding

- A ram system allowing introduction under high pressure of the dosed material into the mould. On some types of injection machine, the screw also acts as the ram.
- A mould with a cooling device to allow cooling of the thermoplastic, which will give part solidification and allow its release from the mould. The mould can be mono- or multi-cavity.

Figure 5.2 shows the principle of injection moulding.

Injection-moulding machines can be characterized by:

- the clamping system type
- the shot capacity
- the plasticizing capacity
- the screw sizes L/D (length/diameter)
- maximum injection pressure
- maximum mould sizes.

Tables 5.1 and 5.2 display some examples of clamping and injection unit characteristics. There are a large number of machines and these data are only examples without claiming to be exhaustive.

Table 5.1 Examples of injection unit characteristics

Screw diameter (mm)	15	18	22
Injection pressure (bar)	2600	2400	1600
Shot capacity (cm^3)	13	23	34
Screw drive (rpm)	375/470	375/470	375/470
Plasticizing rate max., PS (g/s)	2	4	7
Screw diameter (mm)	25	30	35
Injection pressure (bar)	2500	2000	1500
Shot capacity (cm^3)	50	75	100
Screw drive (rpm)	480	480	480
Plasticizing rate max., PS (g/s)	12	18	24
Screw diameter (mm)	50	60	70
Injection pressure (bar)	1900	2400	1800
Shot capacity (cm^3)	380	770	1050
Screw drive (rpm)	330–450	200–300	200–300
Plasticizing rate max., PS (g/s)	35–45	50–70	70–100
Screw diameter (mm)	80	90	100
Injection pressure (bar)	2200	1750	1400
Shot capacity (cm^3)	1500	2000	2400
Screw drive (rpm)	200/280	200/280	200/280
Plasticizing rate max., PS (g/s)	100–150	130–190	160–230
Screw diameter (mm)	135	150	230
Injection pressure (bar)	1800	1500	1700
Shot capacity (cm^3)	10 000	12 000	38 000
Screw drive (rpm)	80–110	80–110	65
Plasticizing rate max., PS (g/s)	190–260	250–350	580

Table 5.2 Example of clamping unit characteristics

Clamping force (kN)	300–500	650–800	1100
Size of mould platens (mm)	540 × 540	600 × 600	850 × 875
Mould height min. (mm)	200	250	250
Clamping force (kN)	1800	2800	3800
Size of mould platens (mm)	900 × 900	1000 × 1000	1300 × 1200
Mould height min. (mm)	350	330	380
Clamping force (kN)	4000	20 000	40 000
Size of mould platens (mm)	2000 × 1800	2600 × 2300	3300 × 2900
Mould height min. (mm)	700	1000	1100
Mould height max. (mm)		1700	2000
Clamping force (kN)	54 000		
Size of mould platens (mm)	3800 × 3200		
Mould height min. (mm)	1400		
Mould height max. (mm)	2300		

Injection moulding:

- permits total automation of the process and high output rates
- has the highest mould and press prices
- has the cheapest labour costs
- is suited for mass production. For standard mass production parts it is the cheapest process
- normally, the whole surface of the part has a good finish, which removes the need for finishing operations
- the optimization of the moulding parameters can be difficult; part warpage and shrinkage are sometimes difficult to predict
- apart from particular cases of resins filled with fibres and other acicular or lamellar fillers, the parts are isotropic if there are no residual constraints
- the part sizes are limited by the mould size and the machinery performances
- shot capacities cover a large range: for example, a few grammes up to more than 100 kg
- over-moulding and co-moulding can be used.

Some basic rules for part design

The following rules are some of the basic ones and are not sufficient to optimize the design, which should be discussed with the producer of the chosen thermoplastic and the moulder. These rules can be modified according to the actual problems.

- Remember that there is always shrinkage after moulding and the part is smaller than the cavity of the mould.
- Design parts to ease demoulding by forecasting sufficient draft if the material does not support stretching. Draft angles are commonly in a range of 0.5–1° but can be reduced for small and flat parts (to 0.2°, for example) or increased for deep parts (2° or 3°, for example). A lack of draft requires building special expensive moulds with movable tool parts.
- Thickness:
  - ○ Minimize wall thickness variations throughout the part. That reduces warpage, sinking and residual stresses to the minimum. The mould is easier to fill and the cycles are shorter. However, it is necessary to consider that cooling in the mould is faster and, for a long path, the thermoplastic flow can solidify before full filling of the mould cavity.
  - ○ Compute the least thickness according to the mechanical performances of the chosen material processed with the chosen method and corrected by safety margins to satisfy regulations, specifications, etc.

    High thickness favours sinking, warpage and shrinkage, porosity and voids. Designing ribs or gussets can reduce wall thickness.

    Generally, injection-moulded parts have wall thicknesses in the range from 1 mm to 4 mm. This range can be enlarged to 0.3–10 mm using particular processing conditions. At the moment, there is a trend to develop high-flow grades to favour the injection of long and thin parts.
- Design parts to improve mechanical performances:
  - ○ Prohibit sharp angles that provide obstacles to the material flow and favour the concentration of constraints in the case of impact. Use a large radius for all corners connecting two different walls. The inside corner radius should be at least equal to one of the two related wall thicknesses.
  - ○ Minimize wall thickness variations and, if unavoidable, use a large radius and/or low slope (3 to 1 for example) to link the two portions of different thicknesses.

  - Avoid thick walls using ribs or gussets to achieve the same mechanical performances and cutting part weight, material cost, and shortening cycle times.
  - Long parts can be divided, notched, split . . . to avoid warpage.
- In mould design, flow balance avoids warpage.
- Inserts can be incorporated into the mould before injection or placed after demoulding into a moulded hole. For neat resins, the first solution is generally avoided because of the big difference between the coefficients of thermal expansion of metals and plastics. In both cases, inserts and embossing must obey some general rules. Among these, some, but not all, are recalled below:
  - Holes must be located as far as possible from the edges and welded lines.
  - The material thickness around the insert must be sufficient, of the same order as the wall thickness.
  - Sizes of holes and inserts must be calculated according to the suppliers' instructions.
  - The insert metal must be compatible with the chosen plastic material. For example, polyamide absorbs moisture, which leads to steel rusting; copper is a catalyst for oxidation of polyolefins; zinc, aluminium and brass are not compatible with polyacetals . . .
  - The insert shape should favour its mechanical anchorage: faces, flat sides, grooves, milling . . . However, sharp angles initiate cracks and the geometric anchors must be located as far as possible from the surface.

Injection moulding leads to the best part tolerances but plastics differ because of their morphology, structure, rheology, etc. The geometry of a part and the complexity of the corresponding mould vary. Consequently, the tolerances of a part depend on:

- polymer type – generally, amorphous plastics filled with isotropic fillers lead to tight tolerances
- part geometry
- processing concerns such as temperature, pressure, demoulding constraints, storage conditions . . .
- acceptable cost.

Table 5.3, as an example, displays thermoplastic part tolerances for the 'normal' and 'precision' classes as defined by the NF-T58000 standard.

Table 5.3 Examples of part tolerances for normal and precision classes

	Size	Tolerance class	
	(mm)	Normal	Precision
		(± mm)	(± mm)
Filled or neat ABS, amorphous PA, PC, PESU, amorphous PET,	10	0.20	0.07
PMMA, PPO, PS, PSU, rigid PVC, SB, SAN.	100	0.50	0.20
Filled PA 6, 66, 6/10, 11, 12. PBT, PET, POM, PPS.	1000	2.90	1.25
Neat CA, CAB, CAP, PA 6, 66, 6/10, 11, 12. Crystalline PBT,	10	0.20	0.09
PET, POM(< 150 mm), EPDM modified PP. Filled ETFE, PP,	100	0.60	0.29
plasticized PVC Shore D> 50. High hardness PEBA, COPE, TPU.	1000	4.40	1.90
Neat ETFE, FEP, PE, PFA, PP, plasticized PVC Shore D< 50.	10	0.20	0.11
TPE hardness Shore D< 50.	100	0.87	0.41
	1000	6.50	2.90

5.1.1.2 Injection micro-moulding

Telecommunications, the watch industry, medical applications, and the automotive and chemical industries are asking for smaller and smaller parts and components made of plastic. Standard injection machines are unsuitable for micro-parts. Here we describe, without claiming to be exhaustive, two examples of special machinery developed by Battenfeld and Medical Murray.

Battenfeld's MicroSystem technology

The system incorporates a screw and a ram of small diameters with a reduced shot capacity:

Screw diameter	**14 mm**
Injection pressure	2500 bar
Injection ram	5 mm
Shot capacity	1.1 cm^3
Screw drive	300 rpm
Clamping force	**50 kN**
Size of mould platens	196 × 156 mm
Mould height min.	100 mm

This machine is suitable for moulding latches and rotors for the watch industry, bearing caps for medical application, and locking wheels for micro-mechanics weighing 0.003 g to 0.02 g.

The Sesame injection machine

Built by Medical Murray, it is made of two rams of small diameter with a reduced shot capacity:

- one of 10 mm diameter moving in a heated chamber to plasticize a small quantity of polymer, as little as one pellet, and push it into an injection chamber
- the other is a needle of 1–3.5 mm diameter to inject the metered quantity of polymer into the mould.

Plasticizing plunger diameter	**10 mm**
Injection pressure	2000–3500 bar
Injection ram	1–3.5 mm
Shot capacity	0.08–0.6 cm^3
Clamping force	**4–17 kN**
Size of mould platens	95 × 90 mm
Mould height min.	82 mm

Basic price is roughly US$60 000.

5.1.1.3 Co-injection, over-moulding

Co-injection and over-moulding involve several processing options:

- Overmoulding of a thermoplastic onto a previously produced part.
- Injection of several materials side by side in the same mould. This is the process used to produce taillights. The thermoplastics must be compatible. It is possible to use moulds with moving parts and inject the materials successively, or use simple moulds and simultaneously inject the materials (Figure 5.3).

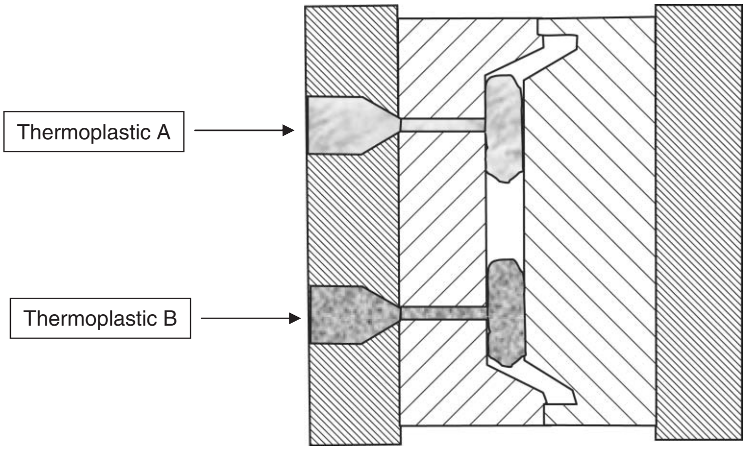


Figure 5.3. Principle of simultaneous co-injection moulding

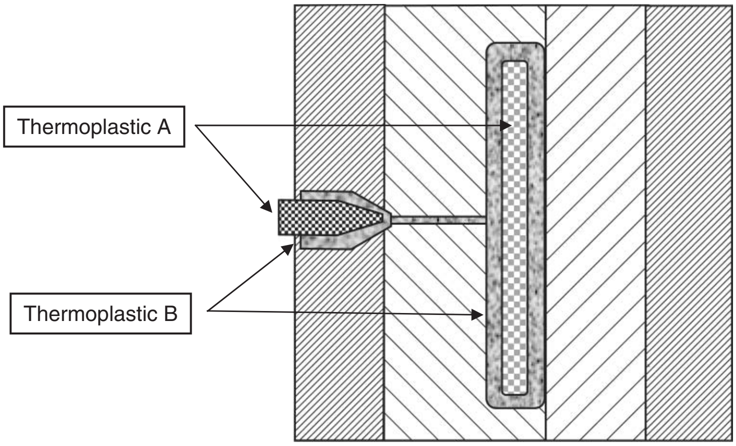


Figure 5.4. Principle of co-injection of core and skin

- Co-injection of a core and a skin of two different thermoplastics. The core can be any thermoplastic, a foam or a recycled material. The thermoplastics must be compatible. Figure 5.4 shows a schematic example.

5.1.1.4 Gas-assisted injection moulding

Gas-assisted injection moulding is a variant of injection moulding suitable for producing parts with internal cavities or hollow parts. It is used for the manufacture of products such as household appliances and automobile parts.

Apart from the injection step itself, which is identical to common injection moulding, there are three steps for mould filling and gas introduction:

- The mould is partially filled with the melted thermoplastic.
- Gas is injected into the material through a specialized nozzle. The plastic in contact with the mould is colder and therefore stronger; thus the gas stays in the core of the plastic and presses it against the wall cavity.
- The pressure is maintained until the part is cold and solidified.
- At the end of the cycle, the gas is vented prior to the mould opening.

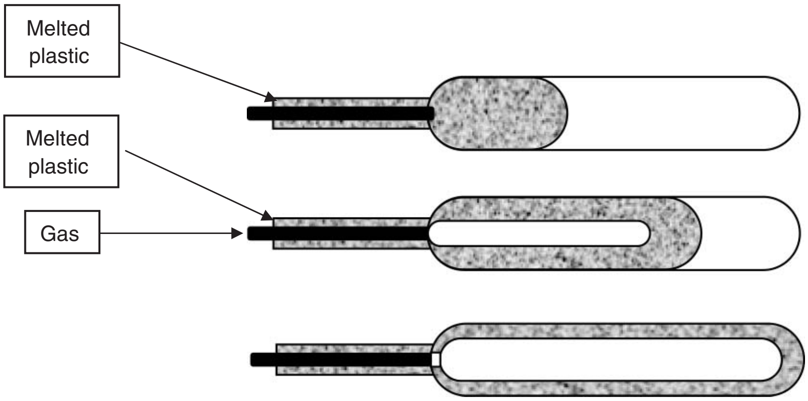


Figure 5.5. Principle of gas assisted injection moulding

Figure 5.5 schematizes the principle of gas-assisted injection moulding.
Adding to the advantages of injection are:

- weight and material savings for the same volume
- cost cutting
- sink mark reduction
- less residual stresses.

On the other hand:

- the technique is less widespread
- the machinery is specialized.

5.1.2 Blow moulding

Plastic bottles, milk or cream cartons, oil cans and other hollow containers can be produced by blow moulding.

The principle (Figure 5.6) is to produce a preform or parison by extrusion or injection, and then to blow it into a cooled mould to obtain the final hollow recipient. There are four steps:

- fabrication of the parison
- closure of the moulds
- blowing
- demoulding.

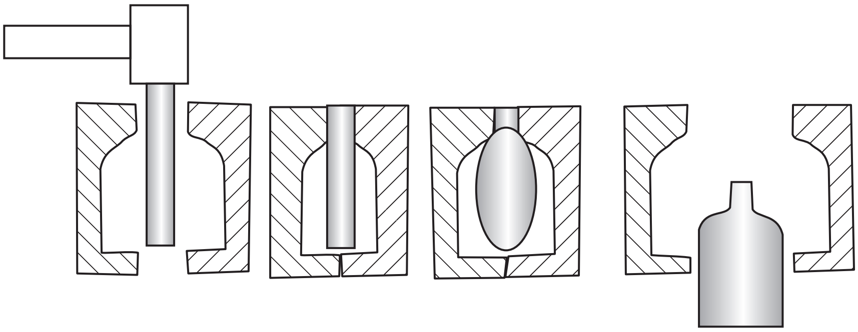


Figure 5.6. Schematic principle of the blow-moulding process

Several versions of blow moulding are used:

- Extrusion blow moulding (the simplest), in which the parison is an extruded tube that is blown with air. Various types of machinery are marketed: shuttle, reciprocating and wheel machines.
- Injection blow moulding, in which the parison is injected into a first mould and then blown in a second mould having the shape of the final recipient. This process is more expensive and the cycle time is a longer. The aspect and dimensional quality are better compared to extrusion blow moulding.
- Injection stretch blow moulding in which all the operations are performed on the same line. The preform is stretched with a 'stretch rod'. Stretching improves the mechanical performances and allows the production of thinner walled bottles.
- Reheat and blow moulding in which parisons are bought from an external furnisher and are blown on an in-house machine.

Among the plastics suitable for blow moulding are polyethylenes, polypropylenes, polyacrylonitrile, thermoplastic polyesters, polycarbonates . . .

The containers often have capacities in the range from 250 cm^3 to 25 litres and can:

- integrate a handle
- be multilayer.

The output can range from, for example, 20 units per hour to more than 5000 units per hour.

5.1.3 Compression moulding

Compression moulding of thermoplastics comprises at least two steps:

- The required quantity of thermoplastic is compressed at high pressure into the hot cavity space between the two parts of the heated mould.
- When the thermoplastic is softened and shaped, the mould is cooled to solidify the material and allow demoulding.

This process is only used for special cases because of the long time needed to heat and then cool the thermoplastic parts before demoulding.

Figure 5.7 shows the principle of compression moulding with:

- the matrix, attached to the lower plate of the press
- the stamp, fixed to the upper plate of the press.

The contact with the hot mould plasticizes the material, which, by the pressure applied, takes the form of the cavity. The cooling of the mould leads to part solidification and allows demoulding.

Certain additional operations can be necessary:

- possible drying of the resin before moulding
- feeding with blanks to ease moulding
- finishing and deflashing of the parts.

The heat-insulating properties of polymers cause some problems: in the first phase of moulding, the hot temperature of the mould is transmitted slowly within the thermoplastic. If the part is rather thick, the softening and shaping of the core is very long. There is the same drawback for the cooling phase.

Compression moulding:

- yields very low output rates
- needs few investments: the mould and press are relatively inexpensive
- needs high labour costs

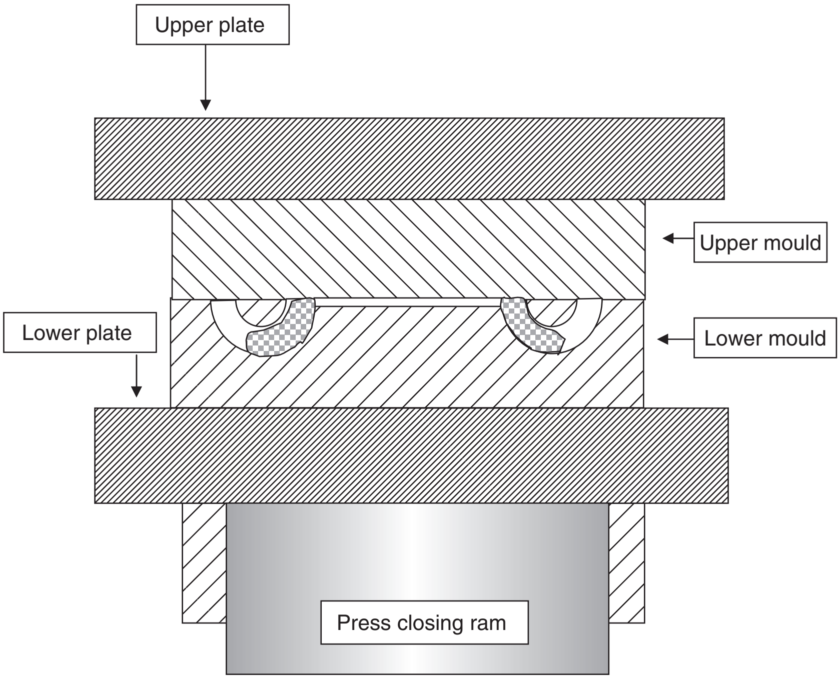


Figure 5.7. Principle of compression moulding

- is consequently suited for small outputs
- risks inducing voids and internal stresses if some air cannot escape
- does not adapt well to the use of inserts
- often needs a finishing step.

5.1.4 Rotational moulding or rotomoulding

The centrifugal force induced by the rotation of the mould is used to splash the resin onto the inner surface of the mould.

In principle:

- the right amount of the compounded resin is filled into the closed mould, which is possibly pre-heated
- the mould is rotated uni- or bi-axially, possibly in an oven to gel (PVC) or melt (polyethylene) the thermoplastic.
- Then, the mould is cooled and the part is demoulded.

Figure 5.8 shows the principle of the rotational moulding of a cylindrical tank.

This process is suitable for:

- liquid or pasty thermoplastics such as plastisols (pasty soft PVC) and liquid polyamide
- powders such as polyethylene, polyamide, PVC, polycarbonate . . .

Advantages of the process:

- convenient equally for the production of small parts and giant ones, such as tanks of more than 75 000 litres capacity
- products are essentially stress-free and there are no weld lines
- the external part face is generally smooth with good surface details

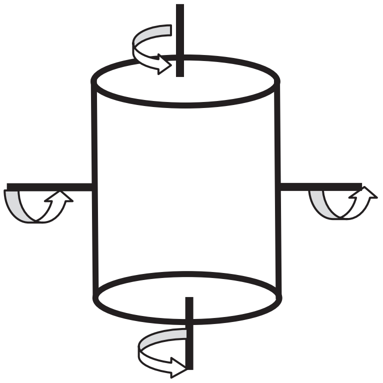


Figure 5.8. Principle of the rotational moulding of a cylindrical tank

- the mould and tool costs are rather moderate
- the investments are reasonable
- the process is convenient for short and medium production runs.

Disadvantages of the process:

- discontinuity
- the choice of resins is limited
- relatively slow
- fabrication of thin parts is difficult
- for the powdered thermoplastics, mechanical performances can be weaker than those of injected materials because of the lack of shear and pressure, which reduces the interpenetration of grains of the powder and decreases the material cohesion
- finishing is often essential
- the labour costs are high.

5.1.5 Slush moulding

A powdered dry-blend of plasticized PVC is introduced into a hot mould for an appropriately adjusted time to obtain a consistent wall thickness of gelled PVC. The dry-blend excess is removed and then the mould is cooled to strengthen the moulded part.

This process is used for the production of dashboards and skins for consoles, door trims and glove boxes for the automotive industry.

Slush moulding is also suitable for other polymer powders such as TPU or for polymer liquids.

5.1.6 Casting

This process, commonly used with thermosets, is sometimes used for specific thermoplastics such as monomers or pre-polymers of PMMA or polyamide (Nyrim). For the latter, a mix is made just before casting with:

- a pre-polymer dissolved in caprolactam
- a catalyst dissolved in caprolactam.

The liquid monomer or the liquid mix is cast by simple gravity without pressure in the open or closed mould, possibly containing a reinforcement.

For batch processes, it can be necessary to deaerate the entrapped air.

The main advantages and drawbacks of simple liquid resin casting in an open or closed mould are:

- the part sizes are limited by the mould size
- reinforcements can be arranged in the mould before casting
- performances can be increased because of a high molecular weight
- the parts are isotropic with neat resin or with isotropic reinforcements
- polymerization can be too highly exothermic and too high a temperature can lead to internal stresses
- shrinkage can be very high, sometimes of the order of 20% in volume
- the aspect is finished for one part surface for open moulding; for the whole part surface for closed moulding
- a finishing step is often essential
- the moulds are cheap and there is no press
- the labour costs are high
- the output rates are low
- the process is suited for small and medium outputs.

5.1.7 RIM

Reaction injection moulding (RIM), commonly used with thermosets, is sometimes used for specific thermoplastics such as Nyrim. Nyrim is supplied in two parts:

- a pre-polymer that is dissolved in caprolactam
- a catalyst that is dissolved in caprolactam.

An injection unit doses and mixes the monomer and catalyst. The mix is discharged under pressure, through an injection cone, into the closed mould. The injection pressure is not negligible and the moulds must be rather rigid and resistant. The precision of the cavity and the quality of its surfaces govern the precision and finish of the parts.

In alternative methods:

- RRIM – reinforced reaction injection moulding – the resin is reinforced with short fibres
- SRIM or SRRIM – structural (reinforced) reaction injection moulding – mats or fabrics are placed in the mould before injection of the resin, possibly reinforced with short glass fibres.

The main advantages and drawbacks of the low-pressure RIM or RRIM processes are:

- the limited part sizes according to the mould size
- the possibility to arrange the reinforcements in the mould before injection
- the isotropy of the parts with neat resin or isotropic reinforcements
- the excellent aspect quality for the whole part surface
- the necessity to have pressure-resistant moulds
- the investment in a press and mixing/injection unit
- the moderate labour costs
- the suitability for medium range outputs.

Figure 5.9 shows the principle of RIM. In the case of Nyrim:

- Part A is the pre-polymer dissolved in caprolactam
- Part B is the catalyst dissolved in caprolactam.

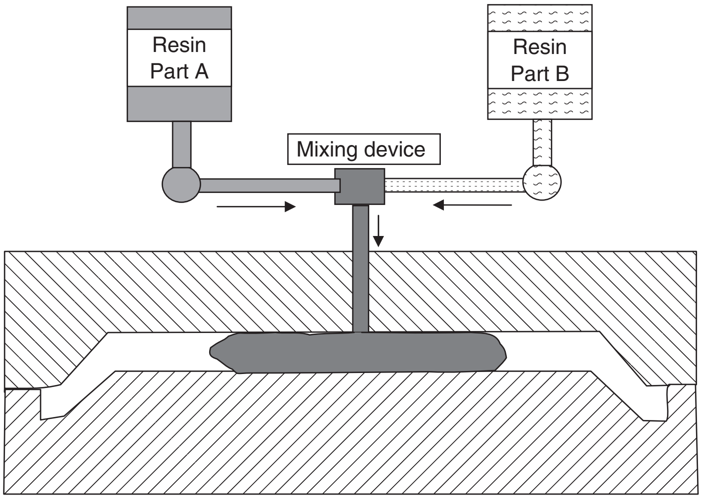


Figure 5.9. Principle of RIM (resin injection moulding)

5.1.8 Dipping

A former having roughly the shape of the article to be moulded is immersed in a suitable liquid compound that forms a deposit onto the former, which is possibly heated to ease the increase in thickness of the deposit. The former can be first sheathed with a knitted fabric to reinforce the dipped polymer. This process is used in special cases:

- to produce PVC gloves dipped in plastisol
- to coat articles.

The main advantages and drawbacks of dipping onto a former are:

- the part sizes are limited by the former size and the dipping bath size. Reinforcements can be arranged onto the former before dipping
- thickness is difficult to control
- the parts are isotropic with neat resin
- the aspect can be poor
- a finishing step is often essential
- the formers are cheap but the machinery can be expensive for high output
- the process is difficult to industrialize
- the workers must be skilled and labour costs are high for the simplest machines
- the output rates are low to medium according to the sophistication of the machinery.

5.1.9 Spraying

A solution of the polymer is sprayed onto a former that has roughly the shape of the article to be moulded. After drying the polymer is demoulded.

This process is used in very special cases to produce, for example, bellows made out of polyurethane. All precautions must be taken concerning health and safety according to local laws and regulations.

The main advantages and drawbacks of spraying onto a former are:

- the part sizes are limited only by the former size. It is possible to fabricate long bellows with specific shapes

- thickness is difficult to control
- material losses are high
- reinforcements can be arranged onto the former before spraying
- the parts are isotropic with neat resin
- shrinkage can be very high
- the aspect can be poor
- a finishing step is often essential
- the formers are cheap and the only other investment is a spraying device
- the workers must be skilled and labour costs are high
- the output rates are low.

5.2 Extrusion and connected processes

5.2.1 Extrusion

Extrusion is the shaping of a plastic by pushing the plasticized or melted material through a die, and possibly a punch forming an air gap, having roughly the form of the final section of the profile.

The total of the necessary equipment constitutes an extrusion line, which includes:

- the extruder (Figure 5.10) – generally with a screw rotating in a barrel – which pushes, heats, plasticizes, homogenizes and pressurizes the material in the barrel before it passes through the die

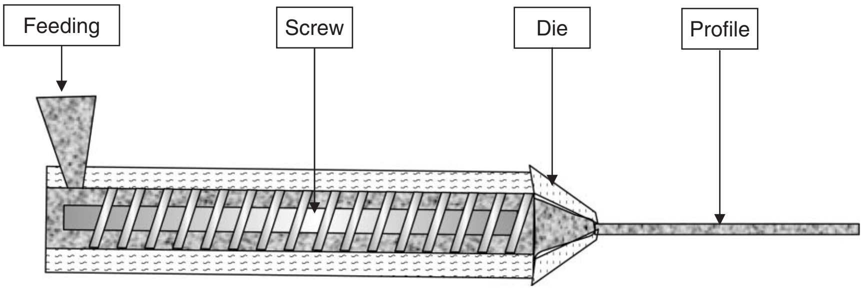


Figure 5.10. Principle of extrusion

- the die and possibly the punch or internal mandrel (Figure 5.11), which will give the desired form to the material flow
- the calibrator and cooling fixtures that precisely and permanently define the shape of the profile
- the cooling device, which cools the profile to strengthen it

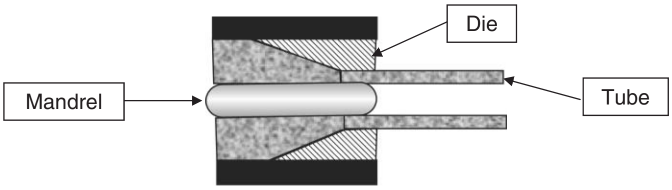


Figure 5.11. Die and internal mandrel for tube extrusion

- ancillary equipment including:
  - the pulling device, which ensures the drive of the cooled section
  - the metering and cutting devices, the marking machines.

Figures 5.10 and 5.11 show the principle of extrusion.

Extruders are used:

- to extrude profiles, tubes, films, sheets . . .
- for wire coating
- for direct compounding and extrusion in a single step
- for compounding, which is outside the framework of this chapter.

Generally:

- the output is medium or high, varying from kg/h to tonnes/h, for example 10 kg/h to 1500 kg/h
- the section sizes are limited by the die size and/or the machinery size. The length is unlimited
- arrangements of reinforcements are limited
- the parts are often anisotropic. Properties are different in the processing and transverse directions
- the aspect is correct for the outer surface but cuts are rough
- several extruders can be arranged to fabricate multi-material profiles
- the cost of the tools and machinery depends on its sophistication. Each tool is appropriate for a single section. Universal screws are not always appropriate and some profiles or materials need special screws or special extruders.

There are multiple types of extruders that can be:

- single-screw, commonly used to extrude profiles
- multiple-screw, used preferably:
  - for direct compounding and extrusion of the profile in a single step
  - extrusion of specific compounds such as wood-fibre composites
  - compounding.

Extruders are characterized, among other parameters, by:

- Output, which depends on the extruded compound. For example, for given compounds extruded with a given extruder, the linked outputs (base 100 for PVC) can roughly be estimated as:

○ PVC	100 (base)
○ polypropylene, TPE	100
○ HDPE, HIPS	130
○ ABS	145
○ alloy	170

- Power: driving and heating/cooling energy
- Screw design:
  - diameter (D)
  - length (L)
  - L/D ratio
  - shape, for example: standard, single-stage; increasing or decreasing pitch; double flighted; two-stage vented . . .
- Barrel zones: number and heating capacity.

Table 5.4 displays some examples, without claiming to be exhaustive.

Table 5.4 Examples of extruder characteristics

Output (kg/h)	Single-screw extruders		
	100 ± 50	200 ± 100	300 ± 100
Screw diameter (mm)	45	60	75
L/D ratio	30	30	30
Screw speed (rpm)	330	230	180
Barrel zones	4	4	4
Drive power (kW)	55	100	140
Heating power (kW)	5	10	20
Output (kg/h)		400 ± 100	
Screw diameter (mm)		90	125
L/D ratio		30	30
Screw speed (rpm)		140	140
Barrel zones		4	4
Drive power (kW)		180	280
Heating power (kW)		25	35
	Twin-screw extruders		
Output (kg/h)	120	240	350
Screw diameter (mm)	50	75	90
L/D ratio	21	26	26
Screw speed (rpm)	40	30	25
Heating/cooling barrel zones	4/3	6/4	6/4
Drive power (kW)	25	32	43
Heating power (kW)	13	20	45
Output (kg/h)	500	700	1200
Screw diameter (mm)	110	130	160
L/D ratio	26	26	26
Screw speed (rpm)	20	18	17
Heating/cooling barrel zones	6/4	6/4	6/4
Drive power (kW)	70	95	170
Heating power (kW)	70	90	1270

Various processes are connected to extrusion:

- blown film extrusion: an extruded sheath is blown with air at the exit of the die to form a giant bubble of film
- extrusion-laminating: an extruded film is coated onto a continuous substrate of paper, metal, fabric or other plastic
- extrusion-coating: electrical wires passing through the die are coated with the thermoplastic
- extrusion-calendering: an extruder feeds a simplified calendar that produces a sheet.

Profile design

The profile may be designed in close cooperation with the producer of the chosen thermoplastic and the specialists at the extrusion company. However, the following rules are some of the basic ones. They can be modified according to the actual problems.

- Thickness:
  - Minimize wall thickness variations throughout the profile. That reduces warpage, sinking and residual stresses to the minimum.
  - Compute the least thickness according to the mechanical performances of the chosen material processed with the chosen method and corrected by safety margins to satisfy regulations, specifications, etc.

  - High thickness favours sinking, warpage and shrinkage, porosity and voids, and increases the cooling time. Designing ribs can reduce wall thickness.
  - Generally, extruded profiles have wall thicknesses in a range from 0.8 mm to 3 mm.
- Design parts to improve mechanical performances:
  - Prohibit sharp angles that provide obstacles to the material flow and favour the concentration of constraints in the case of impact. Use a large radius for all corners connecting two different walls.
  - Minimize the wall thickness variations and, if unavoidable, use a large radius or progressive slope to link the two portions of different thicknesses.
  - Avoid thick walls using ribs to achieve the same mechanical performances and cutting weight, material cost, and shortening cycle times.
  - Ribs and partitions: used to increase rigidity, they can be only in the machine direction. Their shrinkage during cooling can involve longitudinal shrink marks on the opposite surface. If that is not acceptable from an aesthetic point of view, one can voluntarily draw a groove at this place to dissimulate the default. But thus, dies, calibrators and cooling fixtures are more complex and expensive.
- Tolerances: the processing cost increases with the tolerance requirements. Not all dimensions are so easily controlled and one can distinguish three tolerance classes; the tolerance also depends on the thicknesses:
  - A: easily controlled tolerances, for example, 0.3–0.8 mm for a PVC profile with three chambers.
  - B: difficult to control, for example, 0.45–1.2 mm.
  - C: very difficult to control, for example 0.6–2 mm.
  - For a thickness, e, tolerances are of the order of: $\pm 0.1 \times e$ mm up to $e = 1$ mm; $\pm 0.03 \times e + 0.1$ mm for $e > 1$ mm.

Each profile model needs its die, mandrel, calibrators and cooling fixtures whose cost is charged on each run. Consequently, the costs of the profiles depend on:

- material
- section area
- complexity of the section
- tolerances
- quantity produced for a run.

For example, the cost per volume of the same profile indexed on the cost of a PVC profile can be roughly estimated as follows, but prices can differ from these examples according to the actual circumstances:

PVC, LDPE, HDPE, PP, PS	100
ABS	130
PMMA	140
CA, CAB	170
PC	190

5.2.2 Blown film extrusion

This technique is commonly used to produce films of polyolefins for packaging and other applications, competing with cast and calendered films. The thickness is commonly in the 20–500 μm range but more rarely can be in the 10–800 μm range.

The principle is:

- to extrude a sheath
- to blow air (at a convenient pressure) from the centre of the die to form a giant bubble of film between the die and a pair of nip rolls that close the bubble. The bubble diameter is up to four times the diameter of the die. The film is also stretched in the machine direction by accelerating the nip rolls
- to cool the upper part of the bubble and to flatten it before passing between the nip rolls
- to wind up the cold film.

Figure 5.12 displays a diagram of a blown film extrusion line.

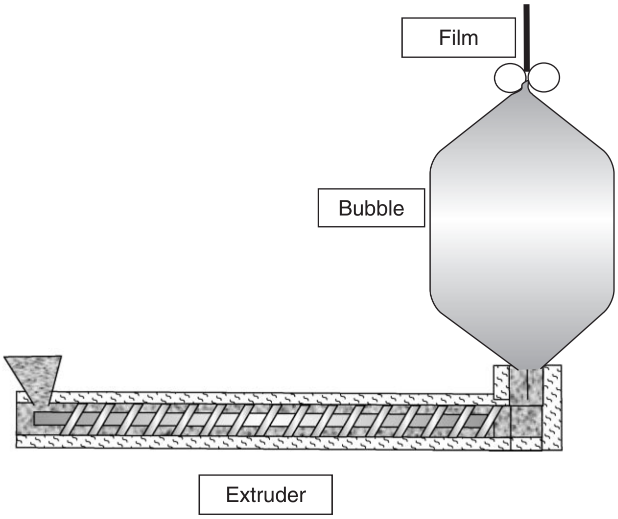


Figure 5.12. Principle of blown film extrusion

The blowing of films is used:

- to process polyethylenes and copolymers, and more rarely polypropylene, polyamide, PETG . . .
- for packaging, stretch films, agricultural films, geomembranes . . .

Multilayer films, generally with three layers but more rarely up to nine layers, are obtainable with a sufficient number of extruders.

Generally:

- the output is medium or high, for example 500 kg/h
- the section sizes are limited by the machinery size. The length is unlimited
- there are no reinforcements
- the final cost is lower than those of calendered or cast films
- the biorientation of the films lead to superior mechanical performances
- the films are often anisotropic. Properties are different in the processing and transverse directions because of the difference in stretching between the two directions
- the aspect is correct
- several extruders can be arranged to fabricate multi-material films
- the cost of the machinery is lesser than that of calendering.

5.3 Calendering

This technique is commonly used to produce sheets and films of PVC and more rarely ABS and EVA. The minimum thickness is commonly of the order of 25 μm.

The principle is:

- to soften or melt the thermoplastic by extrusion
- to laminate the softened or melted thermoplastic between counter-rotating steel rolls to obtain a film or sheet of constant thickness. The thicknesses are in the 80–800 μm range before stretching and 25 μm and more after stretching
- to cool the polymer to strengthen it.

The number of rolls, their sizes and their configuration characterize the calender. Some possibilities are indicated below, without claiming to be exhaustive:

- 3–7 rolls
- 400–900 mm in diameter
- 1800–3000 mm length
- I, L, F, Z . . . configuration.

The calender is included in a calendering line (see Figure 5.13) made up of:

- a feeding device, for example, an extruder and a conveyor belt
- the calender
- a pick-up device with multiple rolls
- post-processing devices for stretching, cooling and winding.

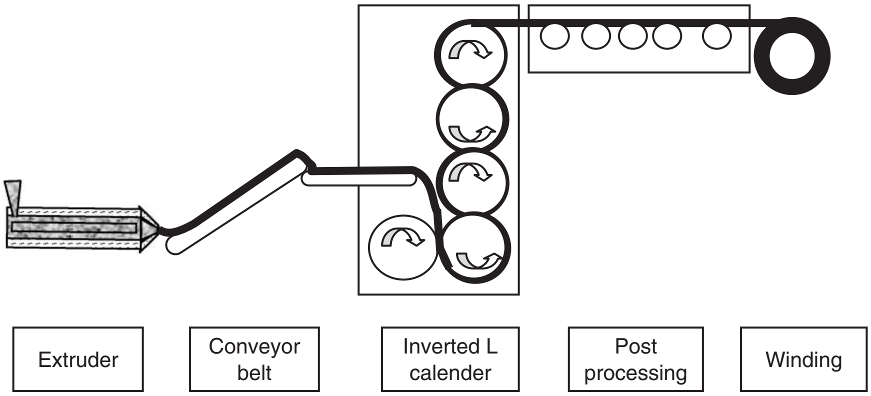


Figure 5.13. Principle of a calendering line with a five-roll calender

Generally:

- Calenders are very expensive and specialized machinery that are only used for high-output productions.
- The section sizes are limited by the roll sizes. The widths are in the 1800–3000 mm range.
- It is necessary to cut the edges.
- The length is practically unlimited.
- Arrangements of reinforcements are limited. It is only possible to calender thermoplastics onto fabrics to obtain a reinforcing effect.
- It is possible to calender two different thermoplastics to fabricate a two-layer article.

- The films and sheets are often anisotropic. Properties are different in the processing and transverse directions. Stretching enhances the performances in the machine direction.
- The aspect is correct.

5.4 Coating

5.4.1 Extrusion coating

This technique is commonly used for wire and cable coating.

The principle is to:

- soften or melt the thermoplastic in an extruder
- direct the melt flow into a crosshead perpendicular to the screw
- insert the wire into the crosshead where it is coated by the molten thermoplastic before coming out through the die
- pull the coated wire, cool and wind it.

Figure 5.14 displays the principle of a wire extrusion-coating line.

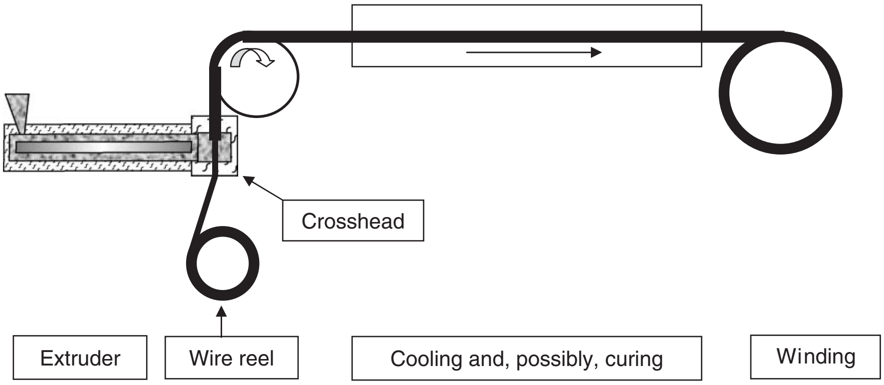


Figure 5.14. Principle of a wire extrusion-coating line

Generally:

- the output is high, for example 1500–3000 m/min
- the length is unlimited
- there are no reinforcements but the wire itself leads to good mechanical properties
- the final cost is low
- the aspect is correct.

Sometimes the thermoplastics, especially polyethylenes, can be cured. In this case, it is necessary to include a curing device in the line and:

- the output decreases
- investments are higher
- the final cost increases
- mechanical and chemical performances are enhanced.

5.4.2 Roll dipping, spreading

These methods process liquid thermoplastics, which are often obtained by dissolving the polymer in solvents. Consequently, it is necessary to obey all health, safety and environmental precautions and regulations.

Discontinuous coating by dipping in a bath of liquid thermoplastic is very similar to moulding by dipping as used for PVC gloves (see Section 5.1.8 above). Wire articles, for example, can be coated with PVC to protect them and obtain a softer touch.

Continuous coating can be obtained by roll coating or spreading. There are three main versions:

- direct dipping in a bath of the liquid thermoplastic
- indirect coating by contact with a spreading roller partially immersed in the dipping bath
- spreading machine.

Figures 5.15 and 5.16 display examples of direct and indirect roll dipping.

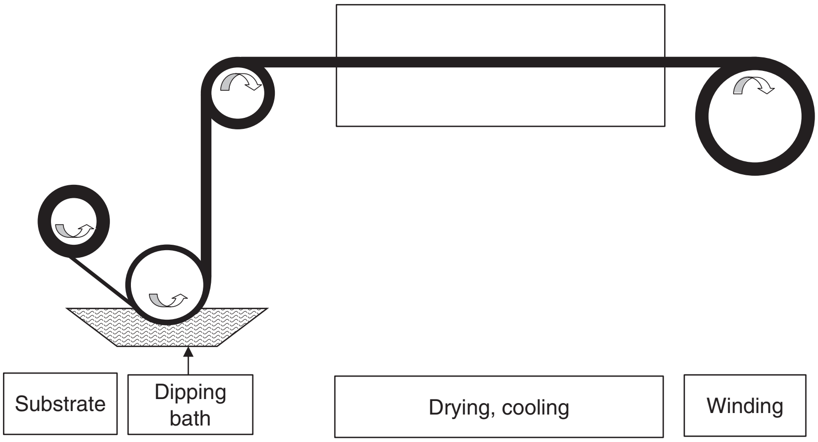


Figure 5.15. Principle of direct roll dipping

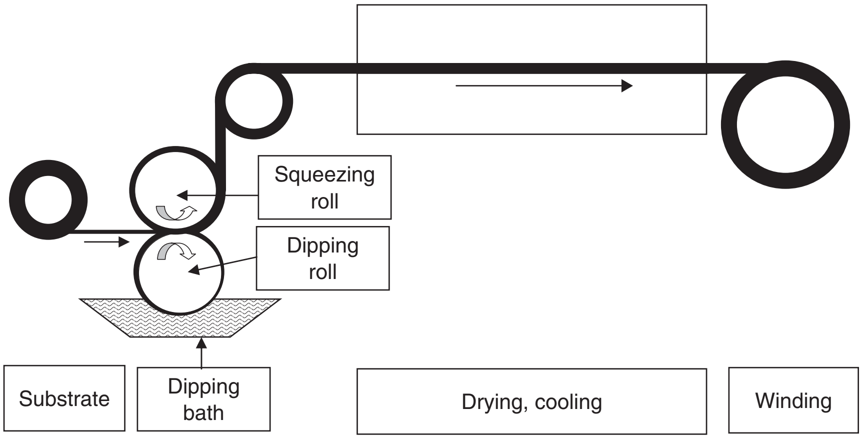


Figure 5.16. Principle of indirect roll dipping

Figure 5.17 shows a diagram of a spreading machine.

The main advantages and drawbacks of coating by dipping are:

- the section sizes are limited by the machinery size but the length is unlimited
- thickness can be difficult to control

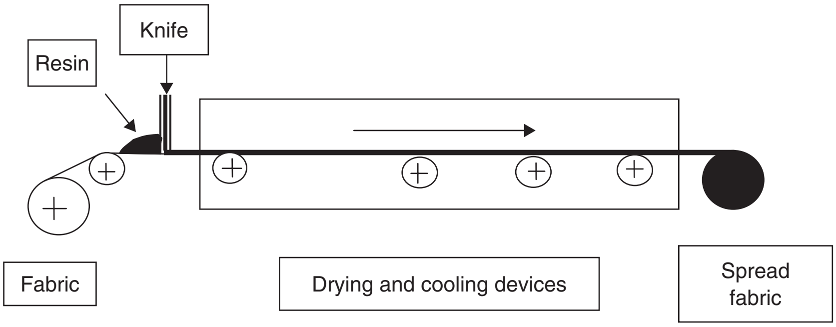


Figure 5.17. Diagram of a spreading machine

- the articles are isotropic with neat resin
- the aspect can be poor to good
- a finishing step is often essential
- the tools are cheap but the machinery cost depends on the output and sophistication
- the process is difficult to industrialize
- the output rates are low to medium according to the sophistication of the machinery.

5.4.3 Powdering, electrostatic deposition

These methods process powdered thermoplastics and may involve high-voltage currents. Consequently, it is necessary to obey all health, safety and environmental precautions and regulations.

The basic principle of powdering comprises three steps:

- hot parts to be coated are immersed in the thermoplastic powder fluidized by an air stream
- the thermoplastic powder melts by contact with the hot part and coats it
- by cooling, the thermoplastic solidifies and forms a continuous coating.

For electrostatic deposition or electrostatic powdering, the scheme is slightly different:

- the thermoplastic powder is charged by a high-voltage current (very low intensity)
- the powder is sprayed towards the grounded conductive part to be coated
- the powder, melted by heating in an oven, forms a continuous coating.

If the part to be coated isn't conductive it is necessary to apply a pre-treatment to make it conductive.

5.4.4 Solvent casting of films

The basic principle is somewhat similar to cast film extrusion but the flow of the polymer is obtained by dissolving it in a solvent instead of heating it during mechanical shearing in an extruder.

This method processes thermoplastics dissolved in solvents. Consequently, it is necessary to obey all health, safety and environmental precautions and regulations.

There are three steps for solvent casting. For example, for a PVC film:

- the ingredients of a soft PVC compound are dissolved in tetrahydrofuran (THF)
- the filtered solution feeds a special flat die to cast a film onto a stainless steel belt
- the cast film is dried in an oven, cooled and wound up.

Figure 5.18 schematizes the principle of solvent casting of film.

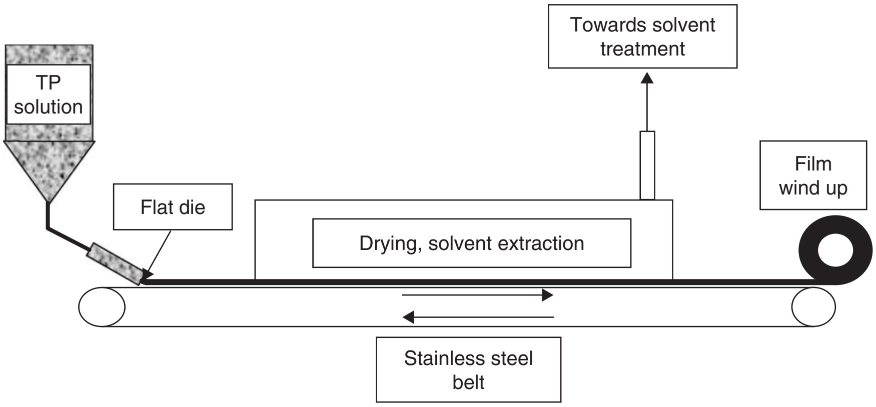


Figure 5.18. Solvent casting of film

5.4.5 Laminating

This technique is used for packaging and industrial multilayer films, often of hybrid nature associating a thermoplastic with paper, cardboard, aluminium foil . . . Some applications are, for example, barrier films, anti-adherent films, credit cards, wallpapers . . .

The basic principle is as follows:

- the substrate (paper, cardboard, aluminium . . .) is continuously coated with a film extruded with a flat die
- the coated substrate is cooled and wound.

If necessary, the process line includes a pre-treatment to make the substrate suitable to adhere to the thermoplastic.

Several extruders can be used to make multilayer films and/or to extrude adhesive layers to glue thermoplastics and substrate.

The hybrid nature of these films leads to several main advantages:

- The thermoplastic(s) bring(s):
  - ○ barrier properties versus moisture, greases, gas
  - ○ sealability.

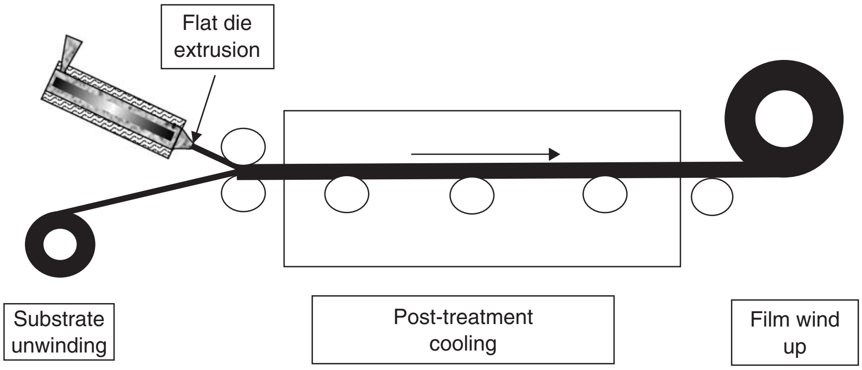


Figure 5.19. The lamination process

- The substrate brings:
  - mechanical performances
  - printability
  - non-plastic aspect and touch.

Figure 5.19 schematizes the principle of lamination.

5.5 Foaming

Generally, lightweight foams are produced by a few specialists on specific equipment with customized methods including the addition of blowing agents or gas injection.

The moulding of expandable beads is commonly used for EPS packaging by some manufacturers.

The structural foams are more widespread and are processed on less-specific equipment by expansion *in situ* of blowing agents.

Gas-assisted processing is developing.

Syntactic foams are composites made up of micro-balloons or hollow macrospheres bound into a plastic matrix.

5.5.1 Moulding of expandable beads

The pentane (or other hydrocarbons) used as the blowing agent is highly inflammable and fire regulations must be considered for transport, handling, storage, processing . . .

The process is commonly used to mould expandable polystyrene (EPS) that is delivered containing some percentage of pentane as the blowing agent. The moulding needs three steps:

- Pre-expansion: a steam flow heats the beads of EPS, which are expanded to about 40 times their original size by the boiling of the pentane. Thus, a closed-cell foam is formed.
- Maturing: the beads, returned to a storage tank, cool for several hours. The pentane condenses, inducing a vacuum in the beads. Consequently, the air from the environment gets into the beads.
- Final moulding: the pre-expanded beads are poured into a mould fitted into a press, are reheated with steam and expand to take the shape of the mould. According to the mould shape, the final product can be a finished part or large blocks. Blocks can be cut into panels, boards, etc.

Advantages of the process:

- the foam density can be very low
- final costs are low
- convenient equally for the production of small parts such as boxes and large ones such as blocks
- the aluminium mould and tool have a rather moderate cost
- the investments are reasonable
- the process is convenient for short and medium production runs
- the final gas in EPS goods is essentially air.

Disadvantages of the process:

- discontinuity
- the external face of the part is generally smooth but surface details are rather rough
- the press and the moulds must have the facility to introduce steam

- the choice of resins is limited
- relatively slow
- fabrication of thin parts is difficult
- mechanical performances can be rather weak because of the lack of cohesion between the beads
- the labour costs are high
- fire risks during storage and processing.

5.5.2 Structural foam injection

Structural foams are made of a cellular core with a dense skin. The technique is used for industrial and aesthetic goods for the automotive, electronics, household appliance and aeronautics sectors, such as housings of machines, TV cabinets, computer housings, roofs for caravans or ships, hard tops of 4WD (Jeep), luggage boxes, parts for washing machines.

Structural foams are processed by thermoplastic injection moulding using:

- the compound containing a blowing agent that is decomposed by the heat of the melted plastic producing a large volume of gas. Standard injection moulding machines are used
- the standard compound and a specialized injection machine allowing the introduction of the gas into the melted plastic. The pressure drop in the mould induces the expansion of the gas.

Advantages of injection moulding of structural foams:

- Almost all thermoplastic materials can be foamed.
- Large parts of more than 40 kg and one metre can be produced.
- Allows the production of parts having a good balance between density and mechanical performances.
- Weight reduction is of the order of 10–35%.
- Basic properties are those of the polymer but foaming reduces some of them.
- Parts are less sensitive to sink marks, thickness variations and residual stresses. Thicknesses, 5–15 mm, can be higher than with dense compounds; bosses and ribs can be oversized.
- Foams are more thermally insulating and are soundproofing.
- Multimaterial parts can be processed with, for example, a foamed core of recycled material and a dense skin made of the same virgin material.
- The combination with glass fibre reinforcement allows enhanced mechanical performances for the same density.
- Total automation of the process and high output rates.
- Low labour costs.
- In certain cases, if feeding pressures are low, tools can be formed in lighter grades of metals.
- Suitable for mass production.
- Normally, the whole surface of the part has a good finish, which makes a final finishing unnecessary. However, the aspect varies with the process. A textured surface can minimize the surface irregularities.
- Apart from particular cases of resins filled with fibres and other acicular or lamellar fillers, the parts are isotropic if there are no residual constraints.
- Shot capacities cover a large range, for example, a few grammes up to more than 50 kg.

Drawbacks of injection moulding of structural foams:

- The blowing agents must be adapted to the polymer because of the decomposition temperature, which must be compatible with the temperatures of the various processing stages.
- The optimization of the moulding parameters can be difficult because of the delicate balance between the blowing agent decomposition and the part shaping. Part warpage and shrinkage are sometimes difficult to predict.
- Part sizes are limited by the mould size and the machinery performances.
- Certain processes are patented.
- The structural foams, because of the reduction of the real section of the material, are less suitable to resist the tensile stresses.
- Processing is more delicate, less widespread and often requires particular materials.
- Low thicknesses are not realizable.
- For high expansion levels, the surface quality often requires sanding and the application of a primer before painting.
- Mould and press prices are the highest.

5.5.3 *Extrusion of thermoplastics containing blowing agents*

The blowing agent can be a hydrocarbon (pentane, for example), which is easily flammable, and precautions against fire must be taken at all the stages of transport, handling, storage, manufacture . . .

The principle of the extrusion of thermoplastics containing blowing agents is theoretically simple:

- Extrusion with a standard extruder of a compound containing the blowing agents. Heating the material produces expansion of the blowing agent after melting. Consequently, the profile expands.
- The temperature profile is then adjusted to control the expansion.

Generally:

- The blowing agents must be suited to the polymer because the expansion temperature must be compatible with the temperatures of the various processing stages.
- Optimization of the extrusion parameters can be difficult because of the delicate balance between the blowing agent expansion and part shaping. Part warpage and shrinkage are sometimes difficult to predict.
- Often the density is in the range of 0.3–0.6 g/cm^3.
- Processing is more delicate, less widespread and often requires particular materials.
- Part sizes are limited by the die size and the machinery performances.
- Certain processes are patented.
- The foams, because of the reduction of the real section of the material, are less suitable to resist the tensile stresses.
- Cooling is retarded because of the high insulating performances of foams.

5.5.4 *Direct gas extrusion process*

Thermoplastic foaming is obtained by injection of high-pressure gas directly into the melt flow.

In this process, the thermoplastic, which does not contain blowing agents:

- feeds an extrusion machine into which a gas is introduced under high pressure after the melting step

- the expansion occurs when the material returns to atmospheric pressure at the exit of the die, before cooling which will fix the physical state of the thermoplastic.

Generally:

- the gas injection requires special extrusion machines
- the high pressure of the gas necessitates sturdy machinery
- optimization of the extrusion parameters can be difficult because of the delicate balance between the gas expansion and the pressure/temperature balance of the extruded material
- the density can be very low, for example as low as 0.03 g/cm^3 or less
- part sizes are limited by the die size and the machinery performances
- certain processes are patented
- the foams, because of the reduction of the real section of the material, are less suitable to resist the tensile stresses
- processing is more delicate, less widespread and requires particular materials
- cooling is retarded because of the high insulating performances of foams.

5.5.5 Liquid foam process

This process is generally used for thermosets, such as polyurethane, polyisocyanurate, phenolic, unsaturated polyester and silicone foams, but it is also used for plastisols or PVC pastes.

Foaming is obtained by:

- decomposition of blowing agents by heat, producing high volumes of gas such as CO_2, N_2
- mixing with air or nitrogen for latex, some silicones and plastisols or PVC pastes
- reaction of components producing a gas
- volatilization of volatile liquids, like halocarbons, by the heat of reaction.

For plastisols, the first two methods are used.

The decomposition of blowing agents by heating can take place:

- Under pressure in a closed mould during gelation. After cooling and demoulding, the expanded parts are re-heated (post-expansion) to obtain closed-cell foams such as life jackets.
- At atmospheric pressure: the foam structure depends on the formulation and processing parameters. Foamed sheets and imitation leathers can be manufactured by this process.

Foaming with air is obtained in special mixers such as the Oakes mixer and the expansion takes place during gelation in hot air or a high-frequency oven.

5.6 Composite processing

Processing methods depend on the fibre length.

We propose one possible classification for the main processes:

- Processing of LFRT or LFT – long fibre (reinforced) thermoplastics: injection, composite insert moulding, compression moulding, extrusion-compression.
- Stamping and compression moulding of GMT sheets.
- Prepreg draping.
- Filament and tape winding.

- Continuous processes:
  - pultrusion
  - pultrusion-coextrusion.
- Thermoplastic sandwich.
- Thermoplastic hybrids.

5.6.1 Processing short fibre reinforced thermoplastics

The methods are the same as those for neat resins but care is needed in:

- ensuring a homogeneous dispersion of the fibres and their random distribution during the whole processing
- designing parts, machines and tools avoiding the stagnation and accumulation of fibres in certain spots
- choosing sufficiently abrasion-resistant metals for machines and tools to withstand the high abrasive effect of fibres.

5.6.2 Processing LFRT or LFT: injection, compression moulding, extrusion-compression, composite insert moulding

The methods depend on the fibre length:

- grades reinforced with fibres 10 mm long can be processed on conventional injection equipment by simply adapting the processes to preserve the fibres
- grades reinforced with fibres 20 mm or more in length cannot be processed on conventional injection equipment. It is necessary to use, for example, the compression moulding or extrusion/compression technique.

Conventional injection moulding is treated in Section 5.1.1 above.

Compression moulding is treated in Section 5.1.3 above.

Extrusion-compression

Two basic processes are combined:

- the thermoplastic composite is heated and plasticized in a screw extrusion machine that feeds a mould
- the part is compression moulded into the cooled mould.

Figure 5.20 shows the principle of the extrusion-compression process.

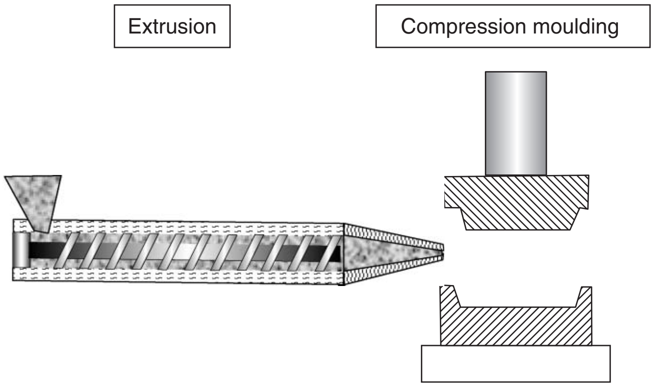


Figure 5.20. Principle of the extrusion-compression process

Advantage of the process:
- it is possible to use longer fibres than with the injection process.

Disadvantages of the process:
- discontinuous fibres
- slower than injection moulding
- limited choice of reinforcements
- higher labour costs
- specialized equipment.

Composite insert moulding, co-moulding

It is possible to use thermoplastic composite inserts to:
- Reinforce injected parts locally. A more lightweight part can be made by reinforcing it at specific spots with an insert of unidirectional composite manufactured, for example, by filament winding.
- Obtain specific properties using, for example, a self-lubricating composite insert.

Discontinuous fibre reinforced thermoplastic composites can also be overmoulded onto GMT sheets.

Figure 5.21 displays the reinforcement of a bush with an inner unidirectional composite insert. The principle is the same for a bush with a self-lubricating insert.

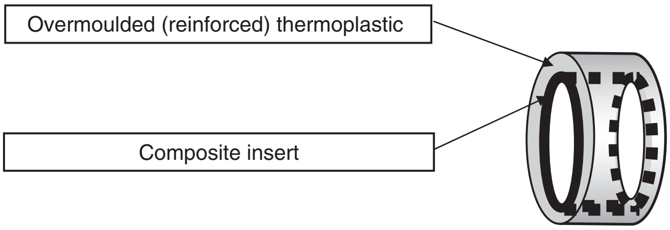


Figure 5.21. Principle of composite insert moulding

5.6.3 Stamping and compression moulding of GMT sheets

Stamping or compression moulding at temperatures close to the melting point of the matrix can be used to produce parts made with GMTs:
- The stamping technique is very similar to the stamping of metal sheets: the pre-cut blanks are heated to their softening point near the melting temperature of the matrix and are quickly transferred into the tools mounted in a stamping press.
- By compression moulding:
  - For fast compression moulding, the pressures are about 15–20 MPa with cycle times of 20–50 seconds. The shapes can be complex and the surface aspect is better. The creep is very significant. The minimum thickness is of the order of 1 mm.
  - Low-pressure compression moulding is carried out under much lower pressures (0.5–3 MPa) and at lower temperatures. The creep is less significant and the shape must be relatively simple and near that of the blank. The surface aspect is not so good but, on the other hand, the process allows a fabric to be laid on it to give a textile effect.

For polypropylene GMT, which is the most commonly used:

- the softening temperature can be of the order of 200°C
- the demoulding temperature is about 100°C.

The main steps of this process are:

- storage of the pre-cut blanks
- heating of the blanks
- stamping.

Automated transport devices handle the blanks and finished parts.

Figure 5.22 shows the principle of stamping.

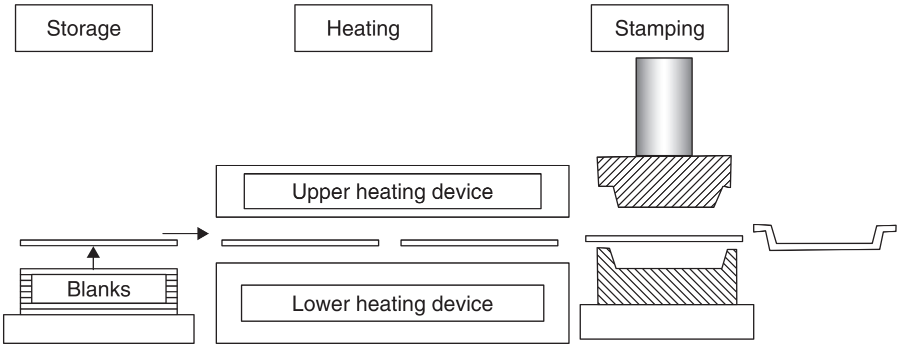


Figure 5.22. Principle of stamping

Advantages of the process:

- high outputs close to those obtained with metals
- possibility of making large parts
- low labour costs
- attractive final prices.

Disadvantages of the process:

- limited choice of matrices
- heavy investments
- limited shapes.

Examples of uses:

- automotive and transport: bumpers, crosspieces, inserts for dashboards, phonic shields, seat frames . . .
- storage, handling: containers, tanks
- miscellaneous: welding helmets, ventilator shells, lawnmower bases.

5.6.4 Prepreg draping and consolidation by vacuum or pressure bag moulding, autoclave . . .

Pre-impregnated rovings, tapes, tows or fabrics, cut to the right shape and size, are laid-up by hand or machine onto a mould surface.

- Hand lay-up: it is possible to use all other types of reinforcements such as honeycombs or foams. All shapes, sizes and thicknesses are feasible.
- Automated lay-up: there are numerous degrees of automation with more or less complex machines.

- The consolidation is obtained by heat and pressure: vacuum or pressure bag moulding, autoclave . . .
- Solidification requires cooling.

Figure 5.23 displays the basic principle for an automated tape placement.

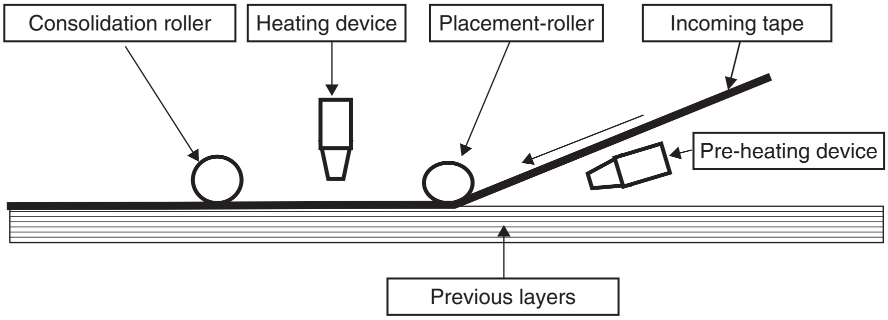


Figure 5.23. Principle of an automated tape placement machine

Advantages of the draping process:

- Hand lay-up:
  - ○ design freedom
  - ○ moulding of complex parts with variations of thickness
  - ○ lower investments.
- Automated lay-up:
  - ○ faster than hand lay-up
  - ○ lower labour costs
  - ○ better repeatability.

Disadvantages of the draping process:

- Hand lay-up:
  - ○ high labour costs
  - ○ skilled labour required
  - ○ risks of placement errors
  - ○ slow.
- Automated lay-up:
  - ○ heavy investments
  - ○ skilled labour required
  - ○ limited design possibilities.

5.6.4.1 Vacuum bag moulding after draping

After the composite has been manufactured onto its mould, an anti-adherent flexible sheet is applied onto it, and then a light vacuum is created by a suitable system (see Figure 5.24).

The vacuum applies the sheet onto the laminate, which creates a compression of the composite and improves the aesthetics of the free face.

Figure 5.24 shows the principle of vacuum bag moulding after draping.

Advantages of the vacuum bag process:

- the upper face has a better finish
- the vacuum makes degassing easier and reduces bubbles and other voids
- it is possible to use a heated oven to accelerate consolidation.

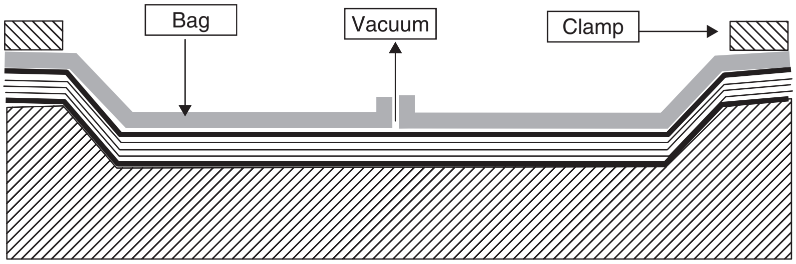


Figure 5.24. Principle of vacuum bag moulding after draping

Disadvantages of the process:
- more complex
- additional investment required in vacuum device
- necessity to tailor the bag according to the part and mould shapes
- part size limited by the mould size.

Pressure bag moulding after draping

This process (Figure 5.25) resembles vacuum bag moulding but the vacuum is replaced by pressure. After the composite has been manufactured onto its mould:
- an anti-adherent flexible sheet is applied onto it
- the mould is closed with a reliable flat cover

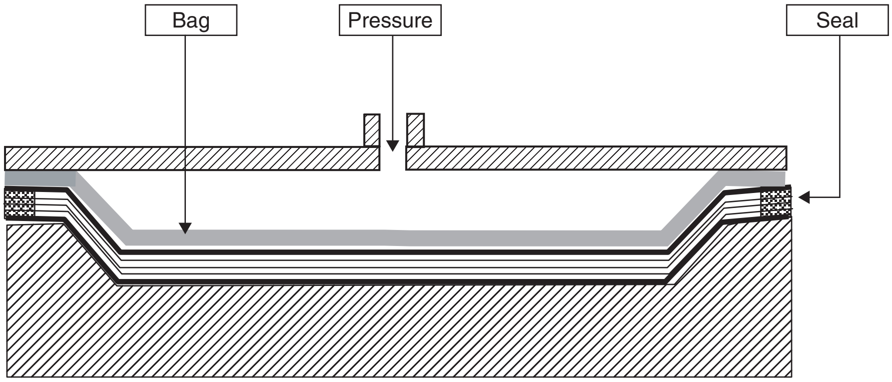


Figure 5.25. Principle of pressure bag moulding after draping

- pressure is created by a suitable system. This pressure applies the sheet onto the laminate, which creates a compression of the composite and improves the aesthetics of the free face.

It is possible to combine vacuum and pressure:
- first, vacuum is created in the bag to remove air, reducing bubbles and other voids
- then pressure is applied outside the bag to increase the compression of the laminate and improve material cohesion and mechanical properties.

Figure 5.25 shows the principle of pressure bag moulding after draping.

Advantages of the pressure bag moulding process:
- improved finish of the upper face
- better material cohesion
- possibility to use a heated oven to accelerate the consolidation.

Drawbacks of the pressure bag moulding process:
- more complex
- additional investment required in pressure device and more-complex and resistant moulds
- necessity to tailor the bag according to the part and mould shapes
- part size limited by the mould size.

Examples of applications:
- hand lay-up: prototypes, technical parts . . .
- automated lay-up: aeronautics elements.

5.6.5 Filament and tape winding

There are several steps:
- the impregnated roving or prepreg is heated by a heating head
- the machine winds up the roving or prepreg on a mandrel, which turns on an axis
- a post-consolidation can be obtained by heat and pressure: specific pressure device, vacuum or pressure bag moulding, autoclave . . .
- solidification requires cooling.

The fibres can be placed:
- perpendicular to the axis: circumferential winding or 90° filament winding
- parallel to the axis: 0° filament winding
- sloped at a defined angle on the axis: helical winding.

The mandrel can be recoverable, or can be integrated in the finished part, for example, in the inner liner of high-pressure tanks.

On-site machines: for construction of very large tanks there are specific machines that build the tank on site, overcoming the transport problems.

Figure 5.26 shows the principle of filament or tape winding.

Advantages of filament or tape winding:
- the reinforcement levels can reach 60% to 75%, even 80%, making it possible to obtain excellent mechanical characteristics
- the properties can be enhanced in chosen directions by modifying the winding angle
- part sizes can be significant.

Disadvantages of the process:
- heavy investments
- limited design and shapes
- the reinforcement placement must be carefully calculated.

Examples of applications:
- high-pressure tanks with metal inner liner
- pipes, masts.

5.6.6 Continuous processes: pultrusion and derived processes

Pultrusion

A heating device softens the pre-impregnated rovings. Rollers consolidate the composite before passing through a cooled die to solidify the thermoplastic matrix.

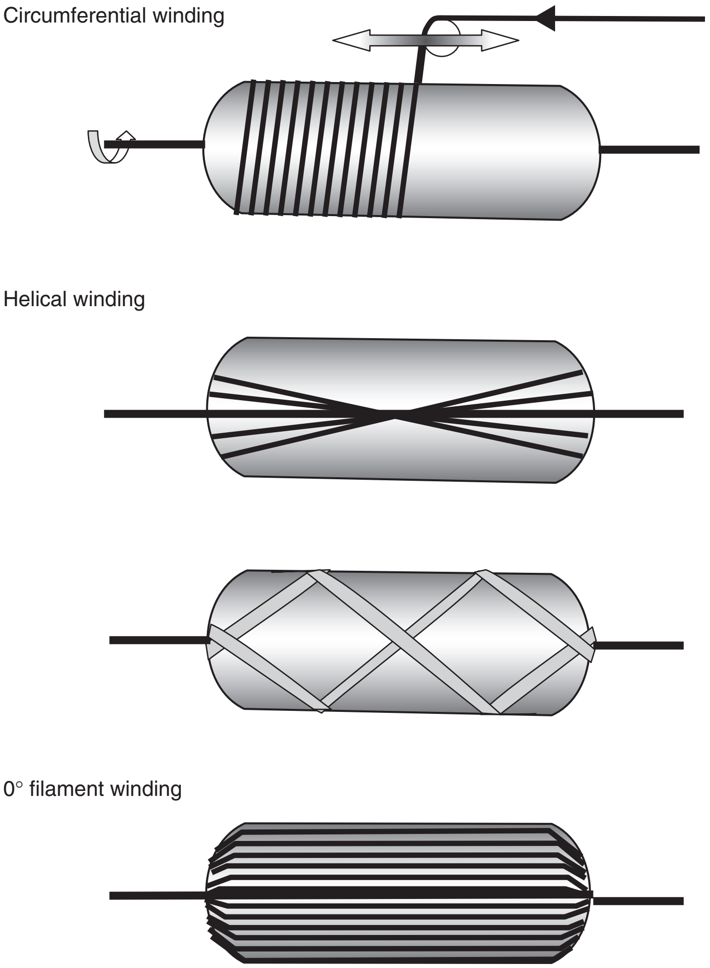


Figure 5.26. Principle of filament or tape winding

- The shape is obtained by going through a die.
- The composite is consolidated in a heated oven.
- A pulling group ensures the drive of the profile.

Additional systems make it possible, subsequently, to curve the profile but the section shape being created by the die is identical over the entire length.

This process is adapted to the realization of complex, hollow or solid sections, with high mechanical characteristics thanks to the high unidirectional reinforcement levels.

Figure 5.27 shows the principle of thermoplastic pultrusion.

Advantages of the pultrusion process:

- excellent mechanical properties in the profile axis
- practically unlimited length
- smooth surfaces except cut ends
- continuous production.

Disadvantages of the process:

- exclusively profile manufacturing
- limited sizes in transverse section

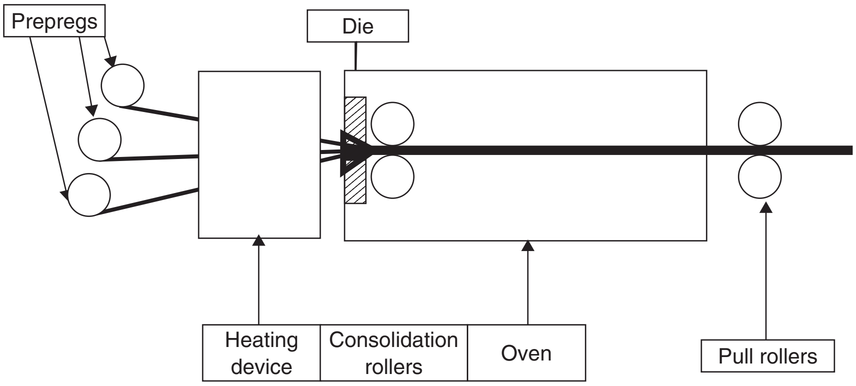


Figure 5.27. Principle of thermoplastic pultrusion

- unidirectional reinforcement
- limited reinforcement choice
- significant investments.

Examples of applications: all rectilinear or curved profiles.

Pullwinding, overbraiding

These processes combine two elementary techniques:

- filament winding or an interlacing reinforcement method from the textile industry, such as braiding
- the pultrusion process.

Pultrusion-extrusion

A thermoplastic is extruded onto the reinforcements impregnated with a thermoset resin before passing through the pultrusion die.

5.6.7 Sandwich composites . . .

Let us recall that a sandwich structure is made up of:

- a core of foam, wood, honeycomb . . .
- two skins of reinforced resin sheets firmly bonded onto the core to obtain high rigidity. The skins can be made of reinforced thermosets, GMTs or metals. Sometimes there is only one skin that surrounds the core completely. This is the case for sailboards, for example.
- subsequent edge protection.

The curing of the adhesive bonding is carried out by heat and pressure: specific device, vacuum bagging, autoclave, press . . .

The cores and the final parts can have any shape: parallelepipedic for a lot of sandwich panels, shaped parts for the hulls of boats or bumpers and so on.

There are several problems to solve:

- The shaping of the core: thermoset and metal cores are generally machinable only. The linear thermoplastic foams are thermoformable.

- The gluing of the skins onto the core uses adhesives in film or liquid form. The small size of the honeycomb areas that are available for bonding makes this difficult.
- Metal and other water- or moisture-sensitive materials need the structural sandwich to be waterproofed.

Several manufacturing methods are used:

- Prefabrication of the two skins and joining on to the two faces of the core.
- Application of a GMT skin on each face of the core.
- Draping of the skins on the shaped core.
- Injection of foam between the two prefabricated skins.
- Use of an expandable polymer insert that expands during the paint setting.

Figure 5.28 shows the principle of the sandwich structure.

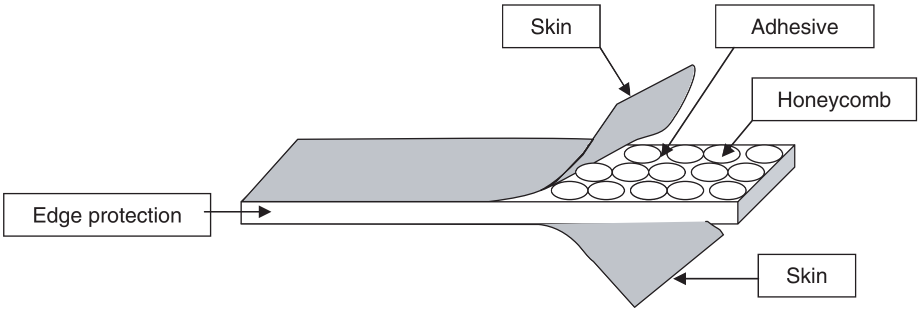


Figure 5.28. Principle of the sandwich structure

Advantages of these processes:

- Foams and honeycombs lead to excellent property/weight ratios.
- Foams are cheaper than honeycombs and are developed in general-purpose applications such as automotive and transport. Honeycombs have higher performances and are used in aerospace applications.
- Plywood leads to very good property/price ratios and better compression strength.

Disadvantages of these processes:

- The compression strength of the foam and honeycomb sandwich composites can be low.
- With wood and honeycombs, it is difficult to make complex shapes.

Examples of applications:

- Automotive and transport, shipbuilding, mass-production sports and leisure: the core is generally made of foams as PVC, polyethylene . . . and the skins can be made of GMT.
- Aerospace, top-of-the-range sports and leisure: the core is generally made of honeycombs or high-performance foams and the skins can be made of carbon fibre reinforced thermoplastic polyimides.

5.6.8 Hybrids

The hybrid techniques associate two (or more) materials and combine the benefits and the processing of both.

Often the material couples are:

- thermoplastics and metals
- thermoplastics and elastomers.

Consequently, the various processing steps are often:

- A thermoplastic method:
    - injection moulding
    - over- or co-moulding.
- A metal method:
    - stamping
    - embossing
    - bending.
- A joining method:
    - Mechanically: the metal bears anchorages such as lugs, holes . . . that interlock the thermoplastic during injection, overmoulding, co-moulding . . . In this case, this step is virtual, taking place during the course of moulding.
    - Chemically: bonding of the polymer to the metal treated with a primer. In this case the step is concrete, consuming time and cost.
    - Direct adhesion of two compatibilized polymers: this step is virtual but often needs special, more-expensive grades of polymers. The bonding of polypropylene and some other materials is difficult.

Advantages of hybrid processing:

- Association of simple and inexpensive plastic processes with simple and inexpensive metal processes.
- Integration, thanks to the plastic elements, of the maximum number of functionalities: mountings, fastening points, fixings, cable holders, housings, embossings, eyelets, clips, etc.
- Elimination of the assembling stages of the eliminated components.
- Reduction of the dimensional defects of the assembled components.
- Removal of welding operations that can cause metal deformations.
- Properties provided by the polymer: aesthetics and style, damping, thermal and electrical insulation.
- Properties provided by the metals: structural properties, impermeability, electrical conductivity.

Several producers such as Bayer, Dow (LFT-PP concept) and Rhodia (PMA – Plastics & Metals Assembly, and MOM – Metal Overmoulding – processes) have developed their own hybrid technologies.

Currently, one of the most important applications is the front-end of recent cars such as the Mini Cooper from BMW, Mazda 6, Audi A6, Ford Focus and VW Polo, associating long glass fibre reinforced polypropylene injected onto stamped metal, which leads to weight savings in the range of 30–35% compared to traditional solutions.

5.7 Curing of thermoplastics

Some thermoplastics, polyethylene or EVA for example, can be cured before use to improve some performances. The main processing methods involve:

- heating to promote chemical reactions of curing agents such as silanes or peroxides leading to crosslinking
- irradiation to promote direct crosslinking.

Heating can be achieved by:

- discontinuous processes such as heated moulds, ovens . . .
- continuous processes such as hot tubes for wire curing, or hot tunnels.

Irradiation can be achieved by:

- Discontinuous processes such as the cobalt bomb:
  - highly penetrating radiation
  - convenient for thick parts
  - slow.
- Continuous processes such as electron beam irradiation:
  - less penetrating
  - suitable for thinner parts
  - speedier.

Advantages of crosslinking:

- improvement of stress cracking
- increase of abrasion resistance
- decrease of the permanent set after loading
- ‘cold’ sterilization for irradiation
- reduction of residual monomers and/or oligomers and VOCs.

Drawbacks of crosslinking:

- cost
- over investment
- safety constraints for radioactive applications
- difficulty of recycling because of the irreversible linking
- possible degradation during irradiation.

5.8 Secondary processing

The secondary transformation processes use semi-manufactured products resulting from a primary transformation, for example:

- thermoforming uses sheets and films
- machining uses rods, tubes, plates . . .
- boilermaking uses sheets, tubes, slabs, plates . . .

5.8.1 Thermoforming

Thermoforming consists of applying a thermoplastic sheet softened by heat onto the walls of a mould to shape it (see Figure 5.29).

There are several processing steps:

- sheet cutting
- heating of the blank
- forming:
  - by the direct action of the mould on the thermoplastic sheet (stamping)
  - by action of the mould combined with vacuum or air pressure to ease shaping.

The mould can be male, female or in two parts and can bear holes for vacuum, air and venting.

- partial or total cooling and demoulding.
- cutting of the edges.

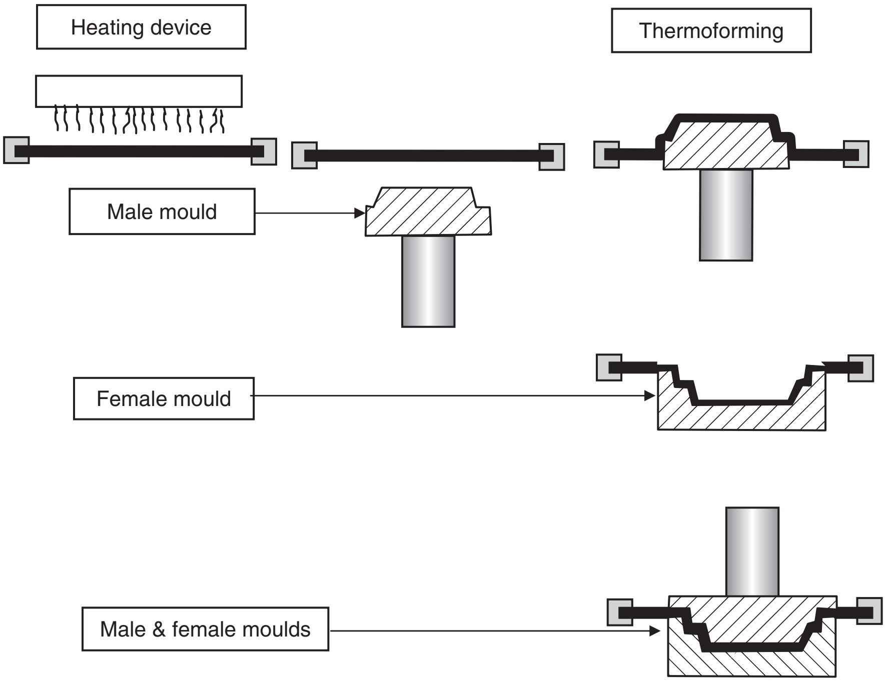


Figure 5.29. Principle of thermoforming

Machines are very diverse (see Table 5.5 for examples) with:

- Simple and cheap manual machines.
- A large range of standard models, mono- or multi-stations, to thermoform sheets or films from 0.1 mm to 8 mm fed in rollers or sheets.
- Specific machines, for example to produce infill domestic door panels.
- High-speed machines integrated into packaging lines for large volume production of milk products, fruits, honey, jellies, creams and various dressings. They can handle a wide range of packaging materials, running from around 10 000 packs an hour up to 48 000 packs per hour with 360° full wrap in-mould labelling for a wide variety of cup sizes and heights. Suitable lid materials are heat-sealable aluminium foils or PET laminates, paper/PET, cardboard/PVC, Surlyn (DuPont ionomer), plastic films or double-layer lids for drink cups. A two-stage thermoforming process (plug-assist preforming with final forming by air) can be used.

Some basic rules for part design

The following rules are some of the basic ones and are not sufficient to optimize the design, which must be discussed with the producer of the chosen thermoplastic and the thermoformer. These rules can be modified according to the actual problems.

- Remember that there is always shrinkage after thermoforming and the part is different from the mould to a greater or lesser degree.
- Design parts to ease demoulding by including sufficient draft if the material does not support stretching.

Table 5.5 Examples of thermoformer characteristics

Feeding S(heet) or R(oll)	Platen size (cm × cm)	Draw depth (cm)	Heating power (kW/m^2)
S	12 × 20	55	30
R	17 × 20	5	300
S	20 × 25	15	
R	20 × 30	10	400
S	30 × 30	30	500
R	30 × 30	12	500
R	35 × 50	10	
S	35 × 50	30	
R	40 × 40	10	
S	40 × 40	10	240
R	75 × 75	15	320–500
S	75 × 75	15	240
R	90 × 90	15	400
S	90 × 90	15	500–800
S	90 × 90	60	500
R	90 × 180	20	350
S	90 × 210	75	600
S	90 × 210	175	600
R	125 × 180	15	500
S	120 × 300	75	400
S	120 × 300	100	800
S	150 × 300	75	600
S	150 × 300	175	600
S	180 × 420	75	600
S	180 × 420	175	600
S	210 × 450	75	600
S	210 × 450	175	600
S	270 × 360	75	600
S	270 × 360	175	600
S	300 × 450	90	
S	300 × 450	120	800
S	300 × 700	90	800
S	300 × 700	150	800
S	700 × 700	60	112

- Avoid over-complicated shapes.
- Thermoforming increases the surface of the starting sheet, leading to a significant thinning of the walls, the more so where drawing is locally high: the depth of the thermoformed parts is limited by admissible thinning for manufacture and use. Over-deep holes, cavities and pressings are not workable. Wall thickness variations are not controllable.
- Embossings, solid ribs, inserts are not suitable.
- Because of the thinning, avoid radii of curvature that are too small, which, moreover, harm the impact resistance.

Choice of thermoplastics: numerous special grades are marketed for various families:

- Commodity thermoplastics:
  - styrenics such as PS, ABS . . .
  - PVC
  - Polyolefins such as polyethylene, polypropylene . . .

- Engineering thermoplastics:
  - acrylics such as PMMA
  - cellulose acetate
  - polyacetal
  - polycarbonate
  - polyamide
  - polyphenylene oxide
  - polysulfone.

Advantages of thermoforming:

- cheap tools and moulds
- convenient for processing from prototype to mass-production parts
- allows the processing of large parts such as car body parts, refrigerator inner doors, domestic inner doors. . . .
- large choice of machinery from very simple lab models to very sophisticated lines.

Consequently, the shapes and tolerances can be rough or precise. Under the best conditions, fine tolerances and sharp details are obtained and with excellent finishing techniques the thermoformed parts can match certain injected ones.

Drawbacks of thermoforming:

- wall thicknesses are not controllable
- parts must be simple with restricted shapes
- limited choice of thermoplastics
- tolerances can be broad
- sheets are expensive and wastes are significant
- finishing is often necessary.

Applications are very varied, from small to large parts, from low output to mass production, from common to high-tech performances, for example:

- transportation: body parts for cars, motorcycles, tractor roofs, hoods, automotive trims . . .
- office automation: housings . . .
- household appliances: inner doors of refrigerators, domestic doors, sanitary ware components . . .
- shipbuilding: hulls, sailboards . . .
- aeronautics: cockpits and windscreens . . .
- signs, domes, display furniture . . .
- packaging: yoghurt cartons, trays, blister shells, chocolate moulds, skin packaging, pallets, cases . . .
- industrial furniture: housings, containers, visors for masks, cases, pumps . . .
- miscellaneous: carnival masks, toys, lawnmowers . . .

5.8.2 Machining of thermoplastics and composites

Practically all the rigid thermoplastics are machined more or less easily by almost all the metal or wood machining methods, after some degree of adaptation of the tools and processes:

- sawing, drilling, turning, milling, tapping, threading, boring, grinding, sanding, polishing, engraving, planing . . .

Other machining techniques can also be used, for example:

- laser cutting
- hyperbar fluid cutting.

Some precautions must be taken:

- The low thermal conductivity and the decrease of the mechanical characteristics at elevated temperature limit the machining temperature and it is necessary to cool and reduce the tool feed motion.
- Machining damages the surface, destroys coatings and gelcoats if they exist and, to avoid the risks of later attack, it is sometimes necessary to (gel)coat after machining.
- For anisotropic parts, machining can be more difficult or impossible in certain directions. Drilling, for example, can only be done perpendicularly to the layers of a composite.
- Carbon and glass fibres are very abrasive and quickly wear away high-speed steel tools. For intensive use, carbide or diamond tools are preferable.

Machining is suited for:

- prototypes and low output of complex parts made from blanks whose mould or manufacturing could be simplified
- correction of parts with tight tolerances
- thick parts.

5.8.3 Boilermaking

Plastic boilermaking, very similarly to metal boilermaking, allows the realization of simple and developable geometrical parts, by cold or hot forming, machining and assembly by welding or joining of plates, tubes and blanks.

Boilermaking is commonly used for the fabrication of large vessels, piping, cisterns, tanks, tubing, geomembranes, etc. from prototypes up to medium output thanks to the use of techniques such as welding, forming, machining, bonding of sheets, slabs, pipes, blanks . . .

The workers must be skilled and the labour costs are high.

This processing method is also commonly used to build inflatable boats, protective clothing, inflatable structures particularly those made of soft PVC.

The most commonly used thermoplastics are:

- PVC, CPVC
- polyolefins such as polyethylene, polypropylenes and copolymers
- engineering thermoplastics such as PVDF, PMMA, polycarbonates.

The implementation requires good knowledge of materials, great experience and skilled and careful labour.

The mechanical characteristics obtained are often higher than 0.8 times those of the starting semi-finished products.

Advantages of boilermaking:

- cheap tools
- allows the fabrication of very long and complex tubing, giant parts such as silos, cisterns . . .
- convenient for processing prototypes up to medium output.

Drawbacks of boilermaking:

- parts must be rather simple with restricted shapes
- limited choice of thermoplastics
- mechanical performances lower than those of injected parts
- tolerances can be broad
- the workers must be skilled and the labour costs are high.

5.8.4 Inserts, outserts

Inserts are any parts of any material located into another plastic part during or after its processing. The best known are metal inserts for assembly by screwing but there are numerous other insert types (plastic parts, films . . .) for numerous other applications.

Outserts are large machined metal plates with holes and other anchorages onto which a plastic is locally overmoulded to ensure specific functions. The metal plate brings high rigidity and the plastic ensures insulation, frictional properties, damping. . . This technique cuts the assembly costs of numerous small plastic parts.

5.8.4.1 Inserts

Inserts are used to improve plastic performances:

- mechanical properties, often to ensure a stronger assembly but also to improve rigidity . . .
- specific behaviour: tribological metals or plastics inserted as bearings . . .
- aesthetics: in-mould decoration with film insertion, labelling . . .

Inserts can be incorporated:

- during the moulding process. The inserts can be loaded in the empty mould by a robot or by the operator. For the neat resins, this solution is generally avoided because of the large difference between the coefficients of thermal expansion of metals and plastics
- inserted into a moulded hole as a post-moulding operation.

Most inserts are made from:

- Metals, usually brass but also, for example, a more-expensive stainless steel if a higher tensile strength is needed. The insert metal must be compatible with the plastic material. For example, polyamide absorbs moisture, which leads to the steel rusting; copper is a oxidation catalyst for polyolefins; zinc, aluminium and brass are not compatible with polyacetals . . .
- Plastic: a pre-moulded plastic insert of differing properties to the moulded polymer can simplify tools and lead to cost savings.
- Film: a pre-decorated film is laid out onto the surface of the part to be decorated.

There are a myriad of insert shapes, which are often patented. The insert shape must favour its mechanical anchorage: faces, flat sides, grooves, milling, barbs, perforations. . . that allow the flowing of the thermoplastic. However, sharp angles initiate cracks and the geometric anchors should be located as far as possible from the surface.

Inserts are often dedicated to specific plastic materials: neat thermoplastics, neat and filled thermosets, reinforced plastics, composites, structural foams . . .

Table 5.6 displays some examples of inserts, the targeted goals and installation processes, without claiming to be exhaustive.

Table 5.6 Examples of inserts

Insert material	Goal	Installation
Metal	Mechanical anchor	During or after moulding, self-tapping inserts
Moulded plastic	Specific mechanical property: bearing inserts . . .	Overmoulding, post-moulding insertion by means of pressure (and heat)
Film	Decoration, protection . . .	In-mould decoration (IMD)
Label	Information . . .	In-mould labelling
Metal fibre mat	Electrical property: RF shielding	Overmoulding

Generally, embossing must obey some basic rules. Among these, some, but not all, are recalled below:

- Holes should be located as far as possible from the edges and welded lines.
- The material thickness around the insert must be sufficient, of the same order as the wall thickness.
- Sizes of holes and inserts must be calculated according to the furnisher's instructions.

5.8.4.2 Installation of inserts

- Moulded-in inserts: the inserts can be loaded in the empty mould by a robot or by the operator. The advantages and drawbacks of this process are:
  - high extraction resistance because the plastic completely encases the insert on its outer wall
  - slowdown of the output if inserts are manually placed inside the mould
  - increase of investments if inserts are automatically placed inside the mould
  - for the neat resins, this solution is generally avoided because of the large difference between the coefficients of thermal expansion of metals and plastics.
- Thermal insertion: a heating tool heats the insert, which in turn heats the plastic part receiving the insert. The tool then presses the insert into the hole in the part. The advantages and drawbacks of this process are:
  - simplicity of tools, usually cylindrical ones, which are easy to machine
  - speed of the process
  - necessity of good temperature control to avoid plastic degradation.
- Ultrasonic insertion: an ultrasonic transducer (horn) vibrates the insert, which heats by vibrating against the plastic. The advantages and drawbacks of this process are:
  - speed of the process
  - low residual stresses
  - special tools adapted for each application for optimum performance
  - more-expensive machinery
  - requires grade of thermoplastic having adapted flowing characteristics.
- Press fitting: the inserts are press fitted inside the hole. The advantages and drawbacks of this process are:
  - speed of the process
  - no special tooling
  - higher hoop stresses needing robust boss design
  - lower stress retention.
- Self-tapping inserts: available in thread-cutting or thread-forming types. The advantages and drawbacks of this process for the thread-forming type are:
  - high tensile values
  - high hoop stress for the thread forming
  - high amount of torque to strip threads
  - large number of cycles of assembly and disassembly possible
  - stress relaxation possible
  - suitable only for non-brittle plastics.

And for the thread-cutting type:

  - lower hoop stress
  - suitable for brittle plastics

- ○ lower tensile pullout
- ○ lower amount of torque to pull the threads.

5.9 Finishing

Many plastic parts are painted to:

- improve aesthetics
- differentiate productions from those of competitors
- differentiate parts for safety applications
- produce a special effect determined by styling or design
- cut costs of coloured parts that can be mass produced in a neutral colour and then painted in the various desired colours
- improve durability, the paint film protecting the plastic from the environment, including UV.

As for metals, many painted parts have to achieve a colour match with other parts.

Thermoplastic painting is similar to the process for metals, apart from some particularities of plastics and notably thermoplastics:

- Sensitivity to heat, which can cause physical and chemical alterations during paint drying and hardening.
- Sensitivity to solvents.
- Low surface tension. Wetting of the surface is more difficult as the surface tension decreases. Surface treatments can improve the surface tension and the wettability.
- Smoothness of the surfaces.
- Insulating properties limiting the use of electrical processes.
- Modification of the surface morphology by:
- ○ additives such as fillers, pigments . . .
- ○ the processing method: moulding, extrusion, thermoforming . . .
- Migration of additives such as plasticizers, internal mould release agents . . . Painting defects can appear a long time after painting.
- External mould release agent residues.

All precautions must be taken concerning health and safety according to local laws and regulations.

There are three main steps to current painting processes:

- ○ cleaning of plastic parts
- ○ surface treatments
- ○ painting.

5.9.1 Cleaning and surface treatments

5.9.1.1 Cleaning of plastic parts

Usually parts are soiled by dust, lint, mould release residues, greases, fingerprints . . .

Cleaning eliminates these pollutants and, for some, the surface oxidation . . .

Two major processes are used:

- Solvent cleaning, the oldest method, preferably in the vapour phase. There are severe restrictions on the use of solvents, chlorinated ones in particular, and safety, environmental and fire risks. Convenient solvents, which must be compatible with the substrate, can dissolve oils, greases and other organic contaminants. Generally, the parts

are then dried to vaporize the solvent but not in some cases. In these cases, the swelling of the polymer favours the adsorption of primers. Solvents can be applied by:
  - vapour degreasing
  - dipping in a simple or ultrasonic bath
  - wiping . . .
- Aqueous cleaning, in which spraying of aqueous acidic or alkaline detergent solutions is followed by normal and deionized water rinses. Strong detergents dissolve greases, oils and possibly oxides. It is necessary to rinse thoroughly to avoid later attacks.

5.9.1.2 Surface treatments of plastic parts

Surface treatments can:
- physically change the surface to permit the mechanical anchorage of the paint
- chemically change the surface material to create active chemical sites or a layer of a new material
- chemically change the surface material to enhance the wettability.

Some processes are usable for metals and polymers; others are specific to polymers or to metals.

These processes are aggressive and can be harmful, hazardous and environmentally damaging, requiring safety precautions in respect of local regulations.

Some of them are described in the following as examples.

Abrasion: to abrade the surface to eliminate oxides, etc. by mechanical means such as brushing, sanding, blasting, sandpapering . . .

If the substrates are greasy, oily or polluted it is necessary to clean them before abrading. Otherwise, the pollutants are carried deep in the grooves created by the abrasion.

Chemical pickling: chemicals are used to eliminate oxides without etching the bulk material.

Chemical etching: chemicals are used to eliminate oxides, to attack the surface layer of the material and/or to create reactive sites. The processes depend on the plastics.

The most commonly used are:
- Chromic or sulfo-chromic acid etching, for polyolefins, polystyrene, ABS, polyacetal, polyphenylene ether . . . These treatments have two effects:
  - forming surface irregularities for a mechanical anchorage.
  - creating reactive sites such as hydroxyl, carbonyl, carboxylic, sulfuryl . . .
- Oxidation by flame treatment for polyolefins: exposure to a flame of methane, propane or butane and oxygen in excess for a very short time (less than 0.2 seconds) to create oxidation and reactive sites such as hydroxyl, carbonyl, carboxyl . . . Particularly used for polyethylene and polypropylene.
- Oxidation by ultra-hot-air treatment for polyolefins: exposition to a blast of hot air (roughly 500°C) for a short time to oxidize the surface and create reactive sites such as hydroxyl, carbonyl, carboxyl, amides . . . Rather similar to flame treatment, it is particularly used for polyethylene and polypropylene.
- Sodium naphthalene etching or Tetra Etch for PTFE: improves the surface roughness and creates unsaturated bonds, carbonyl and carboxyl groups.
- Surface grafting of chemical species to improve the chemical bonding. Can be helped by simultaneous gamma or other irradiation. It is particularly used for polyethylene.
- The attack must be superficial and the parts must be thoroughly rinsed to avoid subsequent degradation.

Physicochemical etching

- Corona discharge: discharge of a high frequency (10–20 kHz), high voltage (20 kV for example), alternating current in air at atmospheric pressure. This treatment has two effects:
  - ○ forming surface irregularities for a mechanical anchorage
  - ○ creating reactive sites such as hydroxyl, carbonyl, carboxylic, hydroperoxide, aldehyde, ether, ester . . .

This process is not suitable for parts with very pronounced 3D shapes. On the other hand, it is well suited to films and sheets. The corona discharge generates ozone that can harshly attack some polymers.

- Plasma treatment: discharge of a high frequency (kHz to GHz), alternating current in gaseous argon, helium, nitrogen, oxygen or CF_4, NH_3 . . . under low pressure. The results depend on the gas used. There are several theories on its effects: surface crosslinking, creation of reactive sites, chain scissions . . . Plasma is used to treat polyethylene, saturated polyesters, PTFE . . .
- UV treatment: exposure to high-intensity UV light promotes chain scissions, crosslinking and reactive site formation. It is particularly used for polyethylene.

5.9.2 Decoration, marking

Numerous processes can be used for the decoration and marking of thermoplastics and thermoplastic composites, including for example, without claiming to be exhaustive:

- painting
- in-mould decoration, in-mould labelling
- metallization
- printing
- laser marking . . .

The choice of the right paint depends on:

- the chemical and physical compatibility with the plastic
- the possibility to obtain the desired decorative effect
- the preservation of all functional properties during the entire service life
- the suitability for the chosen application technique
- the ability of the thermoplastics to be painted to withstand the heat or UV radiation needed for any subsequent paint curing.

The application processes are, for example, spraying, brushing, dipping, roller coating, electrostatic painting . . .

For in-mould decoration or in-mould labelling, a decorated film or printed label is precisely located in the empty mould. The molten plastic then adheres onto the film or label during injection. Film is mechanically clamped. The label can be fixed in the mould by electrostatic charge.

Metallization can be applied by batch or continuous vacuum metallizing, sputtering and electroplating.

There are a multitude of printing techniques such as, for example, silk screen printing, gravure or offset, hot stamping, hot stamping foil, fill and wipe process, pad printing, thermal transfer printing, ink-jet printing, hydrographics, laser marking . . .

EMI shielding: for RF shielding and antenna dishes, a metal wire mat structure can be located in the empty mould and then impregnated by the flowing plastic. The metallizing processes already quoted and zinc arc spray are also available as well as coatings based on nickel and conductive resins such as acrylics or polyurethanes.

5.10 Assembly of fabricated parts

Thermoplastics have different aptitudes for welding and joining. Table 5.7 displays general indications, which should be verified by consultation with the producer of the selected grades and by tests under operating conditions.

The reinforcement of thermoplastics complicates welding, solvent joining and adhesive bonding.

Table 5.7 General indications for the assembly of thermoplastics

	Welding			Adhesive bonding
	Thermal	HF	Ultrasound	
ABS	Good	Fair to good	Good	Good
Cellulosics	Good	Fair to good	Fair	Good
PA	Good	Fair to good	Good	Good
PC	Good		Good	Good
HDPE	Good	Unsatisfactory	Fair	Fair
LDPE	Good	Unsatisfactory	Fair	Fair
PET, PBT	Fair	Fair to poor	Good	Fair
PTFE	Fair	Unsatisfactory		Difficult
PMMA	Good	Fair	Good	Good
POM	Good		Good	Fair
PP	Good	Unsatisfactory	Good	Fair
PPE	Fair		Fair	Good
PS	Good	Unsatisfactory	Good	Good
EPS	Good			Good
TPU	Good	Fair		Good
Soft PVC	Fair	Good	Fair	Fair to good
PVC	Fair	Good	Good	Good
PVDC	Good	Fair to good		
PSU		Unsatisfactory	Good	
Foamed PVC		Good		

5.10.1 Welding

Welding can be very simple or sophisticated allowing short or large runs:

- suitable for short or continuous joining
- can avoid the design and tooling constraints of complex parts by assembling several mass-production pieces (sheets, tubes, films . . .) or more-simple parts produced with economical tools
- needs skilled workers
- machinery is generally relatively inexpensive but there is a lot of labour.

Apart from ferromagnetic welding, to a certain extent, welding is generally unsuitable for assembling materials of different chemical natures. It is even advised to weld only those materials with physicochemical states that are as close as possible. The three main parameters influencing the quality are temperature, time and pressure. Particular care must be taken of cleanliness: one should not hesitate to clean and even refresh by abrasion the surfaces to be welded. For old parts, it is necessary to remove the surface to reach uncorroded and unoxidized matter. In the repair of tanks, pipes, etc., it can be impossible to re-weld if thermoplastics are bulk impregnated with chemicals.

Thermal welding

The thermoplastics to be welded can be directly melted and welded or one can use a rod of the same thermoplastic to make the joint.

Heat can be supplied by a hot tool or by hot air:

- Hot bars or plates are used to weld films, tubes, plates, profiles made out of PVC, PE, PP, etc. Welding correctly carried out makes it possible to reach welding ratios (% of the tensile strength of the original thermoplastic) of the order of 75% up to 90% for PVC, 65% up to 90% for PP, 50% up to 100% for PE. Warming can be generated by a sequence of impulses.
- Welding guns generate hot air to heat the surfaces to be welded and the welding rod.

Friction joining

Heat is generated by friction between the two parts to be welded by:

- Rotation for circular parts: the welding section must be well studied. This process is used, for example, for small lighter tanks.
- Vibration for noncircular objects: the machines are more sophisticated.
- Ultrasound in the 20–30 kHz range.

Radio-frequency welding

Polar thermoplastics whose loss factor is high enough can be welded in a radio-frequency field that excites the polar molecules and generates heat. This method is very much used for the welding of sheets of PVC for clothing, bags, inflatable goods, packaging . . .

Welding by Joule effect

An electric current heats an electrical resistor sunk in a sleeve of thermoplastic and causes its melting by the Joule effect.

The welding of gas pipes made out of PE is a very specialized application.

Electromagnetic bonding

A joint of the same thermoplastic to be welded or compatible with it, containing ferromagnetic particles, is located between the two surfaces to be welded. When passed through an induction coil, this joint melts and causes melting of the surfaces in contact.

This process can permit welding of chemically different thermoplastics and even paper in certain cases.

5.10.2 Adhesive bonding

Joining using adhesives does not present particular difficulties and is used to assemble thermoplastics with plastics, composites or metals. Joining avoids damaging the parts by drilling and allows an excellent distribution of the stresses. The parts can have structural functions if the adhesive is correctly chosen, and if care is taken to:

- make the adhesive joints work in shear and not in peel
- have a sufficient stuck surface to bear the load. In all cases, it should be remembered that a permanent or cyclic loading is more detrimental than an instantaneous one

- prepare surfaces well
- choose an adhesive that is physically and chemically compatible with the two parts to be assembled
- verify the ability of the two parts to be assembled to withstand the possible subsequent curing of the adhesive.

All types of adhesives are usable, for example:

- *Hot-melt adhesives*: the molten adhesive wets the surfaces of the plastics to be assembled and interlocks them while solidifying again on cooling. It is necessary for the materials to be assembled to tolerate the temperature of the molten adhesive. Joining is sensitive to the temperature, which involves the melting of the adhesive joint. However, some hot-melt adhesives crosslink after joining and become less sensitive to heat.
- *Non-reactive solution adhesives*: the solvent wets the surfaces to be assembled, then evaporates involving the cohesion of the parts to be assembled by the adhesive joint. The heat behaviour is generally moderate. If the solvent swells the materials to be assembled, there can be migration of materials and subsequent cracking by residual internal stress relaxation.
- *Reactive adhesive*: after wetting the surfaces to be assembled, there is polymerization of the adhesive joint. The heat behaviour can be better than with the preceding methods.

5.10.3 Mechanical assembly

Clink and spring work, clamping, snap-fit

The impact strength of certain plastics allows their assembly by stretching as click-and-spring work, clamping, snap-fit, etc. To make this task easier, the assembly angle must be shallow, generally lower than 30°, and the strain must be much lower than the elastic limit.

Riveting

If the rivet is not of the same material as the part, it can later induce stresses by differential thermal expansion. Two techniques of riveting are used:

- hot: pre-heating of the rivet, and then crushing of the head
- with ultrasound: properties and durability are generally better.

Screwing

Autotapping screws: the screw type, the diameter of the hole that receives the screw and the tightening torque depend on the plastic used. Repeated screwing and unscrewing is not advised. To a first approximation, and as examples, it is sometimes stated that:

- the external diameter of embossing must be twice as large as the external diameter of the screw
- the length of the threads engaged in the embossing material must be twice as long as the external diameter of the screw
- embossing should not be located on a welded line and the screw should not engage totally.

The use of inserts allows repeated screwing/unscrewing, higher tightening torques and limits the risks of failures.

Press fitting

Subject to correct calculation of the diameters, press fitting of metal and plastic parts gives good results. Durability is conditional on the creep behaviour of the plastic. The metal elements must be round, smooth and clean, and the metal must be compatible with the selected plastic. Embossing must be distant from weld lines and the moulding must be particularly careful to limit residual stresses.

5.11 Repair possibilities: a significant thermoplastic advantage for large parts

Large thermoplastic-made parts have the significant economical advantage of being rather easy to repair.

A skilled professional can correctly repair the most-common thermoplastic parts, such as piping, geomembranes, inflatable boats and structures, by welding or gluing patches after removal of the soiled and damaged part.

5.12 Annealing

To improve the behaviour of the parts in harsh environments, it can be useful to anneal internal constraints by controlled exposure to high temperature. This decreases viscosity allowing a rearrangement of the molecules and a lowering or elimination of the internal constraints.

Annealing is a difficult process that can also bring some drawbacks and must be carefully used. It must be carefully studied in cooperation with the producer of the considered thermoplastic.

To avoid distortion of the parts, it is necessary to choose a treatment temperature lower than the HDT and far from the glass transition temperature. The advised temperature is often 10–15°C below the HDT.

The following examples of procedures are given as general indications. It is crucial to consult the producer of the grade used and rigorous tests must be undertaken before any application. These annealing processes need high temperatures; it is therefore necessary to comply with the health and safety rules.

There are generally three steps:

- heating steps can be from a few hours to one day at constant or increasing temperature in the range from 150°C up to 260°C depending on the thermoplastic
- holding steps depend on the thickness of the parts, varying from tens of minutes to several days
- cooling steps depend on the thickness of the parts and the holding temperature varying from a few hours to one day.

The treatment environment can be, for example, air, nitrogen, oil . . .

References

Technical guides, newsletters, websites

3 M, Arburg, Atofina, Battenfeld, Billion, BMB, Boy, Branson Ultrasons, Coperion, Devcon, Engel, Frimo-Huber, Husky, Illig, Krupp, Loctite, Medical Murray, MuCell, Negri-Bossi, Netstal, Nissei, PPG, PRW, Reifenhauser, Sesame, Sidel, Sika, Sipa, Tubulam, Vetrotex . . .

Reviews

[1] *Modern Plastics Encyclopaedia* (McGraw-Hill Publications)
[2] *Modern Plastics International* (Canon Communications LLC, Los Angeles, CA, USA)
[3] *Reinforced Plastics* (Elsevier Ltd)

Chapter 6

Thermoplastic composites

6.1 Definitions

The composite materials treated here are made of:

- a thermoplastic matrix or binder
- an immiscible reinforcement closely bound to the matrix or the binder: fibres of high aspect ratio (length versus diameter), wires, mats, fabrics, foams, honeycombs, plywood and so on.

Hybrids combine plastics or composites with other materials such as metal, wood, etc.

Plastics filled with talc or other powders are not taken into account in this chapter.

The composite properties depend on:

- the matrix
- the reinforcement
- the adhesion between matrix and reinforcement.

The reinforcement, as its name indicates, bears the stresses. When these reinforcements are not randomly distributed, which is often the case, the properties are anisotropic, being enhanced in the reinforcement direction.

The matrix or binder ensures the cohesion of the composite, and distributes and damps the impacts or stresses to protect the composite from the environment.

The cohesion of the matrix and reinforcements can be damaged, even in the bulk, by moisture or chemical surface attack. The fluids can propagate to some depth by absorption and wicking: consequently it is important that a skin protects the reinforcements from direct contact with the external environment.

Composite processing can obtain nearly all part shapes including: plane or warped surfaces; profiles; hollow parts; bulky parts; sheets, slabs and plates; parts with inserts, etc.

Faced by the diversity of plastic composites and their fast evolution, the information here is deliberately general and treats the most widespread cases only. It will be essential for the designer to work in close cooperation with the producers and manufacturers to fix his final choice.

6.2 Reminder of some basic principles

When designing composites, it is necessary to respect some essential rules:

- Choose the reinforcement according to the loads: if the part properties must be 3D-isotropic, adopt a random reinforcement. If a 2D isotropy is sufficient, it is possible to use a balanced woven or mat reinforcement.
- Lay up the reinforcements according to the stresses so that they really withstand the loads: the planes of the reinforcements will be parallel to the tensile stresses, and perpendicular to the shear, flexural or compressive stresses.
- Choose a matrix compatible with the ambient conditions of use.
- Take care to preserve the matrix or its skin after moulding.
- Proscribe finishing treatments with products or temperatures incompatible with the matrix.

Among the other elementary rules, we will quote:

- Avoid significant thickness variations and maintain those within reasonable limits by arranging reinforcing ribs if the mechanical stresses are too high.
- Avoid sharp angles.
- Draw sufficient draft angles to be able to demould.

- Take care with embossing and insert hole solidity, which could then be zones of maximum stress.

Another important parameter is the choice between thermoplastic and thermoset composites, which are competing for multiple applications. Apart from their characteristic properties, the two families of plastics differ by general features such as:

- thermoplastic composites do not need curing, are easier to recycle and can be welded
- thermoset composites are well-established, well-known and broadly manufactured products, easier to process by certain methods, but they must be cured.

These few elementary concepts are a simple reminder and we should remember that:

- computing software specifically developed for composites is available
- it is imperative that the part design and the processing study are carried out with the manufacturer who will make the part.

The processing methods will be selected according to the importance of the series, part sizes and targeted properties. Table 6.1 suggests some processes, for thermoplastic and thermoset composites, according to the part sizes and production outputs.

Table 6.1 Examples of the suggested process choice versus the part characteristics

Part size (max. area in m^2)	Thickness (mm)	Output (units)	Method	Examples of parts
Limited	Limited	Mass production >10 000	High pressure injection	Electrical & electronic parts
Up to 4	Limited	Medium output	Stamping	Automobile parts
Up to 5	1–6	Mass production	Hot compression moulding of mats and preforms	Car body elements
Up to 5	2–10	Mass production	Hot compression moulding of prepregs	Car body elements
Up to 10		1000–250 000	RRIM	Housings
Up to 15	1–10	200–10 000	Resin injection	Car body elements
Up to 15	3–10	500–20 000	Low-temperature & pressure compression moulding	Car body elements
Up to 20		<5000	Autoclave	Aeronautics elements
Up to 30	3–15		Centrifugal moulding	Tubes, pipes
Limited section	3–20	Continuous	Pultrusion	Profiles
Limited section	1–4	Continuous	Continuous impregnation	Roof sheeting
Diameter up to 25 m with special equipment*	1–10 and more	Low to medium output	Filament winding	Pressurized tanks
Virtually unlimited, <300	Unlimited, often 2–10	<1000	Hand lay-up	Ships
Virtually unlimited	Unlimited, often 2–10	<1000	Spray lay-up	Mine hunters

*Manufacture using specific material developed for a particular part

6.3 Composite mechanical performances according to the reinforcement type

Although the reinforcements are intended to bear the loads, the matrices play a significant role in composite failure by damping sudden stress variations, by distributing the loads and by protecting the reinforcements.

In this section we will present some modelling developments for various forms of composites. The purpose is not to propose a calculation method – excellent computer software programs exist for that – but to show the broad strength range according to the composite structure, to underline the separate effects of fibres and matrix, and to examine the effects of some service conditions. These examples cannot be used for design calculations.

6.3.1 Reinforcement by randomly distributed short fibres

Depending on the rigidity and the ductility of the matrix, when a stress is applied to a short glass fibre reinforced composite the following steps can be observed:

- initiation of cracking of the resin around the fibres
- progressive loss of fibre/matrix cohesion
- propagation of cracks in the matrix
- rupture of fibres
- fibre stripping.

All other things being equal, most of the mechanical performances increase with:

- fibre length above a critical threshold up to a maximum, as shown schematically in Figure 6.1(a)
- fibre aspect ratio
- fibre level, as shown schematically in Figure 6.1(b) (other curve shapes can be encountered).

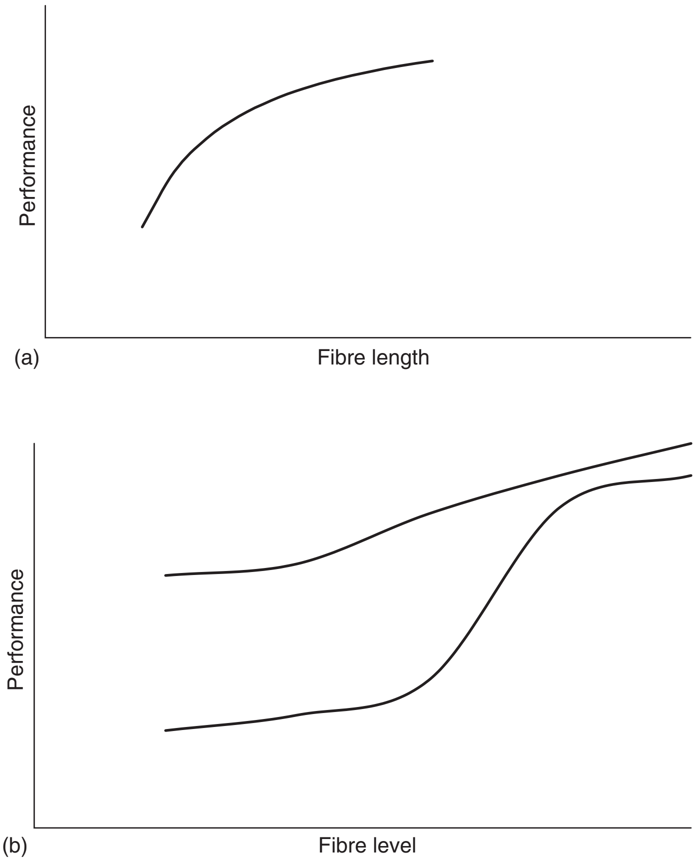


Figure 6.1. (a) Schematic curve of performance versus fibre length; (b) Schematic curve of performance versus fibre level

Modelling of a real case: reinforcement of PA 66 with short glass fibres

Final performance can be considered as the sum of:

- the contribution of the matrix in proportion to its level in the final composite
- the contribution of the fibre in proportion to its level in the final composite.

For example, for a 40% GF reinforced PA:

- the specific tensile strength of PA, measured on samples of pure PA, is 85 MPa
- the weight fraction of PA is 0.6
- the contribution of PA to the tensile strength is $85 \times 0.6 = 51$ MPa
- GF's 'specific tensile strength' is 410 MPa
- the weight fraction of GF is 0.4
- GF's contribution to the tensile strength is $410 \times 0.4 = 164$ MPa
- the tensile strength of the composite is $51 + 164 = 215$ MPa, compared to an experimental value of 225 MPa, that is, an error of −4%.

The 'specific tensile strength' of glass fibres is a theoretical value computed from experimental data relating to several composites with fibre levels varying from 10% up to 50%. This value depends on the glass fibre, its sizing, the matrix, the possible use of coupling agents, and the ambient conditions. For the same composites, if the tensile strengths are measured on samples stored in air at 50% RH, the 'specific tensile strength' of glass fibres is significantly lower (298 MPa).

Note in both cases that the 'specific tensile strength' of glass fibres is very much higher than the specific tensile strength of the matrix. The ratio is 4.8 for dry samples and 3.5 at 50% RH.

Figure 6.2 displays experimental data concerning tensile strengths measured on dry samples (0% RH) and on samples stored in 50% RH air. The continuous lines are modelled tensile strengths.

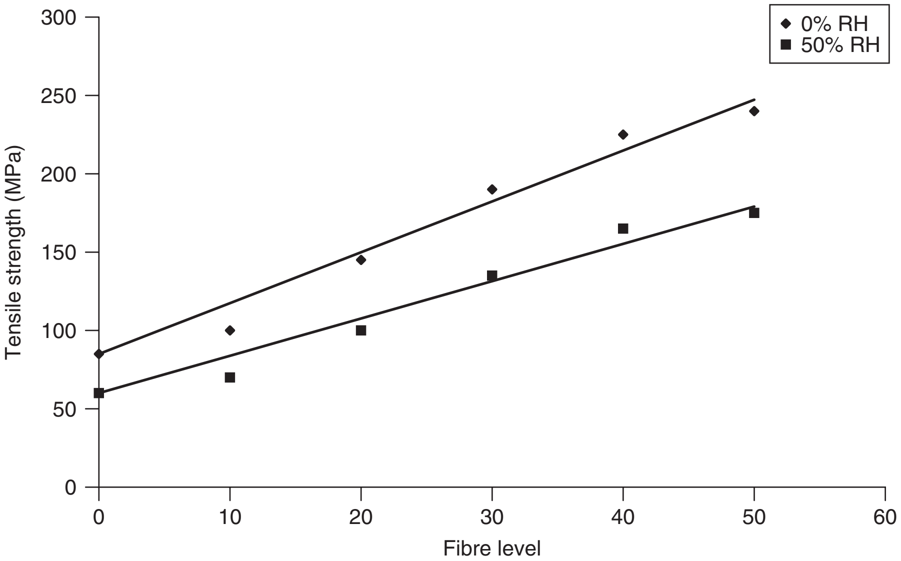


Figure 6.2. Modelling of PA/GF tensile strength versus fibre level

Note in both cases the optimistic modelled values for the low levels of fibres, with an overestimation of 17–18% for the composite reinforced with 10% glass fibre.

6.3.2 Reinforcement by arranged continuous fibres

Again, the following examples of modelling are textbook cases that cannot be used for design purposes.

6.3.2.1 Unidirectional reinforcement

The resistance of the composite in the reinforcement direction can be roughly estimated starting from a simple rule of mixtures, if the matrix transmits the load completely until failure:

$$\sigma = V_{\text{fibre}} \times \sigma_{\text{fibre}} + V_{\text{matrix}} \times \sigma_{\text{matrix}}$$

where V_{fibre} and V_{matrix} are the volume fractions of fibres and matrix, and σ_{fibre} and σ_{matrix} are the strengths of fibres and matrix, respectively.

For example, for a unidirectional (UD) PEEK/carbon fibre composite where $V_{\text{fibre}} = 0.32$ and $V_{\text{matrix}} = 0.68$, $\sigma_{\text{matrix}} = 100\,\text{MPa}$ and $\sigma_{\text{fibre}} = 3530\,\text{MPa}$, the predicted strength is:

$$\sigma = (0.32 \times 3530) + (0.68 \times 100) = 1198\,\text{MPa}$$

The experimental result is 1570 MPa, namely an error of −24%.

In the transverse direction, the strength will be much lower, and at best equals that of the matrix. In the last example, the strength measured in the transverse direction is very close to 100 MPa.

To play its role until failure, the matrix must have an elongation at break better than that of the reinforcement, that is:

- 3–5% for glass fibres
- 0.5–2% for carbon fibres
- 2–4% for aramid fibres.

6.3.2.2 Reinforcement with two orthogonal layers

For the reinforcement direction of one or other layer, the calculation method is the same as in the last example.

For the thickness direction, the modulus of the reinforcement being very much higher (20 times, for example) than that of the matrix, the matrix between the reinforcement layers is subjected to significant deformation that is sometimes qualified as ‘amplified strain’.

6.3.3 General approximate method for strength estimation

Again, these examples cannot be used for design calculations.

PPG in its *Introduction to glass fibre reinforced composites* proposes a calculation method for the strength estimate based on four principles:

- evaluation of the ‘contribution of glass fibres to strength’
- use of a coefficient α assigned to the form of the reinforcement
- use of a coefficient β determined by experiments according to the length of fibres
- application of the law of mixtures.

Evaluation of the 'contribution of glass fibres to strength'

Taking into account the fragility of the fibre to abrasion, the risks of glass fibres breaking during processing, etc., the 'contribution of glass fibres to the strength' of the composite is fixed at a maximum of 2300 MPa in the most favourable case of a matrix with high elongation at break (3.5–5%). For matrices of lower elongations, the contribution of glass fibres to the strength of the composite is reduced, for example:

- 2000 MPa for a matrix with 3% elongation at break
- 1750 MPa for a matrix with 2.5% elongation at break
- 1500 MPa for a matrix with a maximum 2% elongation at break.

An additional reduction coefficient of 0.9 or 0.95 can be assigned to the fabrics according to their armour or treatments such as those intended to remove size.

Use of a reduction factor assigned to the reinforcement form and loading direction

Some values of α are given as examples according to the reinforcement and the relative direction of stresses:

- 1 for UD reinforcement and loading in the reinforcement direction
- 0 for UD reinforcement and loading in the orthogonal direction
- 0.5 for bi-directional reinforcement and loading in one reinforcement direction
- 0.25 for bi-directional reinforcement and loading at 45° to the reinforcement directions
- 0.2 for multidirectional reinforcement in space.

Use of a coefficient β determined by experiments according to the fibre lengths

Examples of coefficient β are indicated for neat and filled matrices:

- 0.25 for 10 mm fibre length and a filled matrix
- 0.45 for 30 mm fibre length and a filled matrix
- 0.6 for 30 mm fibre length and a neat matrix
- 0.55 for 50 mm fibre length and a filled matrix
- 0.65 for 50 mm fibre length and a neat matrix.

Application of the law of mixtures

The law of mixtures is classically applied by replacing the strength of the fibres by their contribution to the strength of the composite, and by taking account of the α and β coefficients:

$$\sigma = \alpha \times \beta \times V_{\text{fibre}} \times \sigma_{\text{fibre}} + V_{\text{matrix}} \times \sigma_{\text{matrix}}$$

Here, σ_{fibre} is the 'contribution' of the glass fibres to the composite strength and not their actual strength.

Examples

1. Glass fabric reinforced polypropylene composite

$$V_{\text{fibre}} = 0.34$$
$$V_{\text{matrix}} = 0.66$$
$$\alpha = 0.5 \text{ in warp or weft direction}$$

The 'contribution to strength' of the glass fibres is valued at its maximum, because of the high elongation at break of the polypropylene, that is, 2300 MPa

$$\sigma_{\text{matrix}} = 40\,\text{MPa}$$

$$\sigma = 0.5 \times 0.34 \times 2300 + 0.66 \times 40 = 417\,\text{MPa}$$

This value exceeds the value recorded in the literature, 350 MPa; that is to say, there is an error of + 19%. However, this result can be usable in the absence of other, more-precise information.

2. Glass mat reinforced polypropylene

$$V_{\text{fibre}} = 0.2$$
$$V_{\text{matrix}} = 0.8$$
$$\alpha = 0.2 \text{ because the distribution of fibres is multidirectional in space}$$
$$\sigma_{\text{matrix}} = 40\,\text{MPa}$$

The elongation at break of the resin is higher than 3%, thus the maximum value of 2300 MPa is used for the 'contribution to strength' of the glass fibres.

$$\sigma = 0.2 \times 0.65 \times 0.20 \times 2300 + 0.8 \times 40 = 92\,\text{MPa}$$

This result is slightly higher than the upper limit of the range recorded in the literature, 70–85 MPa.

6.4 Composite matrices

At the outset of the composites industry, the matrices were unsaturated polyesters. Then other thermosets were developed but some years ago the manufacture of thermoplastic composites began and their development is now faster than that of thermoset-based composites.

At present, the consumption of plastics for matrices is roughly estimated at:

- 65% thermosets
- 35% thermoplastics, particularly polypropylene but also thermoplastic polyester and advanced thermoplastics such as polyetherimide, PEEK, etc.

For the thermoplastics, it is necessary to distinguish:

- Short glass fibre reinforcement: the main thermoplastics are offered in such grades. Some short carbon or aramid fibre reinforced resins are also marketed.
- Mat and continuous glass fibre reinforcements: theoretically all the thermoplastics are usable in these forms, but up to now developments have concentrated on polypropylenes (PP), polyamides (PA) and thermoplastic polyesters (PET); fibre-reinforced PEEK, polyetherimide (PEI) and polyphenylene sulfide (PPS) are used for high-performance applications. They are presented in a range of forms from stampable sheets to pellets, prepregs, ribbons, impregnated or coated continuous fibre rods. More rarely (as in the case of PA 12, for example), the thermoplastic is provided in liquid form.

The thermoplastics can be classified according to their consumption into:

- commodities: polyethylene (PE), polypropylene (PP), PVC, polystyrene (PS)
- technical thermoplastics: polyamide (PA), polyacrylics (PMMA), polyacetal (POM), polycarbonate (PC), polyphenylene oxide (PPO) or polyphenylene ether (PPE), thermoplastic polyesters (PET, PBT). Reinforced cellulosics are scarcely used

- speciality thermoplastics: polysulfone (PSU), PPS, fluoroplastics, PEEK, PEI, polyamide imide (PAI), liquid crystal polymers (LCP).

Advantages of thermoplastics versus thermosets

Suppression of the condensation or reticulation or polymerization step, easier recycling and welding possibilities, but these advantages are often disrupted by the reinforcement. The general properties are those of the basic polymer with a high reinforcement effect.

Drawbacks versus thermosets

Reversibility of thermoplasticity for applications involving heat; lower creep resistance than thermosets; disadvantages of the basic polymer.

Uses

The short glass fibre reinforced grades are used for all sorts of injected parts.

The mat and continuous glass fibre reinforced grades have specific uses:

- Mass production parts: bumpers, soundproofing shields, cross-pieces, inserts for dashboards, seat frames, containers, welding helmets, ventilator housings, base of lawnmowers, taping of pipes, pipelines, tanks, long fibre reinforced injected parts.
- High-tech products with PEEK, PPS, PEI, etc. matrices for aeronautics and other high-tech applications.

6.4.1 Some basic characteristics of thermoplastic matrices

The properties of the thermoplastics are treated in detail in Chapter 4, but for the reader's ease we will briefly recall here the most interesting characteristics relating to their use as a matrix.

Polyethylene (PE)

Advantages

Low cost; easy to process; chemically inert; good impact strength; low water absorption; low density; high insulating properties even in wet environments; low coefficient of friction; suitable grades for food contact.

Drawbacks

Limited UV resistance; risks of environmental stress cracking; heat and creep sensitivity; low rigidity; high shrinkage, difficult gluing.

Cost

The cost roughly ranges from €1 up to less than €2 per kg.

For recycled resins, according to the form and cleanness, the price range is roughly €0.5 up to €1 per kg.

Polypropylene (PP)

Advantages

Good mechanical properties at ambient temperature; price; cost/performance ratios; chemically inert; low absorption of water; low density; good electrical insulating properties even in wet environments; impact and fatigue behaviour for suitable grades and stresses; special grades for food contact.

Drawbacks

Risks of sensitivity to UV; limited impact strength of some grades; low-temperature and creep behaviour; low rigidity; difficult gluing.

Cost

The cost ranges roughly from €1.2 up to €2 per kg.

For recycled resins, according to the form and cleanness, the price range is roughly €0.5 up to €1 per kg.

Polyvinyl chloride (PVC)

Mechanical properties different greatly according to whether the PVC formulation is rigid or plasticized.

Advantages

Rigid PVC: rigidity at ambient temperature; low cost; chemical resistance except to some solvents; possible food contact and transparency; naturally fire retardant; dimensional stability; easy to weld and stick.

Flexible PVC: characteristics depend broadly on the formulations; flexibility; improved low-temperature behaviour; fire-retardant grades; low cost; possible food contact and transparency; easy to weld and stick.

Drawbacks

Environmental standards, regulations and suspicions handicap the development of the PVCs.

Rigid PVC: natural UV sensitivity, but special grades benefit from long-time outdoor-exposure guarantees; sensitivity to heat, creep, aromatic or chlorinated hydrocarbons, esters and ketones; low-temperature brittleness; high density; toxicity and corrosivity of smoke in fires; less easy injection.

Flexible PVC: natural UV sensitivity, but special UV-stabilized grades; higher sensitivity to heat, creep and chemicals; high density; higher flammability if plasticizers are flammable; toxicity and corrosivity of smoke in fires.

Cost

The cost ranges roughly from slightly less than €1 up to less than €2 per kg.

For recycled resins, according to the form and cleanness, the price range is roughly €0.4 up to €0.5 per kg.

Polystyrene (PS)

Polystyrene can be modified, for example:

- polystyrene acrylonitrile: SAN
- acrylonitrile-butadiene-styrene: ABS
- acrylonitrile styrene acrylate: ASA.

Advantages

PS: low cost, transparency, rigidity, impact grades, dimensional stability, food contact grades, insulating properties, easy to weld and stick.
SAN: high rigidity, better chemical resistance, glossy surface, scratch resistance.
ABS: better impact and low-temperature behaviours, better chemical resistance similar to SAN.
ASA: better weathering resistance.

Drawbacks

PS: Sensitivity to UV, low temperatures, impact (apart from butadiene-modified grades), solvents, heat; readily flammable with dripping and dense black smoke; sometimes difficult machining.
SAN: like PS but more difficult to process; cost is a little higher.
ABS: like SAN but opaque except copolymers; lower chemical resistance; higher cost.

Cost

The price ranges are roughly:

- €1.4 up to €2.2 per kg for PS
- €1.5 up to €2.5 per kg for SAN
- €1.5 up to €2.5 per kg for ABS.

For recycled resins, according to the form and cleanness, the price range is roughly €0.4 up to €0.7 per kg for PS or ABS.

Polyamides

The polyamide family is subdivided into very different subfamilies such as PA 66, which is the oldest, the best known and the most used; PA 6, the cheapest and technically very near PA 66 but far less used; and various more specific PAs, for example, PA 11, PA 12, PA 610, PA 612, PA 46, semi-aromatic PAs, liquid PAs . . .

Advantages

Good mechanical properties; dynamic fatigue behaviour; tribological properties; low coefficient of friction; good heat and cold behaviours; resistance to numerous chemicals such as typical hydrocarbons, oils, greases, solvents and oil products.

PA 66 and 6: good ratio of price versus mechanical performances and fatigue resistance; heat and cold behaviours; friction behaviour (coefficient and wear); resistance to oil products and solvents; very high impact strength of special grades.

PA 11 and 12: flexibility; better behaviour at low temperature; less sensitive to water and moisture.

Drawbacks

Water sensitivity and swelling; limited weathering resistance needing protection for outdoor use; significant shrinkage; limited fire ratings except special grades.
PA 66 and 6: highly hygroscopic. Too dry an atmosphere makes them brittle but an excess of moisture causes swelling, plasticization and a reversible decrease of the mechanical and insulating properties. Saturation swelling can reach 10%.
PA 11 and 12: lower rigidity and heat behaviour.

Cost

The costs are roughly:

- €2.5 up to €3 per kg for PA 6 and 66
- €5.4 up to €6.5 per kg for PA 11 and 12.

Thermoplastic polyesters

The most common are polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).

Their properties are relatively similar except for the higher crystallinity of PBT.

Advantages

Good mechanical and electrical properties; rigidity; fair creep behaviour; fatigue resistance; low moisture absorption; broad range of continuous use temperatures −60°C up to 130°C; UHF transparency.

Drawbacks

Sensitivity to water above 60°C; limited fire behaviour except special grades; limited weathering resistance needing protection for outdoor exposure; medium chemical resistance.

Cost

The cost is roughly of the order of:

- €1.5 up to €3 per kg for PET
- €2.4 up to €3 per kg for PBT.

Polyacrylics (PMMA)

Advantages

Transparency; high UV and weathering resistance; gloss and colour stability; fair mechanical properties, rigidity and creep behaviour at ambient temperature; insulating properties notably arc resistance; food contact for suitable grades.

Drawbacks

Low impact strength; sensitivity to heat except acrylic-imides; environmental stress cracking; attacked by some common solvents.

Cost

The range is roughly:

- €1.6 up to €4 per kg for PMMA
- €4 up to €6 per kg for acrylic-imides.

Polyacetal (POM)

The polyacetals are homo- or co-polymers.

Advantages

Good ratio of cost to mechanical properties; elasticity; fair creep resistance and fatigue behaviour; low moisture uptake; heat and cold behaviours; tribological properties (coefficient and wear); oil and solvent resistance; high impact strength of suitable grades.

Drawbacks

High shrinkage due to the high crystallinity; high coefficient of thermal expansion; sensitivity to light; flammability except special grades; opaque; attacked by strong acids and, for certain grades, by weak acids and bases; density is a little high.

Cost

The cost is roughly €1.7 up to €2.5 per kg for general-purpose or glass-reinforced grades.

Polycarbonate

Advantages

High transparency; high mechanical and insulating properties; natural high impact strength; fair creep and fatigue resistances; low shrinkage and moisture uptake; broad range of service temperatures −100°C to +135°C; food contact and sterilization for suitable grades.

Drawbacks

Sensitivity to light, weathering and hydrolysis, requiring protection for outdoor exposure; flammability except special grades; attacked by bases, oils, chlorinated solvents, ketones; price.

Cost

The cost is roughly €3 up to €4 per kg for neat or glass fibre reinforced grades.

Polyphenylene oxide (PPO) and polyphenylene ether (PPE)

Almost always used as an alloy with polystyrene or polyamide. The latter leads to a better heat resistance.

Advantages

Good ratios for cost versus mechanical and electrical properties; fair creep resistance at room temperature; low moisture absorption; fair heat and cold behaviours; moisture and hot-water resistances; low shrinkage.

Drawbacks

Flammability except special grades; attacked by hydrocarbons, oils, chlorinated solvents, strong mineral acids; cost; high friction coefficient.

Cost

The cost is roughly:

- €2.2 up to €3.4 per kg for neat resins
- €3 up to €5 per kg for glass-reinforced resins.

Phenylene polysulfide (PPS)

The properties of PPS are strongly influenced by the degree of crystallinity, which is optimized by hot processing and post-annealing.

Advantages

Good mechanical and electrical properties; rigidity; good creep behaviour; fatigue resistance; broad range of service temperatures −196°C up to 200/240°C; low shrinkage and moisture uptake; good chemical resistance; good fire behaviour.

Drawbacks

Sensitivity to notched impact; price.

Cost

The cost is roughly €4 up to €8 per kg for reinforced and filled resins.

Fluoroplastics

The fluoroplastics can be classified into three categories:

- perfluoroplastics: PTFE (polytetrafluoroethylene)
  FEP [perfluoropoly(ethylene propylene)]
  PFA (perfluoro-alkoxy)
- fluorochlorinated: PCTFE (polychlorotrifluoroethylene)
- partially fluorinated: ETFE (ethylene-tetrafluoroethylene)
  PVDF (polyvinylidene fluoride).

Advantages

PTFE: exceptional chemical resistance; high heat and cold behaviour; high hot and wet insulating properties; UV, light and weathering resistances; low coefficient of friction; anti-adherent; flexural dynamic fatigue endurance; high resistance to fire; food contact and medical grades; very low water absorption.

PFA: injection and extrusion grades with the same advantages as PTFE.

FEP: injection and extrusion grades with the same advantages as PTFE but a slightly lower performance: 200°C maximum continuous use temperature instead of 260°C.

PCTFE, ETFE: the same advantages as PTFE but lower performance: 150°C maximum continuous use temperature instead of 260°C.

PVDF: excellent weathering resistance; other advantages similar to PCTFE and ETFE; piezoelectric properties.

Drawbacks

All these polymers incorporate high halogen levels that are environmentally harmful.

PTFE: creep and abrasion sensitivity; injection and extrusion are impossible by conventional processes; high dimensional variation at glass transition temperature (19°C); high cost; high density; very difficult to stick; corrosive and toxic smoke generated in fires.

PFA: the same drawbacks as PTFE except injection and extrusion possibilities; very high cost.

FEP: the same drawbacks as PTFE except injection and extrusion possibilities; very high cost.

ETFE, PCTFE, PVDF: the same drawbacks as PTFE except injection and extrusion possibilities; high cost; lower resistance to heat and chemicals.

Cost

The costs are roughly:

- PTFE: €10 up to €16 per kg
- FEP: €17 up to €25 per kg
- PFA: €30 up to €45 per kg
- ETFE: €20 up to €30 per kg
- PCTFE: €80 up to €90 per kg
- ECTFE: €21 up to €30 per kg
- PVDF: €12 up to €15 per kg.

Polysulfone (PSU)

Some PSU derivatives are also marketed, such as:

- polyethersulfone – PESU – more heat resistant than PSU
- polyarylsulfone.

Advantages

Good mechanical and electrical properties; fair creep resistance; fatigue behaviour; fair shrinkage; fair moisture uptake; heat and cold behaviours with a broad range of continuous use temperatures −100°C to +150/180°C; optical and UHF transparency; food contact and sterilization for suitable grades.

Drawbacks

Sensitivity to light, requiring protection for outdoor exposure; flammability except special grades; attacked by aromatic hydrocarbons, chlorinated solvents, ketones; cost.

Cost

The costs are roughly:

- PSU: €6 up to €11per kg
- PESU: €6 up to €11 per kg.

Polyetheretherketone (PEEK)

Advantages

Good mechanical, chemical and electrical properties; rigidity; good creep resistance; fatigue behaviour; fair moisture uptake; fair shrinkage; heat behaviour with continuous use temperature up to 250°C; high-energy radiation behaviour.

Drawbacks

Sensitivity to light requiring protection for outdoor exposure; cost justified by the performances.

Cost

The costs are roughly: €44 up to €60 per kg.

Polyetherimide (PEI)

Advantages

Good mechanical and electrical properties; rigidity; fair moisture uptake; fair shrinkage; heat behaviour with continuous use temperatures up to 170/180°C; naturally resistant to UV, light, weathering; naturally fire resistant; optical and UHF transparency; food contact and sterilization for suitable grades.

Drawbacks

Sensitivity to some chemicals; cost justified by the performance.

Cost

The costs are roughly €9 up to €11 per kg.

Polyamide imide (PAI)

Advantages

Good thermo-mechanical and electrical properties; rigidity; impact strength; fatigue endurance; heat behaviour with continuous use temperatures from −196°C up to +220°C; tribological properties for suitable grades.

Drawbacks

Sometimes difficult processing; high cost justified by the performance.

Cost

The costs are roughly:

- €30 up to €52 per kg for neat and glass-filled grades
- €55 up to €67 per kg for carbon fibre reinforced grades.

Liquid crystal polymers

Advantages

Good thermo-mechanical, chemical and electrical properties; rigidity; gamma irradiation resistance; UHF transparency; good creep resistance and fatigue behaviour; low moisture uptake; low shrinkage; heat behaviour; fire resistance; low coefficient of thermal expansion.

Drawbacks

Cost justified by the performance; particular mould and part design; density; anisotropy.

Cost

The cost is roughly €12 up to €37 per kg.

Schematic comparison of thermoplastic matrix properties

Figures 6.3 to 6.6 compare the main mechanical and thermal properties of the main neat thermoplastics.

It should be recalled that the tensile strength and modulus of composites are often mainly determined by fibre performances, the matrix having a lesser effect. In contrast, the continuous use temperature generally depends on the matrix.

6.4.2 Influence of the matrix on composite properties

Table 6.2 (p. 787) displays some examples of properties obtained with various matrices for the same type of reinforcement.

6.5 Reinforcements

The most common reinforcements currently used are:

- fibres and sets containing fibres
- foams
- flat materials: honeycomb, wood, plywood.

Nanofillers are also under development.

Examples of specific ISO standards concerning reinforcements

ISO 1043-2:2000 Plastics – Symbols and abbreviated terms – Part 2: Fillers and reinforcing materials

ISO 3344:1997 Reinforcement products – Determination of moisture content.

6.5.1 Fibres

Glass fibres are the most commonly used reinforcements, accounting for 95% of the consumption of fibres for plastic reinforcement.

Aramid and carbon fibres account for most of the remaining 5%.

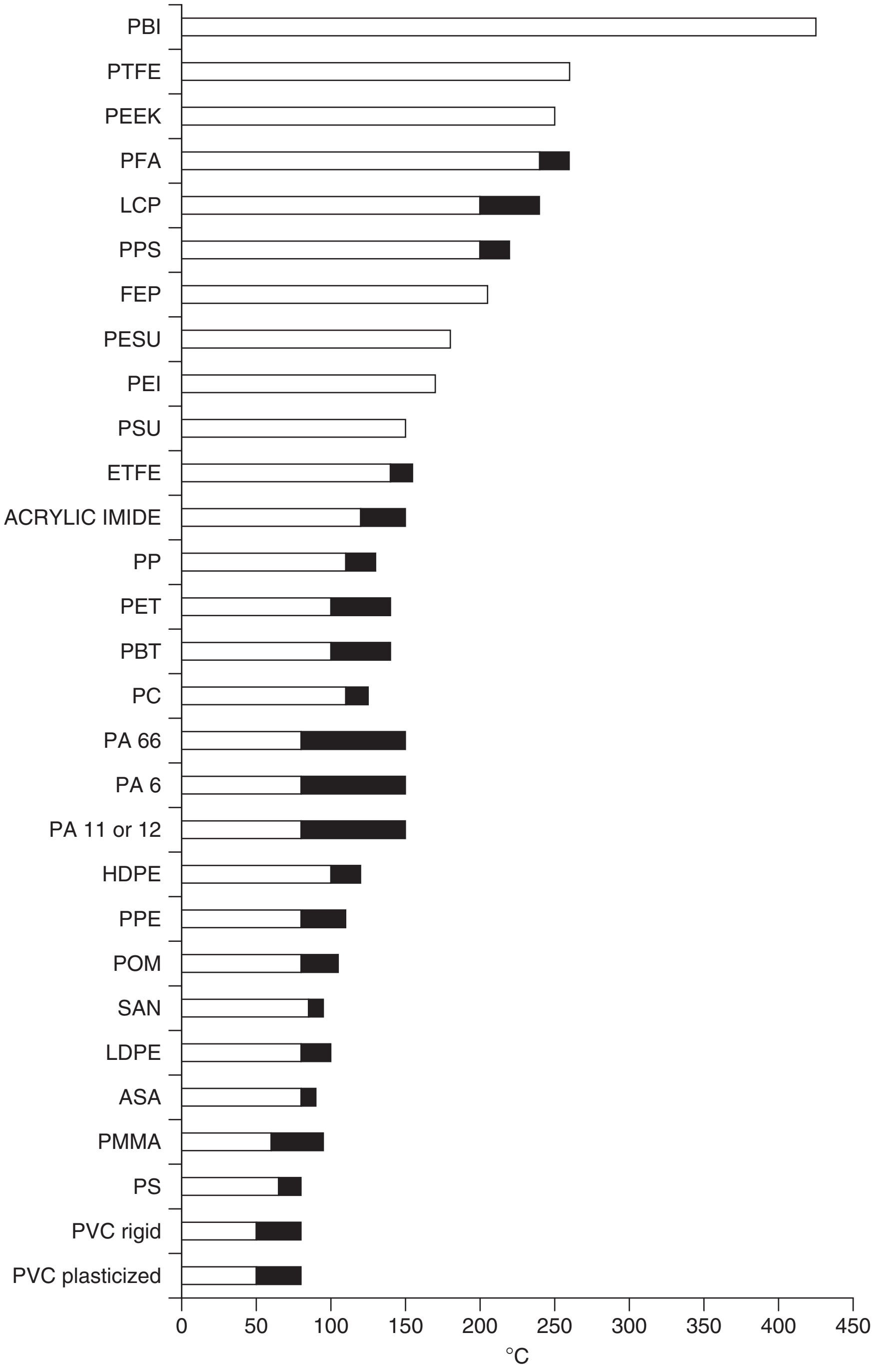


Figure 6.3. Neat thermoplastic matrices: examples of unstressed continuous use temperatures

Numerous other fibres have specific uses:

- textile fibres such as nylon and polyester
- industrial fibres such as PE, PTFE and PBO (polyphenylenebenzooxazole; Zylon)
- natural fibres such as jute, flax and so on

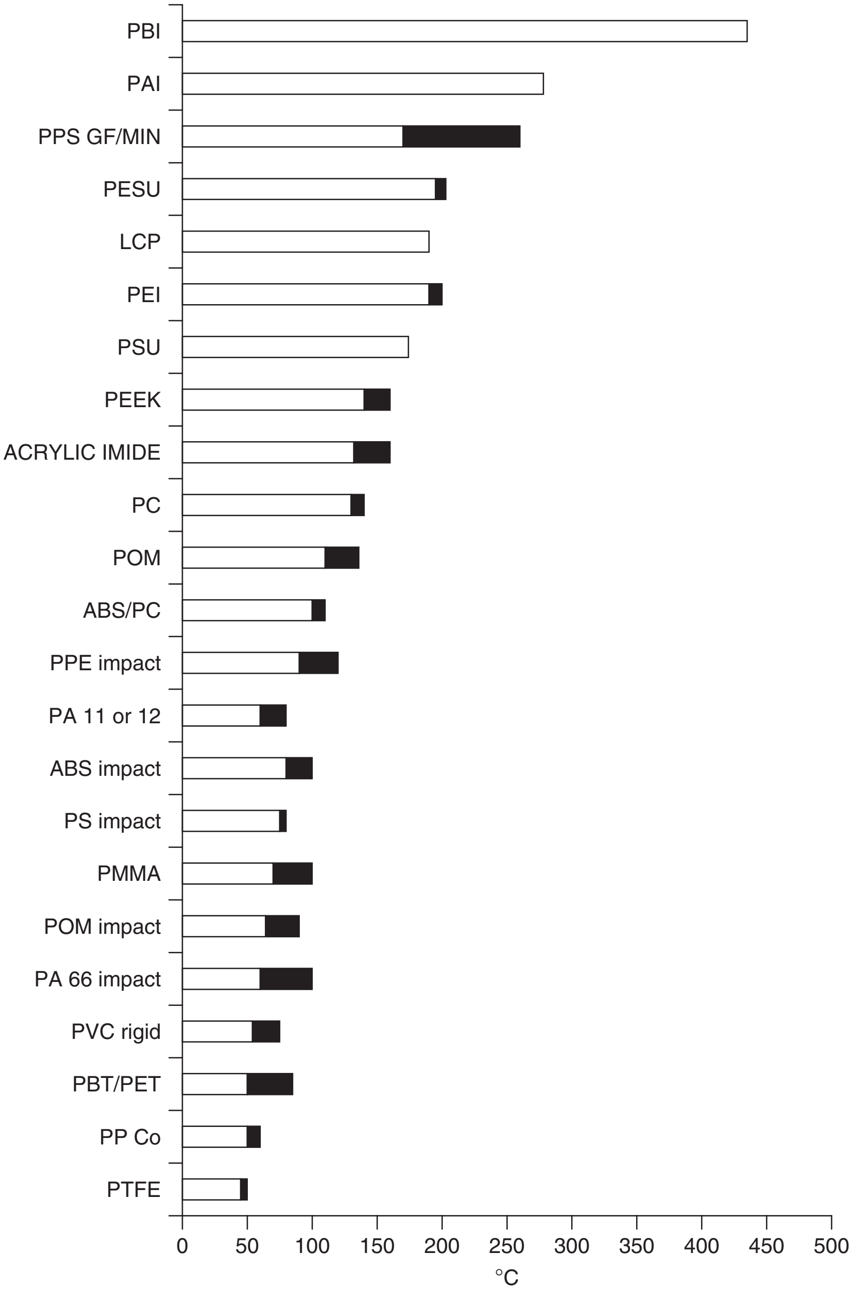


Figure 6.4. Neat thermoplastic matrices: examples of HDT A (1.8MPa) (°C)

- steel fibres and steel cords
- mineral fibres such as boron, quartz and whiskers . . .

In hybrid reinforcement, two or more types of fibres are used in the same composite.

The graph shown in Figure 6.7 plots the strength versus the modulus of some typical fibres. Note the very special performance of the whiskers (single-crystal fibres).

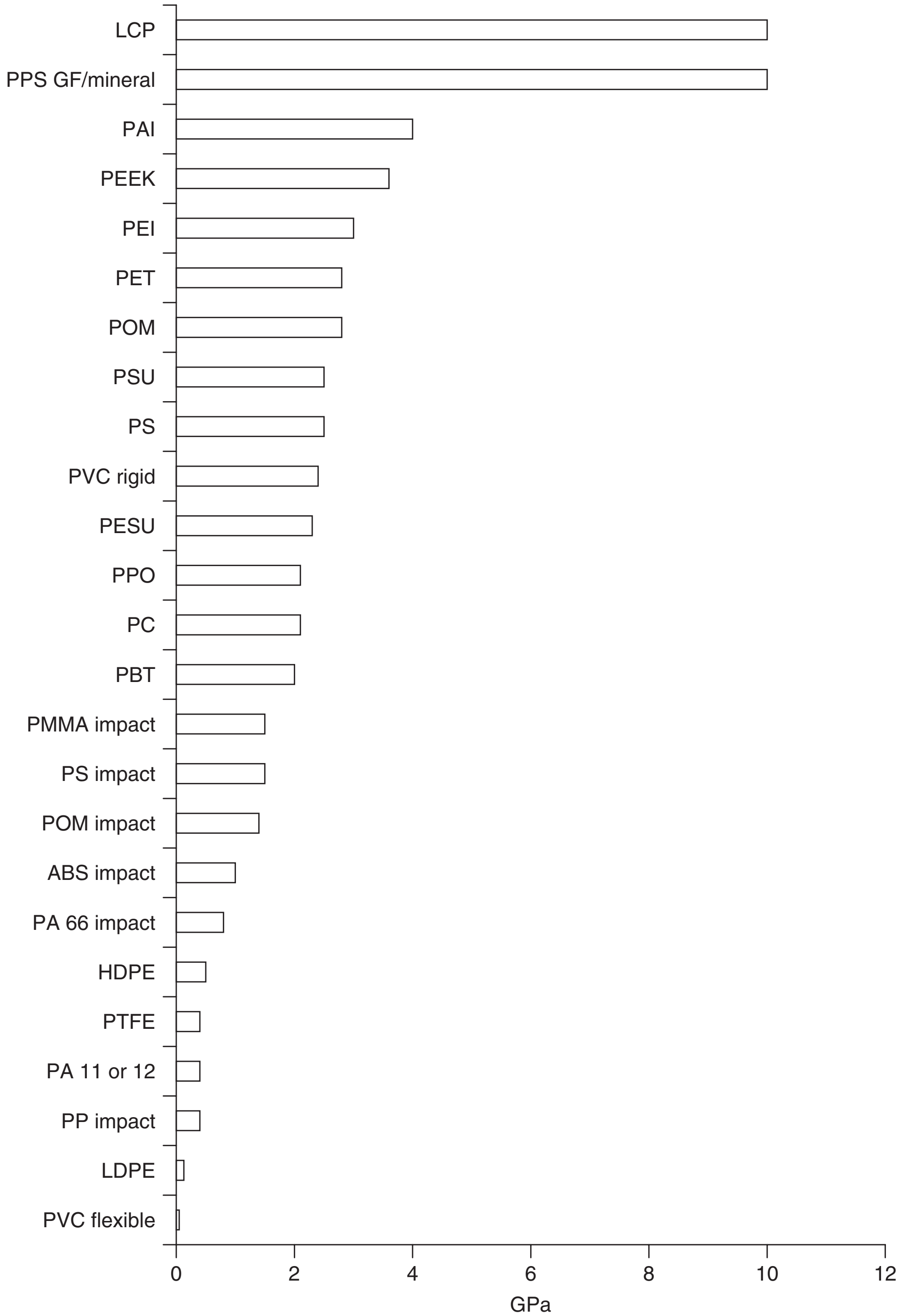


Figure 6.5. *Neat thermoplastic matrices: examples of tensile modulus (GPa)*

The performances of a given fibre and its cost govern its use in composites:
- carbon fibres for advanced composites
- aramid fibres for intermediate composites
- glass fibres for general-purpose composites

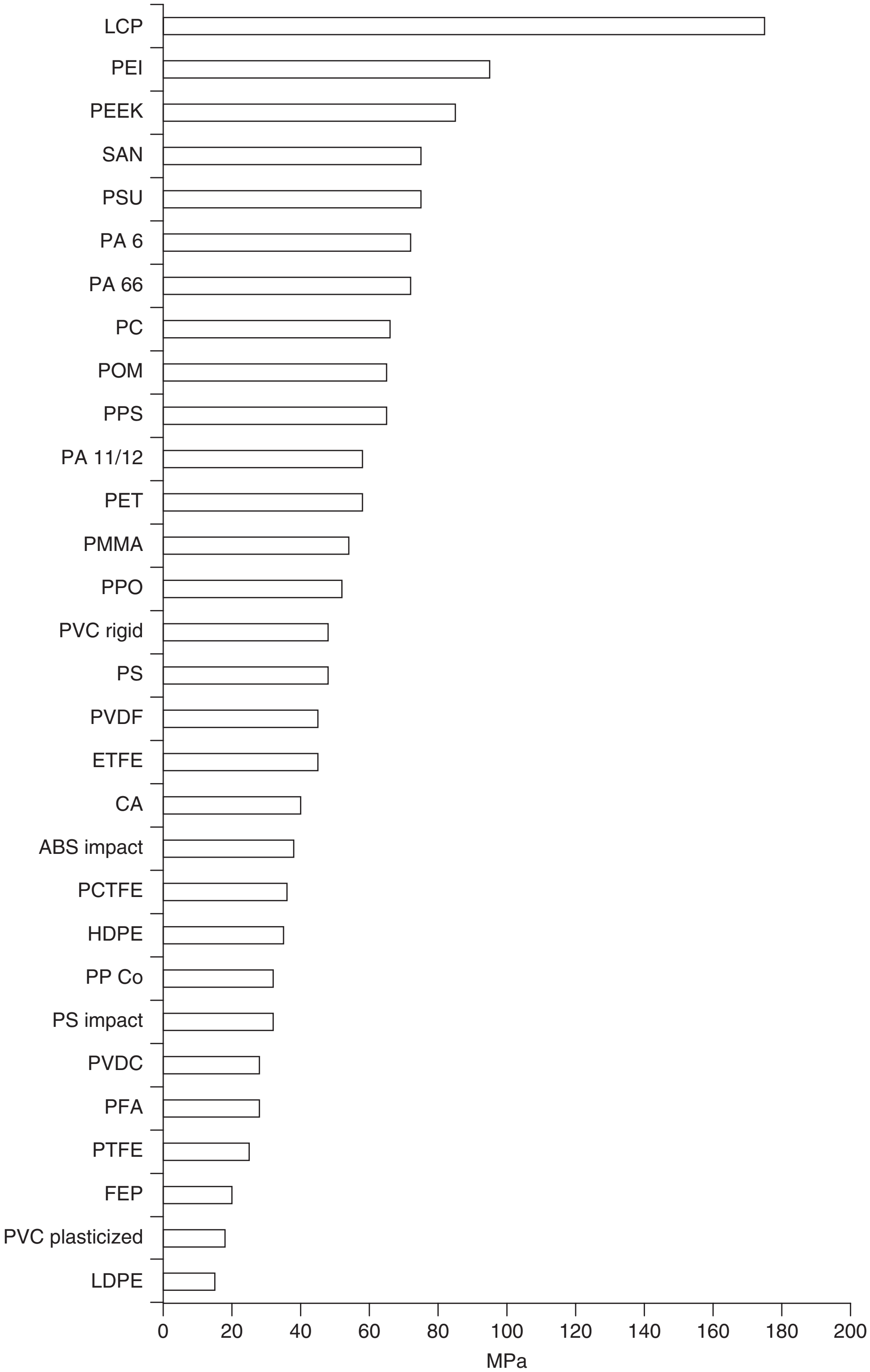


Figure 6.6. Neat thermoplastic matrices: examples of tensile strength (MPa)

Table 6.2 Property examples of 30% glass mat reinforced thermoplastics (GMT)

	PP	PA	PET
Density (g/cm^3)	1.13	1.35	1.5
Tensile strength (MPa)	70–85	73	110
Tensile modulus (GPa)	5	6.8	7.4
Un-notched impact (kJ/m^2)			35–110
HDT (1.8 MPa) (°C)	153	210	210
	PC	**PEI**	**PPS**
Density (g/cm^3)	1.4	1.47	1.4–1.7
Tensile strength (MPa)	160	190	160–370
Tensile modulus (GPa)	8	11	13
Un-notched impact (kJ/m^2)	55	50	
HDT (1.8 MPa) (°C)	160	230	270

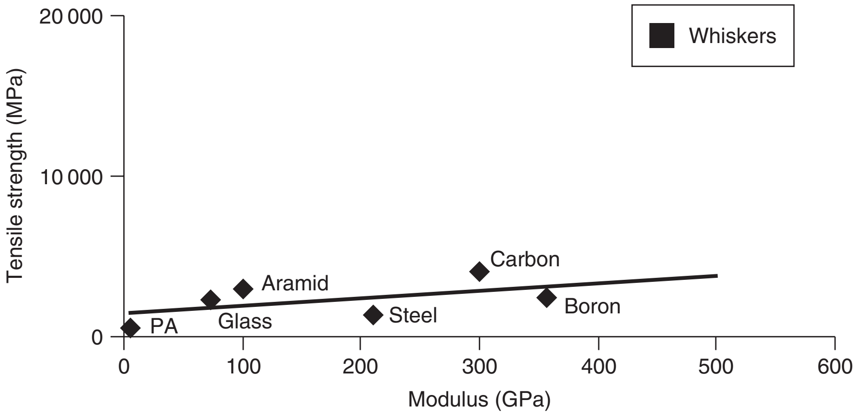


Figure 6.7. Fibres: examples of tensile strength versus modulus

- nylon and other textile fibres for flexible composites
- sustainable fibres for economic and environmental reasons
- steel fibres for tyres, conveyor belts, ESD compounds
- PE for antiballistic composites
- whiskers and boron fibres for very specialized composites.

The practical goals of the fibre reinforcement are:

- to increase the modulus and strength
- to improve the heat deflection temperature (HDT)
- to reduce the tendency to creep under continuous loading
- to save costs by decreasing the material cost used to obtain the same stiffening.

The main difficulties are:

- the risk of shortened fibre length due to breakage during processing.
- anisotropy due to fibre orientation and settling. With some processes, this is an advantage: the appropriate placement of the fibres permits reinforcement at specific points in the right direction.

Cost savings by fibre reinforcement

To cut raw material costs without any change in the stiffness or strength, it is possible to reduce the wall thickness by using a reinforced grade of the same matrix.

Figure 6.8 plots the reinforcement ratios for short glass fibre reinforced polyamide (PA-GF) versus neat polyamide for six important characteristics calculated versus density and material cost. These characteristics are tensile strength, tensile and flexural modulus, impact strength, HDT A and B.

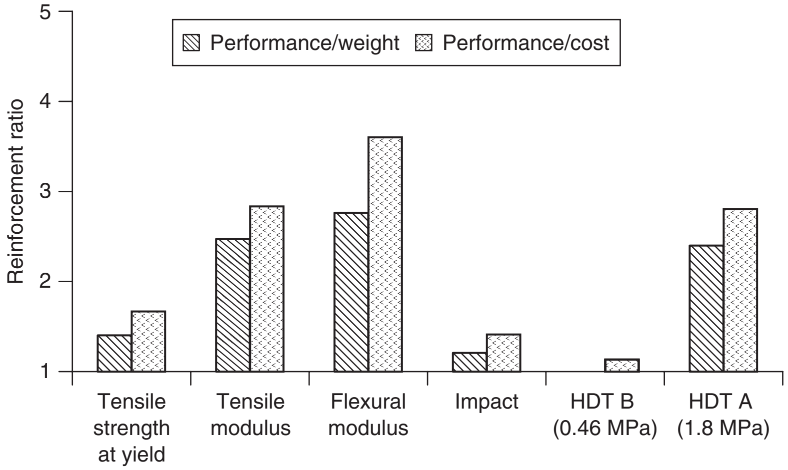


Figure 6.8. Fibres: examples of reinforcement ratios for short glass fibre reinforced PA 6

For example, the flexural modulus (FMw) computed versus density (d) is:

$$FM_{wPA\text{-}GF} = FM_{PA\text{-}GF}/d_{PA\text{-}GF} \text{ for PA-GF}$$

$$\text{and } FM_{wPA} = FM_{PA}/d_{PA} \text{ for neat PA}$$

The reinforcement ratio for performance/weight = $(FM_{wPA\text{-}GF})/FM_{wPA}$

Except for HDT B (reinforcement ratio = 1), all the other reinforcement ratios are greater than one, up to nearly four for the modulus.

To replace a PA with a wall thickness of 2 mm, it is possible to use a PA-GF of wall thickness:

- 1.43 mm for the same tensile strength and save 14% of the weight and 11% of the material cost.
- 0.7 mm for the same modulus and save more than 50% of the weight and the material cost.

Examples of specific ISO standards concerning fibre reinforcement

ISO 1889:1997 Reinforcement yarns – Determination of linear density

ISO 1890:1997 Reinforcement yarns – Determination of twist

ISO 2113:1996 Reinforcement fibres – Woven fabrics – Basis for a specification

ISO 2113:1996/Cor 1:2003

ISO 2558:1974 Textile glass chopped-strand mats for reinforcement of plastics – Determination of time of dissolution of the binder in styrene

ISO 3344:1997 Reinforcement products – Determination of moisture content

ISO 3374:2000 Reinforcement products – Mats and fabrics – Determination of mass per unit area
ISO 4602:1997 Reinforcements – Woven fabrics – Determination of number of yarns per unit length of warp and weft
ISO 5025:1997 Reinforcement products – Woven fabrics – Determination of width and length
ISO 6802:1991 Rubber and plastics hose and hose assemblies with wire reinforcements – Hydraulic impulse test with flexing
ISO 10122:1995 Reinforcement materials – Tubular braided sleeves – Basis for a specification
ISO 10371:1993 Reinforcement materials – Braided tapes – Basis for a specification
ISO 12215-1:2000 Small craft – Hull construction and scantlings – Part 1: Materials: Thermosetting resins, glass-fibre reinforcement, reference laminate
ISO 15100:2000 Plastics – Reinforcement fibres – Chopped strands – Determination of bulk density

6.5.1.1 Glass fibres for polymer reinforcement

The glass fibres are made from glass spun in the melt. They are then assembled and protected by sizing with organic or silane materials.

They exist in various grades:

- E-glass: the general-purpose grade that represents more than 90% of the reinforcement fibres.
- R- or S-glass with high mechanical performances, good fatigue resistance, high thermal and moisture behaviours. The principal applications relate to aeronautics, space, sports, leisure, armaments and antiballistics.
- D-glass with high dielectric properties, transparent to electromagnetic waves. The principal applications relate to the manufacture of radomes, electromagnetic windows and high-tech printed circuit boards.
- C- and ECR-glass with enhanced acid resistance.
- AR-glass, alkali resistant, particularly intended for the reinforcement of concrete.

Table 6.3 displays the average compositions and main features concerning the glass fibres used in polymer reinforcement.

Table 6.3 Average composition and main property examples of the three main types of glass fibres used in polymer reinforcement

	E-glass	R-glass	D-glass
	High performance/ cost ratios	High mechanical performances	Low dielectric loss
Analysis examples (%)			
Silica	53–57	58–60	72–75
Alumina	12–15	23–26	
Calcium and magnesium oxides	22–26	14–17	
Boron oxide	5–8		Up to 23
Applications	General purpose	Aeronautics & space Sports & leisure Antiballistic	Radome EM windows Printed circuit boards
Market share of the reinforcement fibres	90	<10	<10

All the glass fibres have in common:

- high thermal resistance
- insulating properties, with unfortunate consequences for electrostatic discharge
- elastic modulus in the range 50–90 GPa, much higher than the polymer but lower than carbon fibres
- low coefficient of thermal expansion
- high density
- brittleness under high stresses during processing
- abrasive properties harmful for tools.

Table 6.4 displays examples of the mechanical and physical properties of the three most important glass fibre types.

Table 6.4 Typical mechanical and physical properties of various glass fibres

	E-glass	R-glass	D-glass
Density (g/cm^3)	2.6	2.5	2.14
Moisture absorption (%)	<0.1	<0.1	<0.1
Tensile strength of virgin fibres (MPa)	3500	4400	2500
Tensile strength of impregnated fibres (MPa)	2000–2600	3500	1650
Tensile modulus (GPa)	70	85	55
Elongation at break (%)	4	4.8	4.5
Poisson's ratio	0.18		
Thermal properties			
% residual tensile strength after 24 h at 200°C	98	100	
% residual tensile strength after 24 h at 300°C	82	91	
% residual tensile strength after 24 h at 400°C	65	77	
% residual tensile strength after 24 h at 600°C	0		
Coefficient of thermal expansion (10^{-5}/K)	0.5	0.4	0.35
Thermal conductivity (W/m.K)	1	1	0.8
Specific heat (cal/g.°C)	0.19		
(kJ/kg.K)	0.8		
Dielectric properties			
Resistivity (ohm.cm)	10^{12}–10^{15}		
Dielectric constant @ 1 MHz	6.5	6	3.8
Permittivity @ 1 MHz (10^{-4})	15	19	5
Dielectric strength (kV/mm)	10–100		

Glass fibres are used in various forms for the reinforcement of polymers:

- Chopped or milled glass fibres: 0.1–20 mm length, 5–25 µm in diameter, aspect ratio from 4 to 4000. These fibres are dispersed into the polymers.
- Yarns: a defined number of filaments are brought together with a slight twist.
- Plied yarns: a defined number of yarns are brought together with a slight twist.
- Texturized and voluminized products: an air stream leads to the formation of loops in overfed continuous filament and imparts bulk.
- Rovings: a large number of filaments are brought together.
- Mats: chopped fibres (50 mm) are held together with a binder to form a sheet.
- Continuous filament mats: sheet of continuous filament felt with a binder.
- Stratipregs or prepregs: roving impregnated with a resin.

- 2D reinforcing products: mats, woven or knitted fabrics, braidings from yarns or rovings.
- 3D reinforcing structures.

Glass fibres are generally chosen for:

- the versatility of the sizing, which leads to good compatibility with all polymers
- the high specific mechanical performances
- the dimensional stability due to the coefficient of thermal expansion and the low water absorption
- the low cost of the raw material
- the cost-saving possibilities at constant performances
- the insulating properties
- the incombustibility of a mineral material
- the chemical resistance of the glass
- the insensitivity to putrefaction
- the thermal conductivity

Nevertheless, their use in polymers produces some constraints because of:

- the lack of surface conductivity for electrostatic discharge
- the need to employ wear-resistant materials for the equipment parts exposed to the reinforced polymer
- the special design of the equipment and parts to eliminate or reduce the settling of the fibres and abrasion wear.

Examples of the characteristics of some reinforced glass fibre plastics

- Reinforcement with chopped glass fibres dispersed in the polymer matrix. The properties depend on:
  - the fibre content
  - the aspect ratio (length versus diameter)
  - the sizing of the fibres to enhance adhesion to the matrix
  - the real length of the fibres in the final part
  - the quality of the fibre dispersion
  - the anisotropy in the final part.
- Reinforcement with continuous filaments, rovings, fabrics and so on. The properties depend on:
  - the fibre content
  - the form of the glass fibre reinforcement (filament, roving . . .)
  - the orientation of the glass fibres
  - the adhesion of the fibres to the matrix
  - the anisotropy in the final part.

Table 6.5 shows some examples of the modulus and the strength reinforcement ratios for various reinforced thermoplastics. The reinforcement ratio is the performance of the reinforced polymer divided by the performance of the neat polymer.

Effect of short glass fibres on material cost

The addition of short glass fibres has two effects:

- The cost of the raw material is:
  - increased for the cheapest polymers
  - decreased for the most-expensive ones.
- The blending induces a roughly constant supplementary cost.

Table 6.5 Examples of reinforcement ratios based on tensile strength and modulus of various reinforced thermoplastics

	Glass fibre	Strength	Modulus
Polypropylene	None	1	1
	Dispersed short GF	1.8	3.3
	Dispersed long GF	2.5	4.4
	GF mat	2.5	5
	UD GF	18	20
Polyamide	None	1	1
	Dispersed short GF	2.2	5
	Dispersed long GF	3.3	6.7
Polycarbonate	None	1	1
	Dispersed short GF	2.1	3.3

In the end, the cost can be:

- increased by 35% for a PET
- decreased by 35% for an LCP.

Figure 6.9 shows examples of cost ratios (costs of short glass fibre reinforced thermoplastics/costs of the neat thermoplastics) versus costs of the neat grades.

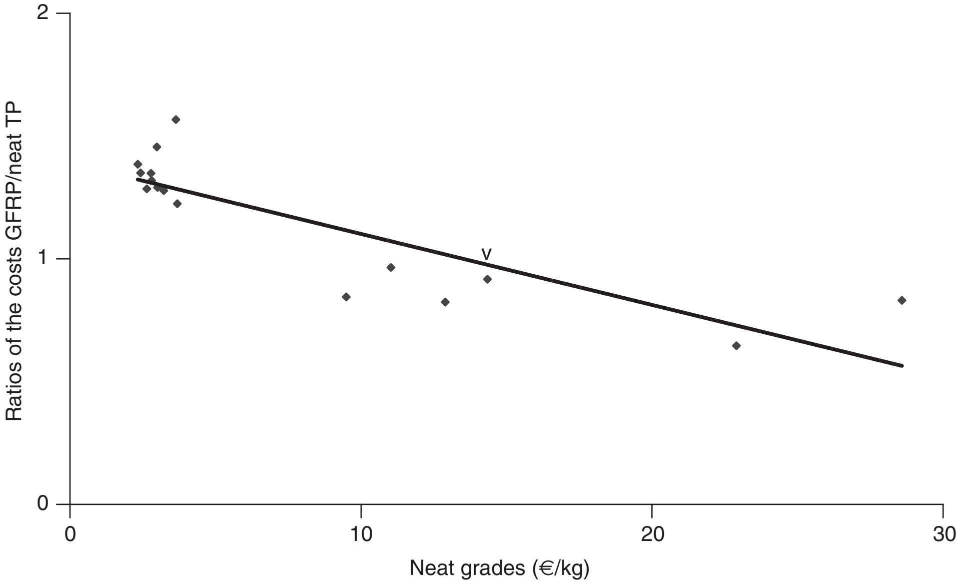


Figure 6.9. Cost ratios for short glass fibre reinforced thermoplastics versus costs of the neat grades

Examples of specific ISO standards concerning glass fibre reinforcement

ISO 1172:1996 Textile-glass-reinforced plastics – Prepregs, moulding compounds and laminates – Determination of the textile-glass and mineral-filler content – Calcination methods

ISO 1268:1974 Plastics – Preparation of glass fibre reinforced, resin bonded, low-pressure laminated plates or panels for test purposes

ISO 1887:1995 Textile glass – Determination of combustible-matter content

ISO 1888:1996 Textile glass – Staple fibres or filaments – Determination of average diameter

ISO 2078:1993 Textile glass – Yarns – Designation

ISO 2558:1974 Textile glass chopped-strand mats for reinforcement of plastics – Determination of time of dissolution of the binder in styrene

ISO 2559:2000 Textile glass – Mats (made from chopped or continuous strands) – Designation and basis for specifications

ISO 2797:1986 Textile glass – Rovings – Basis for a specification

ISO 3341:2000 Textile glass – Yarns – Determination of breaking force and breaking elongation

ISO 3342:1995 Textile glass – Mats – Determination of tensile breaking force

ISO 3343:1984 Textile glass – Yarns – Determination of twist balance index

ISO 3374:2000 Reinforcement products – Mats and fabrics – Determination of mass per unit area

ISO 3375:1975 Textile glass – Determination of stiffness of rovings

ISO 3597-1:2003 Textile-glass-reinforced plastics – Determination of mechanical properties on rods made of roving-reinforced resin – Part 1: General considerations and preparation of rods

ISO 3597-2:2003 Textile-glass-reinforced plastics – Determination of mechanical properties on rods made of roving-reinforced resin – Part 2: Determination of flexural strength

ISO 3597-3:2003 Textile-glass-reinforced plastics – Determination of mechanical properties on rods made of roving-reinforced resin – Part 3: Determination of compressive strength

ISO 3597-4:2003 Textile-glass-reinforced plastics – Determination of mechanical properties on rods made of roving-reinforced resin – Part 4: Determination of apparent interlaminar shear strength

ISO 3598:1986 Textile glass – Yarns – Basis for a specification

ISO 3616:2001 Textile glass – Chopped-strand and continuous-filament mats – Determination of average thickness, thickness under load and recovery after compression

ISO 4603:1993 Textile glass – Woven fabrics – Determination of thickness

ISO 4604:1978 Textile glass – Woven fabrics – Determination of conventional flexural stiffness – Fixed angle flexometer method

ISO 4606:1995 Textile glass – Woven fabric – Determination of tensile breaking force and elongation at break by the strip method

ISO 4900:1990 Textile glass – Mats and fabrics – Determination of contact mouldability

ISO 5025:1997 Reinforcement products – Woven fabrics – Determination of width and length

ISO 7822:1990 Textile glass reinforced plastics – Determination of void content – Loss on ignition, mechanical disintegration, statistical counting methods

ISO 8516:1987 Textile glass – Textured yarns – Basis for a specification

ISO 9163:2005 Textile glass – Rovings – Manufacture of test specimens and determination of tensile strength of impregnated rovings

ISO 9353:1991 Glass-reinforced plastics – Preparation of plates with unidirectional reinforcements by bag moulding

ISO 15039:2003 – Textile-glass rovings – Determination of solubility of size

Trade name examples

The trade names are numerous and only a selection are quoted here:

Araton, Assemblofil, Beta, Chopvantage, Creel-Pak, D-Glass, Fiberglas, G-Glass, Glasslon, Maxichop, Microlith, Miraflex, Q-Fiber, Silenka, Silione, Tufrov, Vetrotex, Vitron.

6.5.1.2 Carbon fibres (CF) for polymer reinforcement

The production of carbon fibres is based on the pyrolysis of organic fibres or precursors. The main starting materials are polyacrylonitrile (PAN) and pitch (coal tar or petroleum asphalt). They can be classified according to their mechanical performances:

- high tenacity
- high modulus
- high modulus and improved tenacity.

Or according to their applications, for example:

- general-purpose
- aeronautics
- aeronautics and high modulus.

The characteristics vary according to the process and the grades, as we can see in Table 6.6.

Table 6.6 Carbon fibres: examples of properties

PAN carbon fibres	High tenacity	High modulus Improved tenacity	High modulus
	Mechanical properties		
Density (g/cm^3)	1.8	1.7–2	1.7–1.8
Tensile strength (MPa)	3500–6400	3400–4700	2700–5500
Elasticity modulus (GPa)	230–300	340–640	290–390
Elongation at break (%)	1.5–2.2	0.5–1.4	0.7–1.9
	Thermal properties		
Coefficient of thermal expansion (10^{-5}/K)	−0.038 to −0.056	−0.073 to −0.11	−0.06 to −0.1
Thermal conductivity (W/m.K)	8–33	38–167	21–113
Specific heat (cal/g.°C)	0.18–0.19	0.17	0.17–0.18
	Electrical properties		
Resistivity (ohm.cm)	$1.4-1.7 \times 10^{-3}$	$0.7-1.1 \times 10^{-3}$	$0.7-1.2 \times 10^{-3}$
Pitch carbon fibres	General purpose	Aeronautics	Aeronautics high modulus
	Mechanical properties		
Density (g/cm^3)	2.12–2.15	2.12–2.15	2.16–2.20
Tensile strength (MPa)	2600–2900	3600–3700	3700–3800
Elasticity modulus (GPa)	640–790	620–790	790–900
Elongation at break (%)	0.4	0.5–0.6	0.4–0.5
	Thermal properties		
Thermal conductivity (W/m.K)	140–220	140–220	220–260
	Electrical properties		
Resistivity (ohm.cm)	$5-7 \times 10^{-6}$	$5-7 \times 10^{-6}$	$2-4 \times 10^{-6}$

Intended for high-performance applications because of their cost, carbon fibres have excellent mechanical properties but are sensitive to impact and abrasion. They are used for their attractive characteristics, such as:

- high tensile strength
- high modulus
- high creep resistance

- high fatigue resistance
- high dielectric conductivity
- high thermal conductivity
- lower density than glass fibres
- low coefficient of friction
- low coefficient of thermal expansion.

On the other hand, their drawbacks are:

- low impact strength
- low abrasion resistance
- high cost.

Carbon fibres are used in various forms for polymer reinforcement:

- short fibres dispersed in the matrix
- yarns, rovings, stratipregs or prepregs, mats, 2D and 3D reinforcing structures.

As for glass fibres, reinforcement with continuous fibres leads to the highest performances.

Compared to short glass fibres, short carbon fibres yield higher reinforcement ratios for the modulus and tensile strength but the impact strength decreases.

Table 6.7 shows examples of:

- The modulus and the strength reinforcement ratios for various carbon fibre reinforced thermoplastics. The reinforcement ratio is the performance of the reinforced polymer divided by the performance of the neat polymer.

Table 6.7 Examples of reinforcement ratios of CFRP and enhancement ratios versus GFRP

	Reinforcement ratios based on tensile strength and modulus of various carbon fibre reinforced polymers		
	Carbon fibre	Strength	Modulus
PEEK	None	1	1
	30% dispersed short CF	2.3	4.4
	40% dispersed short CF	2.7	5.4
PPS	None	1	1
	40% dispersed short CF	2.4	6.5
	Enhancement ratios obtained with short carbon fibre instead of glass fibre in a thermoplastic matrix		
	Property CF composite/property GF composite		
Modulus	1.5–2.7		
Tensile strength	1.2–2.1		
Impact strength	0.7–0.9		
Creep modulus	3.8–6.7		
Creep stress	1.6–1.7		
Fatigue resistance (10^6 cycles)	1.2		

- Enhancement ratios of carbon fibres versus glass fibres. The data used here are the ratios of a property for a carbon fibre reinforced composite (CFRP) versus the same property for the glass fibre reinforced composite (GFRP).

Examples of specific ISO standards concerning carbon fibre reinforcement

ISO 10119:2002 Carbon fibre – Determination of density
ISO 10548:2002 Carbon fibre – Determination of size content

ISO 10618:2004 Carbon fibre – Determination of tensile properties of resin-impregnated yarn

ISO 11566:1996 Carbon fibre – Determination of the tensile properties of single-filament specimens

ISO 11567:1995 Carbon fibre – Determination of filament diameter and cross-sectional area

ISO 13002:1998 Carbon fibre – Designation system for filament yarns

Trade name examples

Selected carbon fibre trade names are:

Besfight, Dialead, Filkar, Fortafil, Grafil, Granoc, Panox, Pyrofil, Pyron, Tenax, Thornel, Torayca.

6.5.1.3 Aramid fibres (AF) for polymer reinforcement

The most widespread and widely known are Kevlar and Twaron. AF are used especially in high- and medium-performance applications; they are also used with other fibres to create a hybrid reinforcement.

Table 6.8 shows examples of properties of Kevlar 29 and 49.

Table 6.8 Aramid fibres: examples of properties

Mechanical properties		
Density (g/cm^3)	1.44	1.44
Moisture level (%)	4.5–7	3.5
Tensile strength (MPa)	2900	3000
Elasticity modulus (GPa)	70	112
Elongation at break (%)	3.6	2.4
Poisson's ratio		0.36
Thermal properties		
Continuous use temperature unstressed (°C)	150–177	150–177
Coefficient of thermal expansion (10^{-5}/K)	–0.4	–0.5
Thermal conductivity (W/m.K)	0.04	0.04
Specific heat (cal/g.°C)	0.34	0.34
Electrical properties		
Resistivity (ohm.cm)	10^{13}–10^{15}	10^{13}–10^{15}

Aramid fibres have high specific mechanical properties and are used for their attractive characteristics such as:

- high tensile strength, particularly specific strength (engineering strength divided by density)
- high modulus
- high creep resistance
- high fatigue resistance
- lower cost than carbon fibre
- lower density than glass and carbon fibres
- low coefficient of friction
- low coefficient of thermal expansion.

On the other hand, their drawbacks are:

- higher cost than glass fibre
- moisture uptake
- sensitivity to UV and weathering
- more limited thermal properties than glass and carbon fibres
- high electrical resistance and a lack of surface conductivity for electrostatic discharge
- more limited compression and flexural strengths
- difficult machining.

Aramid fibres in various forms are used for polymer reinforcement:

- short fibres dispersed in the matrix
- yarns, rovings, stratipregs or prepregs, mats, 2D and 3D reinforcing structures.

Short aramid fibres lead to intermediate reinforcement between those obtained with short glass and carbon fibres.

As for the other fibres, reinforcement with continuous aramid fibres leads to the highest performances.

Table 6.9 shows the enhancement ratios for aramid fibres versus glass fibres used in the same composite type. The enhancement ratios are the ratios of a property for an aramid fibre reinforced composite versus the same property for the glass fibre reinforced composite.

Table 6.9 Examples of enhancement ratios obtained with incorporation of short aramid fibres instead of short glass fibres in a thermoplastic composite

	Property AF composite/ property GF composite
Modulus	1.2
Tensile strength	1.1
Specific modulus	1.3
Specific tensile strength	1.2

Trade name examples

The most well-known trade names are Kevlar and Twaron.

6.5.1.4 Comparison of the three main types of fibre

In all cases, carbon fibres lead to the highest mechanical performances compared to glass and aramid fibres. Nevertheless, their impact behaviour and price restrict their consumption. Glass fibres yield the cheapest composites but performances are more limited. Table 6.10 compares the properties of the main fibre types and shows some examples of properties for a nylon matrix reinforced with short fibres of the three types.

Figure 6.10 shows schematically the relative positions (modulus versus strength) of some composites according to the nature and form of the fibres. These are examples with different reinforcement contents and forms and the comparison is not really representative of all the possibilities.

6.5.1.5 Sustainable natural vegetal fibres

Natural reinforcements have been used for a very long time:

- Wood flour was one of the first fillers used with phenolic resin.
- Wood shavings are used in wood particle boards.

Table 6.10 Example comparisons of characteristics for the three main fibres

Fibre properties	E-glass	Aramid	Carbon
Density (g/cm^3)	2.6	1.44	1.7–2
Tensile strength (MPa)	2000–3500	2900–3000	2000–6400
Tensile modulus (GPa)	70–73	70–130	200–590
Strength/density	770–1350	2000–2080	1000–3760
Modulus/density	28	48–90	100–300
Elongation at break (%)	3–5	2–4	0.5–2
Resistivity	10^{12}–10^{15}	5×10^{15}	10^{-3}
Short fibre reinforced polyamide	E-glass	Aramid	Carbon
Density (g/cm^3)	1.29	1.19	1.23
Tensile strength (MPa)	100	95	207
Tensile modulus (GPa)	5.3	5.1	13
Elongation at break (%)	5	6	
Notched impact (arbitrary units)	10	6	
HDT A (1.8 MPa) (°C)	250	222	250
Coefficient of thermal expansion (10^{-5}/K)	3	2	

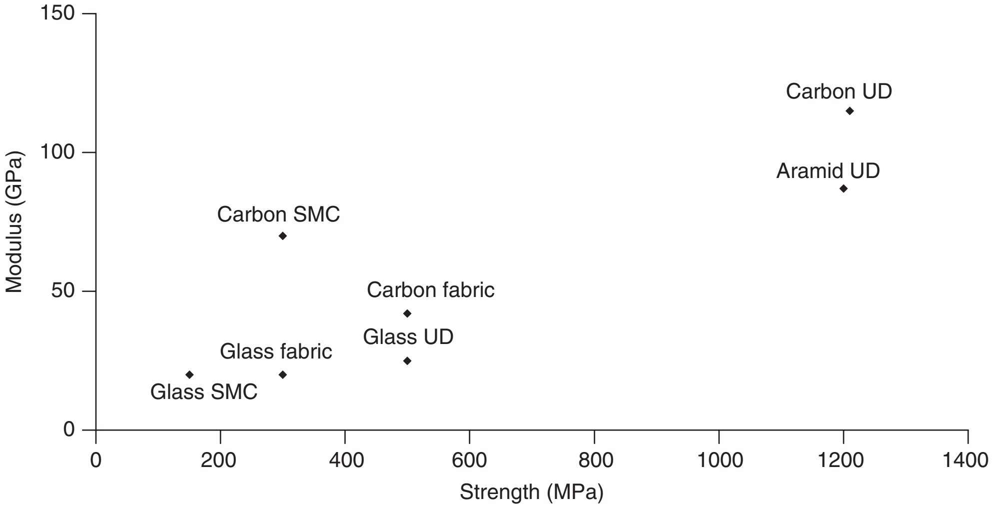


Figure 6.10. Glass, aramid and carbon fibre reinforced composites: tensile modulus versus tensile strength examples

There is a renewed interest in natural fibres as sustainable materials to replace industrial glass fibres in general-purpose composites. Several reasons promote these ideas:

- Environmental and ecological criteria
- Economic considerations, which lead some nations to give priority to local materials
- Increasing plastic consumption, which needs increasing quantities of glass fibres.

Generally, compared to glass fibres, natural vegetal (or plant-based) fibres offer advantages but also drawbacks, for example:

- The outputs are sometimes a little low, which limits development studies and industrialization.
- The price is often attractive but there are exceptions and the performance/price ratios are rarely favourable.

- Density is always attractive.
- Mechanical properties are lower but fair (see Table 6.11).
- Recycling is theoretically easier.
- Long-term effects of temperature, moisture and light are unfavourable.
- Cost savings of up to 60% are claimed when performances are not essential.

Table 6.11 shows the properties of some sustainable fibres compared to glass fibres. Other natural fibres claimed as usable are:

Table 6.11 Properties of some sustainable fibres compared to glass fibres

Fibres	Glass	Flax	Jute	Sisal	Coconut	Ramie
Price (% of GF price)	100	130	20	20	20	
Output (% of GF output)	100	70	280	40	10	
Density (g/cm^3)	2.6	1.5	1.3	1.5	1.2	
Tensile strength (MPa)	3000	350–1000	400–800	500–600	175	400–900
Modulus (GPa)	70	28	27	9–22	5	60–130
Elongation at break (%)	2.5	3	2	2	30	4
Tensile strength/density	1150	230–670	300–600	300–400	150	270–600
Modulus/density	27	20	20	6–15	4	40–90
Tensile strength/price (% versus glass)	100	10–25	70–130	80–100	30	
Modulus/price (% versus glass)	100	30	190	60–150	40	

- Cereal, corn, barley . . . into matrices of PP, PE, ABS, PVC. Composite moduli are claimed in the range of 1.5–3 GPa for prices in the order of €0.75 to €3 per kg. Applications could be in packaging, toys, building and automobile. The properties of the ‘Epitex’ PP composites are, for example:
  - density: 0.94–0.97 g/cm^3
  - flexural strength: 40–46 MPa
  - flexural modulus: 2–2.6 GPa
  - Charpy impact strength: 9–40 kJ/m^2.
- Kenaf (*Hibiscus cannabinus*) is used by Ford, Saab and Volvo for some interior trims.
- A flax nonwoven is used by Opel, Renault and Citroën for interior trims.
- Arboform, a composite of lignin, hemp and flax developed by the Fraunhofer Institute, is proposed to replace more traditional materials in the automotive industry.
- EAC Technologies (of Belgium) produces mats of flax, hemp or jute and composites made of flax, hemp or jute reinforced polypropylene.
- Fasal or Fasalex are completely biodegradable materials of vegetal origin. Some properties are shown below:
  - density: 1.2–1.4 g/cm^3
  - tensile strength: 17–25 MPa
  - tensile modulus: 4–8 GPa
  - flexural strength: 30–50 MPa
  - flexural modulus: 4–6 GPa
  - elongation at break: 0.5%–1%
  - Charpy impact strength: 3–7 kJ/m^2.

Possible applications for Fasal are:

- interior architectural products such as floors, ceilings, walls. . .
- furniture such as skirting, doors, cladding, panels. . .
- technical profiles such as cable channels, supporting poles, fixing elements, vehicle components.

Examples of industrial applications of natural reinforcements:

- interior automotive panels
- truck parts from thermoplastics, rubbers, polyurethanes reinforced with coconut, jute, banana or cotton
- building products: decking, fencing, siding and decorative trims
- infrastructure: boardwalks, marinas and guardrails
- industrial and consumer applications: pallets, playground equipment, benches . . .

The US natural fibre and wood composite market was estimated in *Plastics Additives & Compounding* at 340 000 tonnes in 2001 rising to just over 450 000 tonnes in 2003, that is to say, roughly 1% of the total plastic consumption.

Europe is not such an important market as the USA because of the lack of available wood by-products and the lack of end uses.

6.5.1.6 Other mineral fibres

Other mineral fibres are used for very specialized applications.

Boron fibres and boron/carbon fibre hybrids

Boron fibres were used for specific aeronautic composites, for example by Grumman in the wings of the F 14, because of their structural properties. Now, because of their high cost, they are often replaced by carbon fibres.

Boron fibres have high performances:

- thermal resistance
- high modulus
- high compression strength.

They are generally used in the form of prepregs 70% fibres/30% matrix of epoxy, polyimide or phenolic resin.

The boron/carbon fibre hybrids, Hy-Bor, are sometimes used in sports goods for their ability to provide thinner laminates and save weight for the same stiffness.

Mineral fibres such as silica, quartz, ceramics

These fibres are used for their thermal properties combined with high mechanical performances. Unfortunately, their price is prohibitive and applications are reduced to, for example, rocket motors.

Basalt fibres

These fibres are used for their thermal and fire properties combined with mechanical performances similar to those of glass fibres. Unfortunately, their price is three times higher than that of glass fibres and applications are reduced.

Stainless steel fibres

Stainless steel fibres are used for two main reasons:

- Obtaining electrical conductivity. Short fibres are added to thermoplastics to obtain EMI, ESD or conductive grades. In certain composites, long or continuous fibres partially replace glass fibres.
- Structural properties for flexible composites such as tyres, belts, etc.

Whiskers

Whiskers are single-crystal fibres. They are very expensive and difficult to produce with only a few specific applications, for example, submicron gears or connectors.

6.5.1.7 Other textile fibres

Other textile fibres – polyester, rayon, polyamide – have low moduli (see Table 6.12), which limits their plastic reinforcing power. They are used particularly for the reinforcement of soft thermoplastics such as plasticized PVC.

Thermoplastic polyester fibres are also used in:

- PBT matrix for inner liners of gas pipelines
- PP matrix (by VTS) to lead to very high impact strengths at − 30°C, for example 18 kJ/m^2 with a good modulus of 2.4 GPa.

Table 6.12 compares various fibres with glass fibres.

Table 6.12 Property examples of various fibres

	Density (g/cm^3)	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)	Melt temperature (°C)
Nylon	1.16	1000	5.6	18	254
Polyester	1.38	1200	14	14	256
Glass	2.6	3000	70	2.5–5	750
HS polyethylene	0.97	2600	120	4	149
Steel	7.7	2000	203	2	1500

6.5.1.8 Industrial fibres

Polyethylene fibres

Polyethylene fibres are handicapped by their low melting temperature. They are used for antiballistic products.

Polypropylene fibres

Polypropylene fibres are used to reinforce polypropylene matrices leading to a self-reinforcing polymer.

PTFE fibres

PTFE fibres are used for tribological composites.

Polyetherimide fibres

PEI fibres are used for their resistance to fire in fire barriers for special bedding.

PBO fibres

They are used for their temperature resistance and fire behaviour.

6.5.2 The different fibre forms used for reinforcement

During manufacturing, the filaments are sized with organic materials. Later in the process it may be necessary to desize.

The spun filaments are assembled in strands, yarns, rovings that can be woven or knitted. A variety of forms are available:

- Chopped or milled fibres: 0.1–20 mm length, 5–5 μm in diameter, aspect ratio from 4 to 4000. These fibres are dispersed into the polymers.
- Strands: an assembly of filaments.
- Yarns: a defined number of filaments are brought together with a slight Z- or S-twist.
- Plied yarns: a defined number of yarns are brought together with a slight twist.

- Cabled yarns: a defined number of plied yarns are brought together with a slight twist.
- Texturized and voluminized products: an air stream leads to the formation of loops in overfed continuous filament and imparts bulk.
- Rovings: a large number of filaments are brought together.
- Mats: chopped fibres (50 mm) are held together with a binder to form a sheet.
- Continuous filament mats: sheets of felt of continuous filaments with a binder.
- Stratipregs or prepregs: rovings impregnated with a resin.

These fibre products can be:

- woven: with a few differences, the technology is similar to textile weaving
- braided to produce tubular sleeves.

The products obtained are, for example:

- 2D reinforcing products: mats, woven or knitted fabrics, braidings from yarns or rovings.
- 3D reinforcing structures.
- Fabrics. These are characterized by:
  - the weave pattern or crossing scheme of the warp (lengthwise) and weft (perpendicular to the warp) yarns
  - the count or number per centimetre of warp and weft yarns
  - the yarn types.

Influence of the reinforcement form on composite properties

As the reinforcements have the structural role, their form is essential. Let us recall that:

- For an example of UD continuous carbon fibre reinforcement, the tensile strength is 1760 MPa in the fibre direction and 80 MPa in the perpendicular direction.
- The reinforcement obtained with a given level of a given type of fibres is a function of the length, the aspect ratio and the orientation of the fibres.
- Unless otherwise specified, the mechanical properties are indicated for the favourable fibre direction but the engineering properties really depend on the stress direction.

Table 6.13 displays the strength and modulus of a 60% glass fibre reinforced resin for various fibre forms. The properties are roughly:

- strength: 80–900 MPa – a range of more than 150% of the average value.
- modulus: 8–30 GPa – a range of more than 100% of the average value.

Table 6.13 Examples of properties for a 60% glass fibre reinforced resin according to the fibre forms

	Strength (MPa)	Modulus (GPa)
Mat	200	15
Balanced fabric	200–400	20
UD fabric, fibre direction	700–800	30
UD fabric, perpendicular direction	80	8
UD roving, fibre direction	800–900	30
UD roving, perpendicular direction	80	8

6.5.3 Foams for sandwich technology

In a sandwich structure, the foam is used as the core with two skins of reinforced resin sheets firmly stuck on the foam to obtain high rigidity. The sandwich composite behaves as an I-beam: see Figure 6.11.

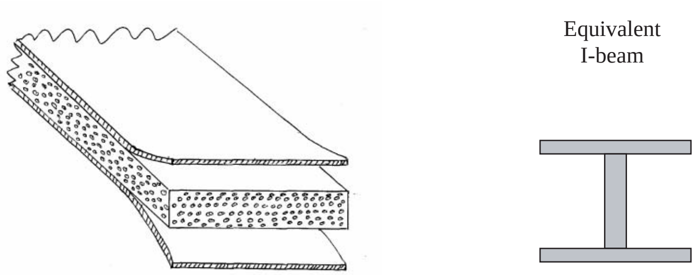


Figure 6.11. Schematic principle of a sandwich composite with a foamed core

Sandwich composites are used in:

- general-purpose applications such as railway and road transport; body elements for isothermal or refrigerated vehicles; sports and leisure (skiing, cycling, hockey); nautical structural components; thermal and phonic insulation panels in buildings . . .
- high-tech applications such as aeronautics, blades of wind turbines, competition sports, racing motorboats, shipbuilding . . .

The core and the final parts can have any shape: parallelepipedic for a lot of sandwich panels, shaped parts for the hulls of boats or bumpers and so on.

These lightweight composites have a superior stiffness/mass ratio with excellent thermal and phonic insulating properties.

Foams can be flexible or rigid, with open or closed cells, reinforced or not. Their properties depend on:

- the chemical nature of the polymer
- the manufacturing process
- the density
- the cell morphology: open or closed, diameter, wall thickness, etc.

The foams can be classified into four categories:

- general-purpose foams: PVC, polyurethane, polystyrene
- for technical applications: polyethylene, polypropylene, methacrylimide
- speciality foams: polyetherimide, polysulfone
- syntactic foams.

The following information concerns foams for sandwich technology only and not foams used for packaging or insulation.

Rigid PVC foams

PVC foams used as sandwich cores generally have:

- densities in the range of 30–700 kg/m^3
- closed cells
- crosslinked or linear structures. Often, the crosslinking improves the mechanical properties and chemical resistance, leading to a more rigid but perhaps more fragile sandwich composite than linear foam.

The water or moisture permeability and absorption are low and the hydrolysis resistance is generally good. PVC is naturally fire resistant and an appropriate formulation can improve its behaviour. However, the high chlorine level in PVC is released in the event of combustion and can involve corrosion during processing, and the thermal behaviour is limited.

Table 6.14 shows some examples of PVC foam properties.

Table 6.14 PVC foams: examples of properties

Linear PVC foams			
Density (kg/m^3)	60	90	140
Compression strength (MPa)	0.380	0.900	1.600
Compression modulus (GPa)	0.030	0.056	0.135
Tensile strength (MPa)	0.900	1.400	2.400
Tensile modulus (GPa)	0.030	0.050	0.090
Thermal conductivity (W/m.K)	0.034	0.037	0.039
Crosslinked PVC foams			
Density (kg/m^3)	30	100	400
Maximum service temperature (°C)	70–80	70–80	70–80
Minimum service temperature (°C)	−200*	−200*	−200*
Compression strength (MPa)	0.220	1.700	11.240
Compression modulus (GPa)	0.012	0.125	0.500
Tensile strength (MPa)	0.510	3.100	12.400
Tensile modulus (GPa)	0.020	0.105	0.469
Thermal conductivity (W/m.K)	0.03	0.04	0.06
Water absorption, 7 days, 40°C (%)	0.1	0.06	0.02
Poisson's ratio		0.32	
Coefficient of thermal expansion (10^{-5}/°C)	4	3.5	2.2

*Except mechanical stresses because embrittlement occurs at higher temperatures

Examples of applications

- Sandwich panels: body structures of refrigerated lorries and similar vehicles; roofs of coaches; structural components; containers for maritime, road, railway and air transport; wagons to carry and store food onboard aircraft; shelters, bodies of military light machines.
- Nautical structural components: hulls, decks, superstructures and partitions of motorboats; vessels for fishing or racing.
- Structural and interior components for aeronautic, automotive and railway equipment: floors, radomes, bodies of buses and coaches (Neoplan), front end components, drivers' cabs, partition walls, luggage racks in high-speed trains.

Polyurethane foams

Polyurethane foams can be flexible or rigid polyesters or polyethers.

Compared to polyethers, polyester foams generally present:

- better mechanical resistance
- better capacity for soundproofing and damping
- more-limited resistance to ageing
- better behaviour with hydrocarbons
- greater sensitivity to water and hydrolysis.

Table 6.15 shows some examples of polyurethane foam properties.

Examples of applications

- Sandwich panels for containers or bodies of isothermal trucks (rigid foams), panels for cold stores.
- Cores for polyester boats, sailboards.

Table 6.15 Polyurethane foams: examples of properties

Type	Soft	Semi-rigid	Rigid
Density (kg/m^3)		20–30	30–70
10% compression stress (MPa)			0.14–0.6
40% compression stress (MPa)		0.02–0.07	
Tensile strength (MPa)	0.100–0.160	0.14–0.18	
Elongation at break (%)	200–300	35–60	
Thermal conductivity (W/m.K)			0.022–0.035

- Walls of prefabricated dwellings.
- Self-supporting panels.
- Seats made of sandwich composite with foamed core and thermoplastic skins.
- Soundproofing screens with foamed core and thermoplastic skins.
- Insulated doors or double doors for buildings, dwellings or offices.

Polystyrene foams

Generally, the properties of the polystyrene foams used for sandwich technology are:

- low densities, usually of 10–50 kg/m^3
- damping, thermal and acoustic insulating properties
- low permeability to water vapour, limited water absorption, good hydrolysis behaviour
- sometimes low mechanical properties depending on the processing method
- limited or weak resistance to solvents and hydrocarbons
- naturally low fire resistance that can be improved by an adequate formulation.

Table 6.16 shows some examples of polystyrene foam properties.

Table 6.16 Polystyrene foams: examples of properties

10% compression stress (MPa)	0.06–0.7
Compression strength for long-term service (MPa)	0.015–0.45
Thermal conductivity (W/m.K)	0.027–0.038
Water absorption, 28 days (%)	0.1–3

Examples of applications

- Insulating panels for refrigerated warehouses and other cold storage.
- Structural insulating panels.
- Sea sailboards or surfboards with laminate skins.
- External panels of houses or buildings with laminate skins.

Polyethylene foams

Generally, the properties of polyethylene foams for sandwich technology are:

- densities of 25–330 kg/m^3
- semi-rigid to flexible
- closed cells
- crosslinked or linear structure. Often, the crosslinking improves the mechanical properties and chemical resistance.

Polyethylene foams have:

- suitable mechanical characteristics
- insulating and damping properties
- low permeability to water vapour, limited water absorption, good hydrolysis behaviour
- limited or weak resistance to solvents and hydrocarbons
- a naturally low fire resistance that can be improved by an adequate formulation.

Table 6.17 shows some examples of the properties of polyethylene foam.

Table 6.17 Polyethylene foams: examples of properties

Density (kg/m^3)	25–185
Thermal conductivity (W/m.K)	0.034–0.067
10% compression stress (MPa)	0.012–0.160
50% compression stress (MPa)	0.080–0.33
Compression set, 22 h, 25% (%)	2–13
Tensile strength (MPa)	0.140–3.9
Elongation at break (%)	80–425
Water absorption, 7 days (%)	<1 to <2.5
Service temperatures (°C)	−80 to 100

Examples of applications:

- panels and sandwich structures for protection of oil wellheads
- multilayer composites for damping, sometimes in combination with polypropylene foam some helmets, for example, are made of thermoplastic skins and a core of one layer of PE foam with a second layer of polypropylene foam

Polypropylene foams

The typical properties of polypropylene foams for sandwich technology are:

- densities of 23–70 kg/m^3
- closed cells
- crosslinked or linear. As with PE and PVC foams, the crosslinking often improves the mechanical properties and chemical resistance.

Polypropylene foams have:

- suitable mechanical characteristics
- good resistance to multi-cycle impacts
- insulating and damping properties
- low permeability to water vapour, limited water absorption, good hydrolysis behaviour
- a naturally weak fire resistance that can be improved by an adequate formulation.

Table 6.18 shows some examples of polypropylene foam properties.

Table 6.18 Polypropylene foams: examples of properties

Density (kg/m^3)	23–70
Service temperatures (°C)	−40 (or −80) to +120
10% compression stress (MPa)	0.02–0.07
50% compression stress (MPa)	0.11–0.56
Compression set, 22 h, 25% (%)	6–11
Tensile strength (MPa)	0.2–1.2
Elongation at break (%)	15–400
Thermal conductivity (W/m.K)	0.034–0.042
Water absorption, 7 days (%)	1–2.5

The major application is in the damping cores of car bumpers.

An interesting development originating from Neste and Norsk Hydro is a multilayer coating for the insulation of deep-water pipelines. The steel pipe is protected by a layer of solid thermoplastic, a core of polypropylene foam and a coating of solid plastic. All the layers are built up by cross head extrusion.

Styrene-acrylonitrile foam: 'Core-Cell' by ATC Chemicals

This rigid linear foam with closed cells was developed by ATC Chemicals Company to be used as the core in lightweight structural sandwich composites particularly intended for boatbuilding.

SAN foams have:

- linear structure
- properties close to those for toughened crosslinked PVC
- better thermal stability than PVC
- thermoformability.

Table 6.19 shows some examples of the properties of styrene-acrylonitrile foams.

Table 6.19 Styrene-acrylonitrile foams: examples of properties

Density (kg/m^3)	58–210
Compression modulus (GPa)	0.042–0.420
Compression strength (MPa)	0.6–4.3
Tensile modulus (GPa)	0.045–0.340
Tensile strength (MPa)	0.9–4.2
Thermal conductivity (W/m.K)	0.032–0.046

Application examples in boatbuilding: hulls, engine stringers, bulkheads, decks and superstructures.

Polymethacrylimide foam: 'Rohacell' by Röhm

This rigid foam with closed cells was developed by the Röhm Company of the Hüls group to be used as the core in lightweight structural sandwich composites particularly used in transport applications.

Polymethacrylimide foams have:

- a density range of 30–300 kg/m^3
- excellent mechanical properties with a high thermal stability
- good resistance to the solvents used for processing composites
- low thermal conductivity
- high damping properties to impact
- low oxygen index, 19 to 20, which limits the fire resistance
- a low X-ray absorption.

Table 6.20 shows some examples of the properties of polymethacrylimide foam.

Table 6.20 Polymethacrylimide foams: examples of properties

Density (kg/m^3)	32	75	110	190
Compression strength (MPa)	0.4	1.5	3	3.2–7.8
Tensile strength (MPa)	1	2.8	3.5	8.5
Elastic modulus (GPa)	0.036	0.092	0.160	0.380
Elongation at break (%)	3.5	4.5	4.5	6
Flexural strength (MPa)	0.8	2.5	4.5	12–12.5
Thermal conductivity (W/m.K)	0.031	0.030	0.032	
Dimensional stability (°C)	180	180	180	130

Application examples:

- aeronautics: parts of Airbus, ATR, Eurocopter, Dassault, McDouglas Donnell; radomes
- car parts: Matra and Volvo
- railway: two-stage version of the TGV; front-end of the Italian Pendolino
- medical: radiography tables (low X-ray absorption)
- naval: sports boats, yachts, catamarans, racing motorboats
- sports: parts for skis, rackets (Head, Dynastar, Atomic), wheels and frameworks of racing bikes.

Polyetherimide foam: 'Airex R82' by Airex

This low-density foam with closed cells is associated with:

- a high impact strength
- broad range of service temperatures: −194°C to 180°C
- good fire resistance
- high thermal behaviour
- low water absorption
- attractive dielectric properties.

Table 6.21 shows some examples of polyetherimide foam properties.

Table 6.21 Polyetherimide foam: examples of properties

Density (kg/m^3)	80
Compression strength (about 6%) (MPa)	0.950
Compression modulus (GPa)	0.054
Flexural strength (MPa)	1.8
Flexural modulus (GPa)	0.052
Service temperature (°C)	−194 to +180
Thermal conductivity (W/m.K)	0.025

Application examples:

- aeronautics: equipment for planes, radomes and communication systems
- automotive and transport: structures for railway and road vehicles
- industry: structures in high-temperature and cryogenic applications.

Polyethersulfone foams

The low-density specific foam named 'Airex R80.90', specially developed by Airex, has:

- good fire resistance
- high thermal behaviour
- transparency to radar frequencies.

The 'Ultratect foam' from BASF is used as the core with glass fibre reinforced polypropylene skins for the sandwich rear seat backrest of the M3 CSL sports car by BMW. The weight saving is 50% versus a metal part.

Table 6.22 shows some examples of polyethersulfone foam properties.

Table 6.22 Polyethersulfone foams: examples of properties

Density (kg/m^3)	90
Compression strength (MPa)	0.790
Compression modulus (GPa)	0.025
Flexural strength (MPa)	1.5
Flexural modulus (GPa)	0.045
Thermal conductivity (W/m.K)	0.039

The major application markets of this foam are sandwich structures for:

- aeronautics and aerospace
- transmissions and telecommunications (transparency to radar frequencies).

Syntactic foams

Syntactic foams are obtained by mixing hollow micro- or macro-balloons, generally made of glass but sometimes of polymer, directly with a liquid resin, generally a thermoset. Some extend this definition to all composites with a foamed core.

For information, Table 6.23 shows some property examples of syntactic foams with thermoset matrices.

Table 6.23 High-performance syntactic foams: property examples

Density (kg/m^3)	500	600
Uni-axial compression strength (MPa)	44	90
Hydrostatic compression strength (MPa)	60	120
Compression modulus (GPa)	2	3
Flexural strength (MPa)	28	38
Thermal conductivity (W/m.K)	0.12	0.13

6.5.4 Honeycombs

Honeycombs are structures with hexagonal or cylindrical cells made from thin sheets of aluminium, aramid (Nomex), paper or extruded polypropylene. The dimensions of the cells are generally in the range of 5 mm to 10 mm. The two faces are covered with a firmly adherent composite (or sometimes metal) skin.

Figure 6.12 shows an example of a sandwich panel made from an extruded polypropylene honeycomb core (from Tubulam, Bagneux, France).

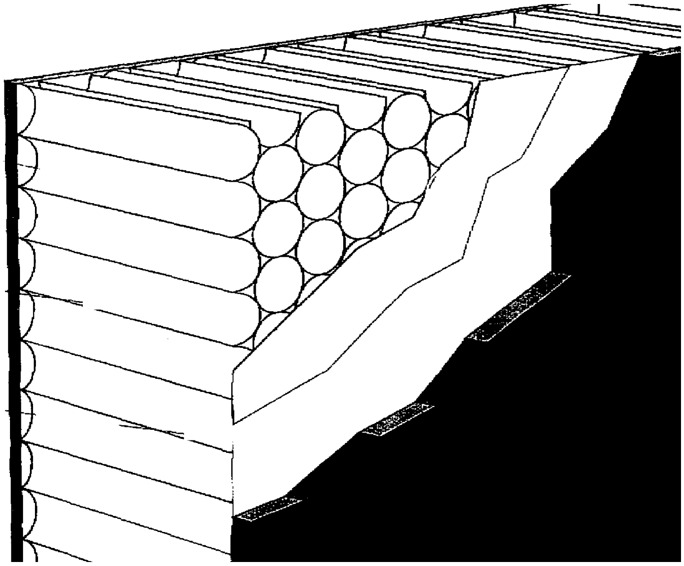


Figure 6.12. Example of a sandwich panel made from an extruded polypropylene honeycomb core

The density is low, 80 kg/m^3 or 140 kg/m^3 for example, with attractive mechanical properties but the skin adherence on the honeycomb section is delicate.

Generally, the sandwich composites combine light weight, good flexural stiffness and good stress distribution without weak points. Tensile and compression properties, particularly punching, can be weak.

Aramid honeycombs

The aramid honeycombs, for example Nomex, generally have:

- fair impact behaviour except punching
- good electrical insulating properties
- high ratio of flexural strength/weight
- high cost
- low lateral strength
- high moisture absorption needing a good waterproofing
- limited tensile and compression strengths.

Aluminium honeycombs

Aluminium honeycombs generally have:

- relatively attractive cost
- high ratio of flexural strength/weight
- good damping properties
- electrical conductivity
- surface finish difficult to obtain
- limited tensile and compression strengths
- sensitivity to corrosion needing special anticorrosion treatments.

The composites obtained can be used as structural elements in:

- Aircraft and space industry:
  - ○ floors of planes; wall, ceiling and flooring panels; soundproofing panels . . .
  - ○ vertical stabilizers, careenages for Atlantique2, helicopter rotor blades, ATR72 jib cowls . . .
  - ○ satellite solar panels, satellite antenna reflectors, radomes . . .
  - ○ storage bins.
- Automotive and transport:
  - ○ buses, trams, intercity trains, cable cars, caravan bodies.
- Buildings and furniture:
  - ○ frontages of Heathrow airport
  - ○ lightweight structural floors
  - ○ one-off range of furniture for an exceptional hotel room (Brochier room).
- Shipbuilding:
  - ○ bulkheads, partitions, watertight bulkheads
  - ○ mega yachts 40 m length.

6.5.5 Plywood and wood

Wood-based composites often use balsa, which has:

- relatively low density: 100 kg/m^3 and above
- attractive cost

- fair mechanical properties:
  - ○ compressive strength: 5–20 MPa in grain direction; 0.6–1.4 MPa in transverse direction
  - ○ compressive modulus: 2–8 GPa in grain direction; 0.1–0.4 GPa in transverse direction
  - ○ flexural strength: 6–17 MPa in grain direction.
- good impact behaviour
- fair thermal, acoustic and electrical insulation
- sensitivity to water and moisture needing a good waterproofing.

Plywood is the cheapest wood-based material and offers:

- good mechanical properties
- good impact behaviour
- good ratio of mechanical properties/cost
- sensitivity to water and moisture needing a good waterproofing
- relatively high density.

The composites obtained can be used in:

- shipbuilding: floor panels, decks, bulkheads, partitions, watertight bulkheads, fishing boats . . .
- road and railway transport: floors of refrigerated trailers or semitrailers, refrigerated vans, containers, etc.

6.5.6 Influence of the core on the sandwich properties

For 15 mm thick panels with GRP skins, the weights are roughly:

- 3 kg/m^2 for a 80 kg/m^3 honeycomb or foam
- 4 kg/m^2 for a 140 kg/m^3 honeycomb or foam
- 5 kg/m^2 for a balsa core
- 8 kg/m^2 for a plywood core.

Figures 6.13 and 6.14 compare sandwiches with a 13 mm core thickness and GFRP skins.

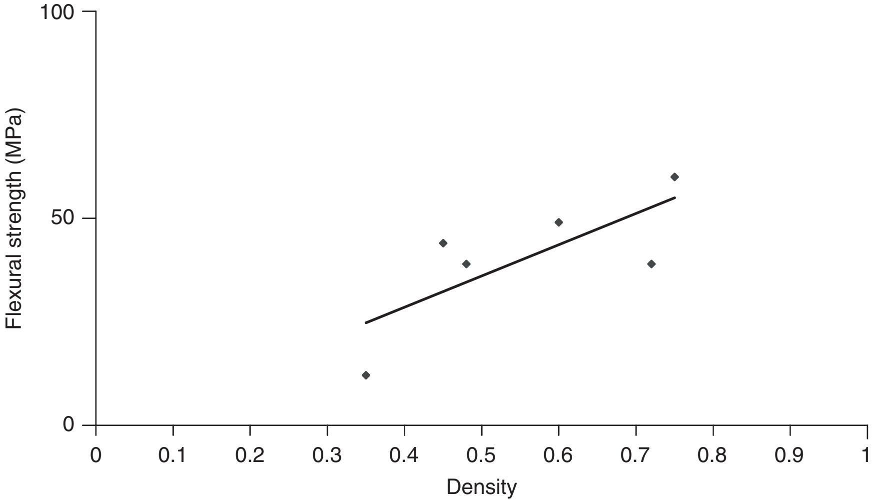


Figure 6.13. Sandwich structure examples: flexural strength versus density

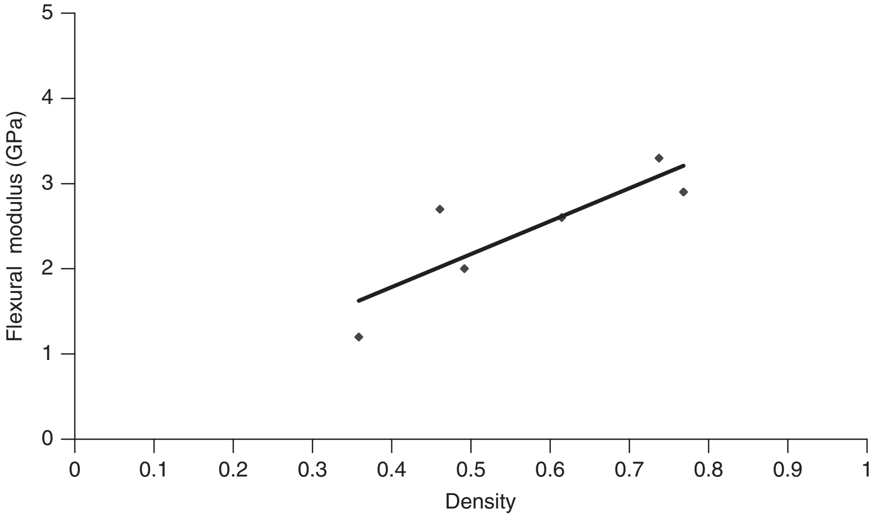


Figure 6.14. Sandwich structure examples: flexural modulus versus density

6.5.7 Nanofillers

Nanofillers (see Figure 6.15) are made up of:

- elementary particles in platelet form with a thickness of the order of a nanometre and diameter of the order of 100 nm
- primary particles made by stacking several elementary particles. The thickness is about 10 nm
- aggregates of numerous elementary particles.

Figure 6.15 shows schematically the structure of nanofillers.

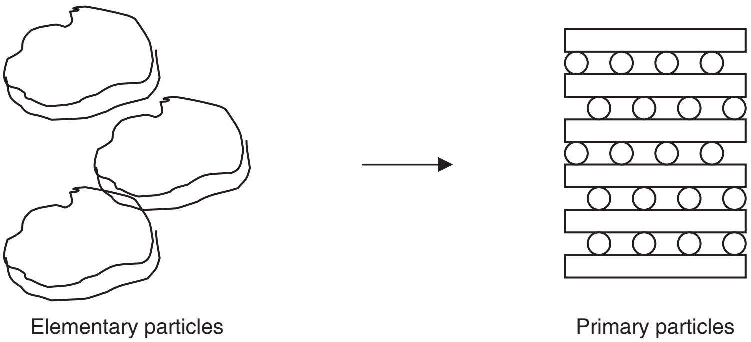


Figure 6.15. Schematic structure of nanofillers

To exceed the usual reinforcement offered by a filler and obtain a real nanocomposite it is necessary to destroy the primary particle structure:

- either completely, by dispersing the elementary particles into the macromolecules, giving a delaminated nanocomposite

- or partially, by intercalating macromolecules between the elementary particles, giving an intercalated nanocomposite.

Figure 6.16 shows schematically the structures of nanocomposites.

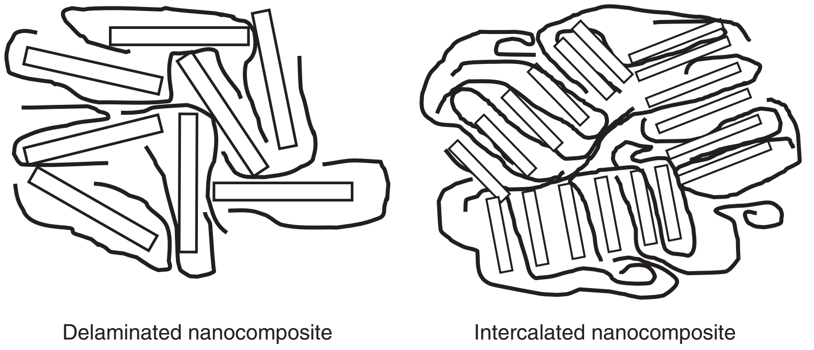

Delaminated nanocomposite
Intercalated nanocomposite

Figure 6.16. Schematic structures of nanocomposites

The most popular nanofiller is the natural layered silicate montmorillonite, which is subjected to specific treatments. The properties of the final nanocomposite depend on the nanocomposite treatments and the mixing efficiency.

Table 6.24 displays examples of polyamide nanocomposite properties according to the processing method.

Table 6.24 Property examples for polyamide nanocomposites processed by various methods

	Neat PA	PA nanocomposite	
		Property	Reinforcement ratios
Tensile modulus (GPa)	2.7	3.3–4.3	1.2–1.6
Tensile strength at yield (MPa)	64	69–85	1.1–1.3
Elongation at break (%)	40	8–60	Not available
Izod notched impact (J/m)	37	36–50	1–1.3

Practically all polymers can be processed to make nanocomposites:

- thermoplastics: some polyamide and TPO nanocomposites are used in the automotive industry and there are experiments with saturated polyesters, acrylics, polystyrenes . . .
- thermosets: studies have been carried out on epoxides, unsaturated polyesters, polyurethanes . . .
- elastomers: studies on nitriles . . .

The nanosilicates, because of their high aspect ratio, high surface area and nanometric scale, provide reinforcement at low levels of incorporation.

The main nanocomposite properties are:

- mechanical performances between those of the neat polymer and short glass fibre reinforced grades
- higher HDT than neat polymer but lower than short glass fibre reinforced grades
- density much lower than conventional reinforced grades
- lower gas permeability
- better fire behaviour.

Taking an industrial example (see Table 6.25), the reinforcement ratios – that is, the ratio of the nanocomposite performance versus that of the neat polymer – obtained with a nanosilicate level as low as 2% are noteworthy. For a very similar density, the nanocomposite has significantly better thermomechanical properties than the neat polyamide, as Table 6.25 shows.

Table 6.25 Property examples of a 2% nanosilicate-filled polyamide

	Property examples	Reinforcement ratios
Density (g/cm^3)	1.15	1
Tensile strength (MPa)	100	1.25
Flexural modulus (GPa)	3.9	1.3
HDT A (1.8 MPa) (°C)	140	1.9

6.6 Intermediate semi-manufactured materials

Some materials are moulded or shaped by means of semi-manufactured products: the thermoplastic matrix and the reinforcement are already assembled before processing, for example:

- GMT
- prepregs.

6.6.1 Glass mat thermoplastics (GMTs)

GMTs are thermoplastic resin sheets or blanks reinforced with glass mat. Possibly, unidirectional continuous fibres can also be used.

The blanks of this consolidated material can be shaped in steel tools by heating under pressure to a semi-molten state. The matrix is generally polypropylene (in more than 95% of GMTs) or, more rarely, thermoplastic polyester.

The parts have good mechanical properties but the creep behaviour is not as good as for thermoset composites.

High-performance GMTs are being developed with matrices such as polyethersulfone, polyetherimide, polyamide-imide, PPS, PEEK.

Two manufacturing processes, dry and wet, are in competition leading to some significantly different properties, particularly for the impact resistance:

- dry process: a mat covered above and below by melted polymer is compacted by heating under pressure
- wet process: discontinuous fibres (of shorter length than in the dry process) and thermoplastic powder are mixed and suspended in water. They are bound in a sheet form before being dried and compacted.

Because of the thermoplastic matrix, the shelf life is unlimited at room temperature.

The graphs in Figures 6.17 and 6.18 display two examples of polypropylene GMTs and two examples of thermoplastic polyester GMTs obtained by dry or wet processes. In each case, note the differences between the impact resistances.

6.6.2 Prepregs

Reinforcements of all forms such as fabrics, rovings, tapes, ribbons, etc. (made of aramid, glass or carbon fibres) can be impregnated with thermoplastic resins to give prepregs. The resin level can be as high as 85%. After or during shaping, consolidation is achieved by heating under pressure.

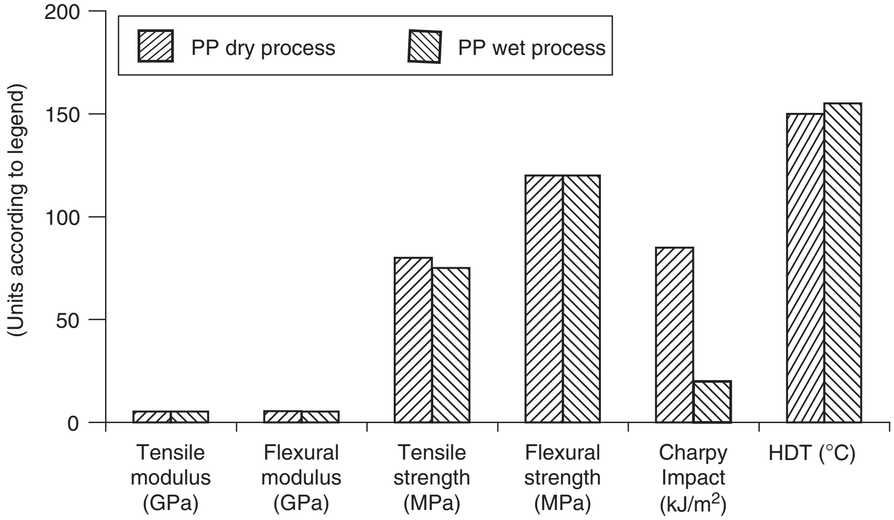


Figure 6.17. *Polypropylene GMT examples: thermal and mechanical property examples*

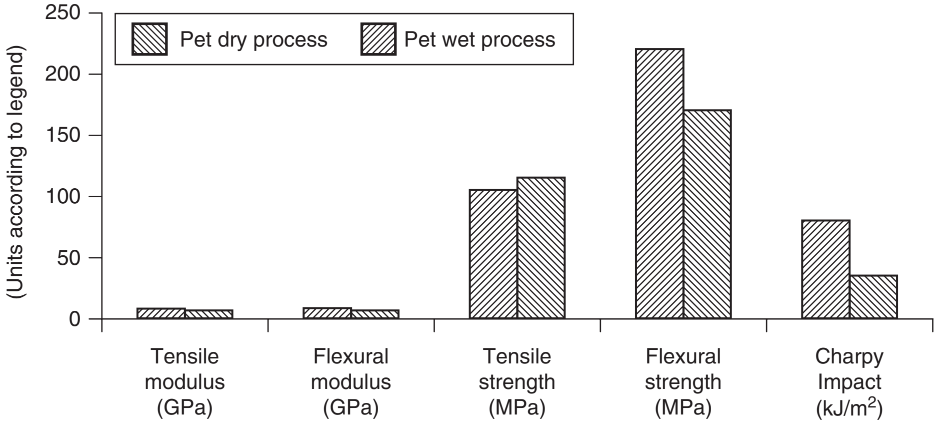


Figure 6.18. *Polyester GMT examples: thermal and mechanical property examples*

There are numerous variations for this technology, for example:

- Twintex R PP (from Saint-Gobain) is a roving composed of commingled E-glass and polypropylene filaments. It is suitable for filament winding and pultrusion. Consolidation is achieved by heating (180–230°C) under pressure.
- Twintex T PP is a fabric woven with commingled E-glass and polypropylene rovings. It is suitable for pressure moulding. Consolidation is accomplished by heating (180–230°C) under pressure.
- Twintex G PP is based on commingled E-glass and polypropylene rovings. Delivered in pellet form, it is suitable for injection or extrusion-compression. Consolidation is again achieved by heating (180–230°C) under pressure.
- Towflex (Hexcel Composites) is based on carbon, glass or aramid fibres impregnated with polypropylene, polyamide, PPS, polyetherimide, PEEK. Product forms include flexible Towpreg, woven fabric, braided sleeving, UD tape, chopped compression moulding compound, moulded plates, thermoformable laminates.

- Tepex (Bond-Laminates) is delivered as sheets of 0.25–3 mm thickness based on carbon, glass or aramid fibres impregnated with polyamide or thermoplastic polyester. Fibre levels range from 35% up to 85%.
- SUPreM, Plytron, Quadrax (Gurit Suprem): consolidated tapes or fabrics are made from continuous fibres impregnated with thermoplastic powder. The fibres can be glass, aramid, carbon, steel and the matrices are polyethylene, polypropylene, polyamide, PPS, polyetherimide, PEEK, thermoplastic polyimide, or fluorothermoplastic. High levels of fibres can be obtained, 65% in volume, for example.
- Fulcrum (Fulcrum Composites) is a unidirectional prepreg with fibre levels up to 70% in volume.
- EMS' hybrid yarns' or Schappe's 'preimpregnated yarns' are a combination of reinforcing fibres (glass, aramid or carbon) and polyamide 12.

Because of the thermoplastic matrix, the shelf life is unlimited at room temperature.

6.6.3 Property examples of intermediate semi-manufactured composites

Table 6.26 and Figure 6.19 display some property examples for various thermoplastic composites. These are examples, some other figures exist and the classification is arbitrary but, as already noted, the mechanical performances at room temperature are especially influenced by the nature, form and size of the reinforcements.

Table 6.26 Property examples for various intermediate semi-manufactured thermoplastic composites

	Short fibres	LFRT	GMT	UD
% of glass	30	50	40	60–70
Tensile strength (MPa)	42	165	100–250	350–450
Tensile modulus (GPa)	4	10–11	5–8	15–75
Flexural modulus (GPa)		11	6–10	
Impact strength, index	1.1	3	5–10	
General-purpose thermoplastic prepregs				
	Pellets	Balanced fabric	Roving	
% of glass	20–40	60	60–75	
Tensile strength (MPa)	85–120	350	700–800	
Tensile modulus (GPa)	5–9	15	28–38	
Flexural strength (MPa)	135–200	280	470–600	
Flexural modulus (GPa)	4–8	13	24–32	
Advanced fibre reinforced thermoplastic prepregs				
Matrix		PEEK	PEEK	PA
Fibres, nature	Glass	Carbon	Carbon	Carbon
Fibres (%)	55–75	40	65	
Tensile strength (MPa)	980–1100	1570	2600	800–2800
Tensile modulus (GPa)	43	78	150	63–245
Flexural strength (MPa)	1100–1340		2000	
Flexural modulus (GPa)	44		120	

6.6.4 Advanced all-polymer prepregs or self-reinforced polymers

This new solution to recycling problems uses the same polymer for the matrix and the reinforcement.

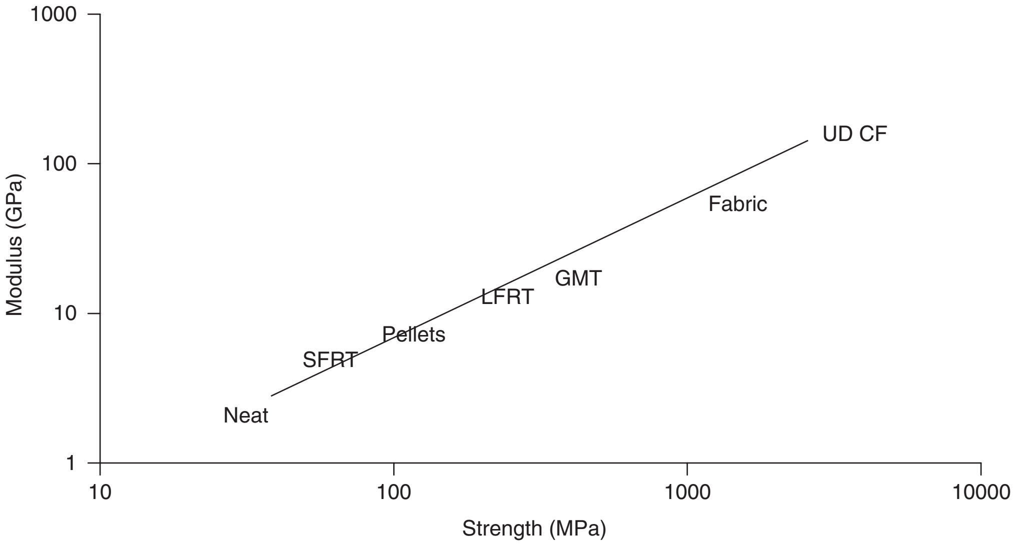


Figure 6.19. Examples of various intermediate semi-manufactured composites: modulus versus strength

The first industrial development is CURV by BP, a highly-stretched polypropylene fibre reinforced polypropylene delivered in sheets of 0.3 mm to 3 mm thickness.

In addition to the polypropylene properties and the ease of thermoplastic processing, these materials have:

- high mechanical performances including the impact strength
- a low density
- suitability for recycling because of the absence of glass fibre
- an attractive cost, €4 to €4.5 per kg.

Table 6.27 compares some self-reinforced polypropylene properties with those of other general-purpose solutions.

The (property/density) ratios show that the self-reinforced polypropylene is comparable to the general-purpose GMTs with a much higher impact resistance ratio.

The (property/volume cost) ratios show that the self-reinforced polypropylene has a much higher impact resistance ratio than general-purpose GMTs and glass fibre reinforced thermoplastics but a slightly lower modulus ratio.

Other self-reinforced polymers are being developed. For example, PURE is based on highly oriented co-extruded tapes of polypropylene and a consolidation binder. Properties vary according to the form (see Table 6.27) – sheets, tapes or fabrics.

6.7 Examples of composite characteristics

6.7.1 Basic principles

The reinforcement is the most important parameter in determining the mechanical properties.

Table 6.28 suggests a possible classification of the numerous reinforcement possibilities:

- Approximately, the reinforcement performance of the fibres increases from the top to the bottom of the table.

Table 6.27 Examples of self-reinforced polypropylene properties compared to other general-purpose solutions

	Self-reinforced polypropylene	Neat polypropylene	GMT
Density (g/cm^3)	0.92	0.9	1.19
Tensile strength (MPa)	180	27	70–100
Tensile modulus (GPa)	5	1.1	4–6
Notched Izod impact D256 at 20°C (J/m)	4750	200	670
Notched Izod impact D256 at −40°C (J/m)	7500	Brittle	Brittle
Examples of (property/density) ratios			
	Self-reinforced PP	GMT	Short GF Reinforced PA
Tensile strength/density	195	60–84	100
Tensile modulus/density	5.4	4–5	5.5
Notched Izod impact D256/density	5160	500–600	100–120
Examples of (property/volume cost) ratios			
	Self-reinforced PP	GMT	Short GF Reinforced PA
Tensile strength/volume cost	40	20–40	30
Tensile modulus/volume cost	1.1	1–2	1.7
Notched Izod impact D256/volume cost	1050	100–300	20–40
Examples of properties of self-reinforced polypropylene tapes and sheets			
	Sheets	Tapes	
Density (g/cm^3)	0.75–0.8	0.76	
Tensile strength (MPa)	200	500	
Tensile modulus (GPa)	6–7	13–17	
Notched Izod impact D256 at 20°C (kJ/m^2)	65		
Notched Izod impact D256 at −40°C (kJ/m^2)	>65		

- There is no possible comparison between fibre, flat core and 3D preform reinforcements.
- The matrix is the most important parameter in determining the other properties:
  - thermal behaviour, durability, chemical and fire resistance
  - however, the matrix makes a significant contribution to the mechanical performance in nanocomposites and discontinuous fibre composites.
- The reinforcement/matrix adhesion is essential to the final properties.

6.7.2 Nanocomposites

The reinforcement ratios are moderate but there are other advantages:

- the low filler level leads to a small density increase
- it is possible to decrease the gas permeability
- better fire-retardant behaviour.

On the other hand:

- nanocomposites are newly developing materials
- exfoliation is essential for efficiency but is difficult to obtain.

Table 6.29 displays some examples of nanocomposite properties.

Table 6.28 Classification of the main reinforcement possibilities

Morphology	Nature	Form	Arrangement
	Nanofiller reinforcement		
Nanofillers	Nanosilicates	Unit	Random
	Fibre reinforcement		
Short fibres:	Glass fibres	Unit	Random
	Aramid fibres	Unit	Random
	Carbon fibres	Unit	Random
'Long' fibres:	Glass fibres	Unit	Random
'Continuous' fibres	Natural fibres	Matted	Mat
	Glass fibres	Matted	Mat
		Interlaced	Woven, braided . . .
		Unit	Unidirectional
	Aramid fibres	Matted	Mat
		Interlaced	Woven, braided . . .
		Unit	Unidirectional
	Carbon fibres	Matted	Mat
		Interlaced	Woven, braided . . .
		Unit	Unidirectional
	Flat cores and 3D performs		
Flat cores	Wood, plywood	Flat	Core
	Foams	All shapes	Core
	Honeycombs	Flat	Core
3D preforms			

Table 6.29 Examples of nanocomposite properties

	Polyamide	Polypropylene
Density (g/cm^3)	1.15	0.9
Tensile or flexural modulus (GPa)	3.3–4.3	1.8–2.2
Tensile or flexural strength (MPa)	69–92	35–46
Elongation at break (%)	8–60	
Izod notched impact (J/m)	34–50	
HDT A (1.8 MPa) (°C)	100–140	

6.7.3 Short fibre composites

6.7.3.1 Significant parameters

Practically all the properties are influenced by the addition of fibres. The significant parameters are:

- nature of the fibre
- addition level
- real sizes of fibres in the finished part, the aspect ratio particularly
- homogeneity of the fibre distribution in the finished part
- sizing, which governs the fibre/matrix adhesion.

Generally, the addition of fibres:

- increases the mechanical property retention when the temperature rises
- improves creep behaviour

- can cause some anisotropy according to the fibre orientation. This leads, for example, to different shrinkage in different directions
- increases viscosity and makes the processing more difficult.

Effect of the fibre nature

Table 6.30 shows the properties of the same thermoplastic (short fibre reinforced polyamide) reinforced with the same level of the three main reinforcement fibres, illustrating the effect of the fibre nature.

Table 6.30 Property examples of short fibre reinforced polyamide reinforced with the same level of the three main reinforcement fibres

	E-glass	Aramid	Carbon
Density (g/cm^3)	1.29	1.19	1.23
Tensile strength (MPa)	100	95	207
Tensile modulus (GPa)	5.3	5.1	13
Elongation at break (%)	5	6	
HDT A (1.8 MPa) (°C)	250	222	250
Coefficient of thermal expansion (10^{-5}/°C)	3	2	
Resistivity (ohm.cm)	10^{12}	10^{13}	10^4–10^6
Charpy notched impact (kJ/m^2)	10	6	

Effect of the fibre level

Table 6.31 shows the properties of the same thermoplastic reinforced with increasing levels of the same short glass fibre.

Table 6.31 Property examples of the same thermoplastic reinforced with increasing levels of the same short glass fibre

Glass fibre (% by weight)	0	10	20	30	40	50
Density (g/cm^3)	1.14	1.21	1.29	1.37	1.46	1.57
Water absorption, 24 h (%)	1.3	1.2	1	0.8	0.7	0.6
Coefficient of thermal expansion (10^{-5}/K)	7	4	3	2.5	2	1.5
HDT A (1.8 MPa) (°C)	75	232	250	255	255	255
Shrinkage (%)	1.9	0.9–1.3	0.7–0.9	0.5–0.8	0.4–0.7	0.3–0.5
Strength (MPa)	50–60	70–95	100–135	135–175	165–210	175–250
Modulus (GPa)	1.5	2.4–3.2	4.2–5.3	6–7.5	8–10	9–13
Elongation at break (%)	55	10	5	4	3	2.5
Izod notched impact (kJ/m^2)	12	8	13	16	18	17
Resistivity (ohm.cm)	10^{13}	10^{13}	10^{13}	10^{13}	10^{13}	10^{13}

The effect of the fibre content varies for different properties:

- Some of them, such as density and water absorption, obey a law of mixtures.
- Others continuously decrease or increase as the fibre level increases.
- The impact strength decreases for small fibre levels and then increases.
- The resistivity is almost constant for glass fibre reinforcement but decreases in the case of carbon fibre reinforcement.

Effect of heterogeneity of fibre distribution

Fibres can gather at specific spots in a mould or can be diversely oriented leading to variations in the mechanical properties.

For a 40% glass fibre reinforced nylon, all other things being equal, a relative change of ±10% in the actual glass fibre level at a specific spot leads to a tensile strength change of about ±6%.

Mould shrinkage and coefficient of thermal expansion also vary by several percent and can lead to warpage.

6.7.3.2 *Short glass fibres*

Table 6.32 shows some basic property examples of short glass fibre reinforced thermoplastics. In some cases the glass fibres can be combined with mineral fillers.

Table 6.32 Property examples of short glass fibre reinforced thermoplastics

	PP	PA	PBT	POM
Density (g/cm^3)	1.1–1.2	1.3–1.4	1.5–1.6	1.5–1.6
Tensile or flexural strength (MPa)	40–70	100–160	110–160	130–140
Tensile or flexural modulus (GPa)	4–8	5–9	7–12	9–11
Elongation at break (%)	2–3	4–7	2–7	3–12
Izod notched impact (J/m)	45–160	130–160	50–230	50–100
HDT A (1.8 MPa) (°C)	120–140	230–260	195–240	145–163
Coefficient of thermal expansion (10^{-5}/°C)	2–3	2–3	2–5	2–3
Resistivity (ohm.cm)	10^{16}–10^{17}	10^{12}–10^{13}	10^{15}–10^{16}	10^{15}–10^{16}
	PC	**PSU**	**PPS**	**PEEK**
Density (g/cm^3)	1.35–1.5	1.4–1.5	1.8–2	1.5
Tensile or flexural strength (MPa)	90–160	100–125	60–150	150–180
Tensile or flexural modulus (GPa)	6–10	7–10	10–17	9–12
Elongation at break (%)	2–4	2–3	1–3	2–3
Izod notched impact (J/m)	90–200	55–80	25–70	95–130
HDT A (1.8 MPa) (°C)	140–150	175–185	170–260	290–315
Coefficient of thermal expansion (10^{-5}/°C)	2–4	2–3	1–2	1.5–2
Resistivity (ohm.cm)	10^{15}–10^{16}	10^{15}–10^{16}	10^{15}–10^{16}	10^{15}–10^{17}

6.7.3.3 *Short carbon fibres*

Table 6.33 shows the properties of the same thermoplastic (polyamide) reinforced with increasing levels of carbon fibres.

Table 6.33 Property examples of the same thermoplastic (PA) reinforced with increasing levels of carbon fibres

Carbon fibre (%)	Tensile strength (MPa)	Flexural modulus (GPa)	Izod notched impact (J/m)
0	81	2.8	48
10	152	6.5	43
20	207	13	75
30	241	18	96
40	255	24	100
50	262	34	107

As already seen, the effect of the carbon fibre content varies depending on the property that is being considered:

- some of them, such as density and water absorption, obey a law of mixtures.
- others, tensile strength or modulus, increase as the fibre level increases. The strength reaches a ceiling but the modulus continuously increases.

- The impact strength decreases for small levels and then increases.
- The resistivity decreases significantly; for example, the resistivity of neat PA is roughly 10^{12} but that of PA 6 with 30% CF is 10^{2}.

Generally, the addition of carbon fibres:

- increases the mechanical property retention when the temperature rises
- improves the creep behaviour
- decreases the resistivity
- can cause some anisotropy according to the fibre orientation. This leads, for example, to different shrinkage according to the direction
- increases viscosity and makes the processing more difficult.

Where glass fibre is replaced by the same level of carbon fibre:

- the modulus of a carbon fibre reinforced resin is roughly twice that of the same resin reinforced with the same weight of glass fibres
- the tensile strength is enhanced by 15–50%
- the impact strength of a carbon fibre reinforced resin is lower than that of a glass fibre reinforced resin, but the modulus is much higher.

Table 6.34 shows some basic property examples of short carbon fibre reinforced thermoplastics.

Table 6.34 Basic property examples of short carbon fibre reinforced thermoplastics

	PPE	POM	PBT	PC	PA 6 or 66	PA Ar
Carbon fibre (%)	<20	20	30	30	30	30
Density (g/cm^3)	1.2	1.46	1.41	1.31	1.26	1.34
Tensile strength (MPa)	140	170	160	170	230	240
Tensile modulus (GPa)	10	17	17	16	19	25
Izod notched impact (J/m)	70		60	100–130	80–100	50
HDT A (1.8 MPa) (°C)	115–135	160	220	140	215–255	220
Resistivity (ohm.cm)	10^2	10^3	10^3	10^3	10^2	10^3
	PSU	PESU	PEI	PPS	PEEK	LCP
Carbon fibre (%)	30	20–30	25	30	30	30
Density (g/cm^3)	1.36	1.45	1.37	1.46	1.44	1.5
Tensile strength (MPa)	160	150–190	200	170	210	190–240
Tensile modulus (GPa)	17	16	16	18	13–20	34
Izod notched impact (J/m)	80	45–75		55	80–110	350–100
HDT A (1.8 MPa) (°C)	185	215	210	260	315	220
Resistivity (ohm.cm)	10^2	10^2	10^4	10^2	10^5	10^3–10^4

6.7.3.4 Short aramid fibres

The reinforcing effect is similar to that of glass fibres with some minor differences:

- 10% lower density
- lower HDT
- higher moisture take-up, similar to the neat resin.

Some basic property examples of short aramid, glass and carbon fibre reinforced polyamide are shown earlier in Table 6.30.

6.7.4 Long fibre reinforced thermoplastics (LFRT)

LFRT (long fibre reinforced thermoplastics) are reinforced with fibres about 2 cm long, far from the length of 'continuous' fibres. Practically all the properties are influenced by the addition of fibres. The most significant parameters are:

- addition level
- real sizes of fibres in the finished part, the aspect ratio particularly
- homogeneity of the fibre distribution in the finished part
- sizing, which governs the fibre/matrix adhesion.

LFRT processing:

- Grades reinforced with fibres 10 mm long can be processed on conventional injection moulding equipment by simply adapting the processes to preserve the fibres.
- Grades reinforced with fibres 20 mm and more in length cannot be processed on conventional equipment. It is necessary to use, for example, the extrusion-compression technique. The process differs too much from conventional injection used for short glass fibre reinforced thermoplastics to measure the influence of fibre length alone.

Table 6.35 displays some basic property examples of long glass fibre reinforced polyamides and polypropylenes.

Table 6.35 Basic property examples of long glass fibre reinforced polyamides and polypropylenes

Polypropylenes				
Glass fibre weight (%)	30	40	50	60
Density (g/cm^3)	1.12	1.22	1.34	1.59
Tensile strength (MPa)	46–107	55–124	92–131	262
Tensile modulus (GPa)	4–6.9	4.2–9.0	7.8–13.8	18.6
Notched Izod impact (J/m)	213	265	295	295
Polyamides				
Glass fibre weight (%)	30	40	50	60
Density (g/cm^3)	1.36	1.45	1.56	1.69
Tensile strength (MPa)	197	155–257	190–304	230–323
Tensile modulus (GPa)	10.4	11.4–14.4	12.8–18.6	22–23.5
Notched Izod impact (J/m)	270	213–373	347–621	375–670

Long glass fibres lead to:

- maximum values of the strengths and moduli of the same order as those obtained with short carbon fibres, definitely higher than for short glass fibres
- attractive (impact strength/modulus) ratios
- a better retention of properties than with short glass fibres when the temperature increases.

Trade name examples

Celstran, Compel, Pryltex, Twintex, Verton.

6.7.5 'Continuous' fibre composites

In this category, not all the reinforcement fibres are truly continuous (certain GMT, for example) but they all have a longer length than in the LFRT.

The mechanical performances vary with:

- the fibre nature
- the fibre level

- the aspect ratio (length versus diameter) for the chopped fibres or the form of the fibres (filament, roving, fabrics . . .) for the truly continuous fibres
- the orientation and the quality of the fibre dispersion, and the anisotropy in the final part. For example, the tensile strength of unidirectional composites can be greater than 2000 MPa in the fibre direction and less than 100 MPa in the transverse direction
- the treatment of the fibres to enhance adhesion to the matrix
- the real length of the fibres in the final part.

Table 6.36 displays basic property examples of: glass mat thermoplastics (GMT); thermoplastic prepregs; and glass or carbon reinforced unidirectional composites.

Table 6.36 Basic property examples of fibre composites

	Glass mat reinforced polypropylene				
Glass fibre (%)	30	40	40	40	43
Density (g/cm^3)	1.13	1.19	1.2	1.2	1.21
Tensile strength (MPa)	70–85	77	95	105	250
Flexural strength (MPa)	120	145	155	155	160
Elongation at break (%)	3	4	3	2	2
Tensile modulus (GPa)	5	5.8	7	4.8	8
Notched impact (kJ/m^2)	54	10			132
HDT A (1.8 MPa) (°C)	153	154	165	156	158
Melting or softening point (°C)	170	170	170	170	170
Coefficient of thermal expansion (10^{-5}/°C)	1.4–2.9	2.7	2.7	2.7	2.6

	Glass mat reinforced thermoplastics			
	PET	PA	PPO	PC
Glass fibre (%)	30	30	30	30
Density (g/cm^3)	1.55	1.35	1.28	1.4
Tensile strength (MPa)	110	73	125	160
Flexural strength (MPa)	185	122	205	185
Elongation at break (%)	3	3		
Tensile modulus (GPa)	7.4	6.8	7	8
Un-notched impact strength (kJ/m^2)	35–110		50	55
HDT A (1.8 MPa) (°C)	210	210	220	160
Melting or softening point (°C)	256	215	290	230
Coefficient of thermal expansion (10^{-5}/°C)	1.5			

	PEI	PPS
Glass fibre (%)	30	Unknown
Density (g/cm^3)	1.47	1.36–1.66
Tensile strength (MPa)	190	160–370
Flexural strength (MPa)	210	280–450
Tensile modulus (GPa)	11	13
Un-notched impact strength (kJ/m^2)	50	
HDT A (1.8 MPa) (°C)	230	270
Melting or softening point (°C)		280

	Property examples of thermoplastic prepregs		
Thermoplastic	PP	PP	PET
Glass fibre (%)	60	75	65
Density (g/cm^3)	1.5	1.75	1.95
Tensile strength (MPa)	180–500	420	440
Compression strength (MPa)	100–230	140–160	410
Tensile modulus (GPa)	8–24	21	25
Un-notched impact strength (kJ/m^2)	90–330	300	300
HDT A (1.8 MPa) (°C)	159	159	257

Table 6.36 (Continued)

	Property examples of UD thermoplastics		
Thermoplastic	PP		PP
Glass fibre (%)	60		75
Direction	Machine	Transverse	
Density (g/cm^3)	1.5	1.5	1.75
Tensile strength (MPa)	720	11	700
Compression strength (MPa)	170–366		170
Tensile modulus (GPa)	28–32	3.7	32–38
Un-notched impact strength (kJ/m^2)	445		445
Notched impact strength (J/m^2) @ 23°C	383		
Notched impact strength (J/m^2) @ −30°C	425		
HDT A (1.8 MPa) (°C)	156–159	156–159	159
Coefficient of thermal expansion (10^{-5}/°C)	0.7	9	

	Property examples of UD thermoplastics
Thermoplastic	PA 12 & carbon fibre hybrids
Carbon fibre (% volume)	56
Density (g/cm^3)	1.44
Tensile strength (MPa)	830
Tensile modulus (GPa)	65
Un-notched impact strength (kJ/m^2)	445

Thermoplastic	UD CF/PEEK		
Carbon fibre (% volume)	40	50	60
Density (g/cm^3)			
Tensile strength (MPa)	1570	1960	2400–2800
Tensile modulus (GPa)	78	98	125–142
Flexural strength (MPa)			2000
Flexural modulus (GPa)			120

Trade name examples

APC 2, Fulcrum, Plytron, SUPreM, Tepex, Towflex, TPS, Twintex . . .

6.7.6 Sandwich composites

The sandwich composites combine the following:

- Light weight: densities are often less than 1 g/cm^3 compared to more than 1.5 g/cm^3 for the composites discussed above.
- High flexural rigidity.
- Medium to low tensile properties according to the tensile properties of the core. The tensile strength and modulus of a 100 kg/m^3 foam are roughly as low as 3 MPa and 0.1 GPa, respectively.
- Good compression properties for cores made of honeycombs, wood and plywood. Low compression properties for foamed cores. The compression strength and modulus of a 100 kg/m^3 foam are roughly as low as 2 MPa and 0.1 GPa, respectively. On the other hand, pinpoint impact is distributed across the whole surface facing, provided it is sufficiently resistant.

Figure 6.20 displays schematically a symmetrical sandwich panel made up of:

- an upper facing of composite having modulus E_f and thickness t
- a core of foam having modulus E_c and thickness C
- a lower facing of the same composite having modulus E_f and thickness t.

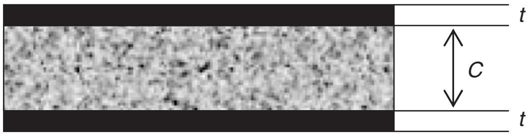


Figure 6.20. Schematic of a sandwich panel

For a beam of width b, the formula for flexural rigidity (D) can be expressed as:

$$D = E_f bt^3/6 + 0.5E_f bt(C + t)^2 + E_c bC^3/12$$

E_c is negligible compared to E_f and the last term can be omitted to lead to a simpler expression:

$$D = E_f bt^3/6 + 0.5E_f bt(C + t)^2$$

And, if we compare various sandwich structures of the same materials and same facings with increasing core thickness only, we can write:

$$D/(E_f b) = t^3/6 + 0.5t\,(C + t)^2$$

By application of this equation for a facing thickness of 0.5 ($t = 0.5$), Figure 6.21 shows the ratio of $D/(E_f b)$ for a sandwich panel to$D/(E_f b)$ for the facings without foam, as a function of the foam core thickness. Note that rigidity can be multiplied by 50 for a core thickness of 3.6, that is to say, a panel thickness of 4.6 and a practically unchanged weight.

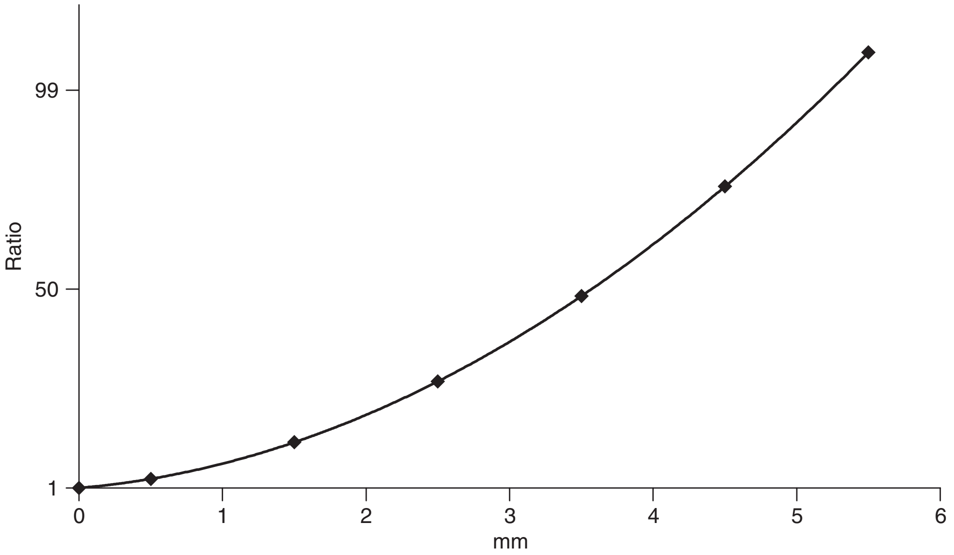


Figure 6.21. Example of panel rigidity/facing rigidity ratio versus foam thickness

All these considerations are purely theoretical and cannot be used for designing, but they give an idea of the broad possibilities of sandwich structures that are also illustrated by Figure 6.22, showing some examples of sandwich flexural moduli.

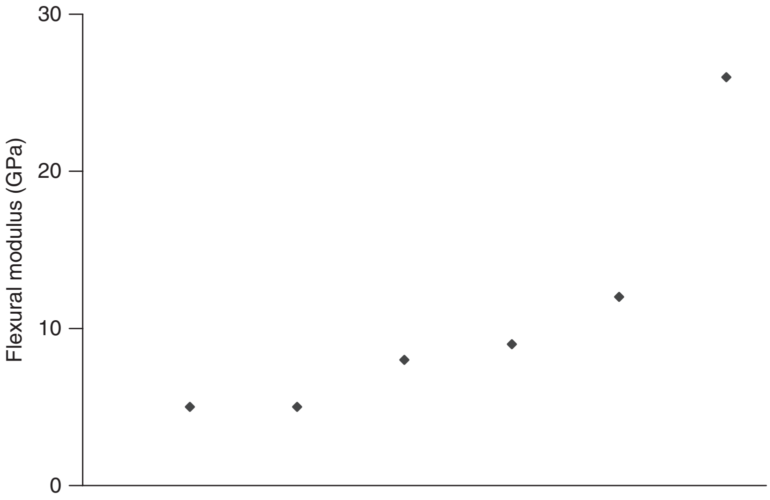


Figure 6.22. Example of flexural modulus (GPa) for various sandwich structures

Considering another point of view, Swedish manufacturer DIAB quotes an example of a sandwich and a laminate of approximately the same flexural rigidity: the laminate is 2.8 times heavier than the sandwich panel.

6.7.7 Conductive composites

Composites can be rendered conductive, antistatic or resistant to EMI by several methods, such as:

- metal coatings: application of sheets or strips of metal, metallization
- addition of conductive ingredients in sufficient quantity to exceed the threshold of percolation: metal powders, graphite, metal fibrils, carbon blacks
- use of conductive reinforcements: metallized glass fibres, carbon fibres, steel fibres.

The resistivities range from less than 1 ohm.cm up to 10^6 ohm.cm. The mechanical properties can be affected.

Table 6.37 compares some properties of conductive and neat plastics.

Table 6.37 Examples of properties of conductive and neat plastics

	Polypropylene					
Fibres	None		Stainless steel			Carbon
Resistivity (ohm.cm)	10^{17}		10^3			10^3
Tensile or flexural strength (MPa)	30–40		41			41
Flexural modulus (GPa)	1.3		1.4			4.3
	ABS		PA 66		PPO	
Aluminium powder (%)	0	40	0	40	0	40
Density (g/cm^3)	1.1	1.57	1.1	1.48	1.1	1.45
Tensile strength (MPa)	30–65	23–29	40–85	41	45–65	45
Elongation at break (%)	3–60	2–5	150	4	2–60	3
Tensile modulus (GPa)	1–3	2.5	1–3.5	5	2.5	5.2
Thermal expansion coefficient (10^{-5}/°C)	6–10	4	5–14	2.2	3–8	1.1
HDT A (1.8 MPa) (°C)	100	95	85	190	110	110

References

Technical guides, newsletters, websites

3M, 3Tex, AES, Airex, Akzo Plastics, Allied Signal, Alusuisse, Amcel, Amoco, Alveo, Arkema, Asahi Fibre Glass, Asahi Kasei, Astar, Ashland, Azdel, Baltek, BASF, Bayer, Besfight, BF Goodrich, BFG Int, Bond Laminates, BP, Borealis, Bryte, Ciba, COI Materials, Cray Valley, Cytec, Degussa, DIAB, Dow, DSM, DuPont, Eastman Chemical, Elastogran, EMS, European Alliance for SMC, European Alliance for Thermoplastic Composites, Exxon, Ferro, Fibre Glast, GE, Goodyear, Haufler, Haysite, Hexcel, Hoechst, Hüls, Hydro Polymers, ICI, Isosport, Jet Moulding Compounds, Kraton Polymers, Kuraray, Lankhorst Indutec, LNP, MatWeb, MFC, Mitsubishi, Montell, Multibase, Neste, Nippon Zeon, Owens Corning, Parabeam, Philips Petroleum, Plascore, PPG, PRW, Quadrant, Rhodia, Röhm, RTP, Sabic, Saint-Gobain, Schulman, Scott Bader, Shell, Silenka, Sintimid, SNIA polimeri, Soficar, Solvay, SP Systems, Stratime Capello Systems, Sulzer Composites, Sumitomo, Symalit, Thermotite, Ticona, Toray, Tubulam, Twaron, Ube, Vetrotex, YLA, Zherco Plastics, Zoltek, Zyex.

Reviews

[1] *Plastics Additives & Compounding* (Elsevier Science)
[2] *Engineering & Manufacturing Solutions for Industry Composites* (Ray Publishing, Wheat Ridge, CO 80033, USA)
[3] *High-Performance Composites* (Ray Publishing)
[4] *Modern Plastics* (ModPlas.com)
[5] *Reinforced Plastics* (Elsevier Science)
[6] *Techniwatch* (CRIF)

Papers

[1] A. Garcia-Rejon *et al.*, Antec 2002, p. 410
[2] A.K. Bledzki, J. Gassan, M. Lucka, *International Polymer Science and Technology*, Vol 27, No. 8, (2000), p. T/75
[3] A.R. Bunsell, *Fibre Reinforcements for Composite Materials*, Elsevier
[4] J. Klunder, *Introduction to glass fibre reinforced composites*, Second edition, (1993) [available from: PPG Industries Fiber Glass bv, Mail Box 50, 9600 AB Hoogezand, The Netherlands]

Chapter 7

Future prospects for thermoplastics and thermoplastic composites

The consumption of thermoplastics and thermoplastic composites is controlled by:

- user market demand
- the ability to adapt these materials to economic and technical market requirements and to propose technological advancements
- the capacity for innovation in terms of materials and processes
- the adaptability to environmental constraints: recycling, sustainable matrices and reinforcements.

The purpose of this exploratory study is to provide some background information on these various points.

7.1 The laws and requirements of the market

Apart from exceptional cases, any manufacturer is subject to general regulations induced by the economics of competition, customers' rights and requirements, and the legislative arsenal.

Figure 7.1 points out some of the main market constraints.

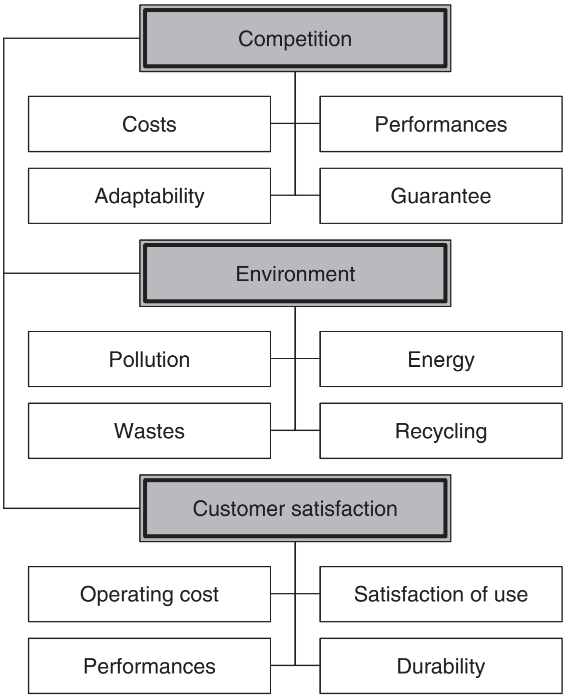


Figure 7.1. Laws and requirements of the market

While the majority of these points speak for themselves, others need to be restated.

Reduction of production costs

Cost prices are optimized by reductions in:

- the number of parts necessary to satisfy all the functions
- raw material costs

- part weights
- investments
- payroll
- scrap
- manufacturing costs
- finishing costs
- joining and assembly costs.

Adaptability

Customers' requirements, changing fashions and technological developments involve a shortening of product life cycles. So, the manufacturers turn to materials that allow fast and economic design and easy adaptation of the production equipment.

Guarantee

The extension of warranty periods is viable only if the performance and the durability of the product make it technically possible.

Operating cost

This depends on:

- the costs in energy, process fluids and others
- maintenance expenses: simplification of maintenance and cleaning; reduction of repair and restoration operations
- durability.

User satisfaction

This is a combination of a multitude of objective or subjective parameters, for example:

- ease of use and maintenance
- reliability
- aesthetics
- lack of noise and vibration in operation.

7.2 Thermoplastic and thermoplastic composite answers and assets

The use of thermoplastics and thermoplastic composites makes it possible to satisfy some of the requirements listed above, provided all the players are involved from the beginning of the project and problems such as the process of transformation and downstream recycling are taken into account from the start of the design phase.

The diagrams in Figures 7.2 and 7.3 propose general schemes of the services to involve and the parameters to be taken into account.

At the **design stage** it is necessary to seek:

- The best performance/density/cost compromise giving the best cost with the lowest weight and sufficient performance levels to meet the requirements. Plastic/metal or plastic/wood/metal hybrid materials are sometimes excellent solutions.
- Integration of functions to reduce the number of parts and minimize the costs of materials, processing, finishing, assembly/joining and intermediate storage.

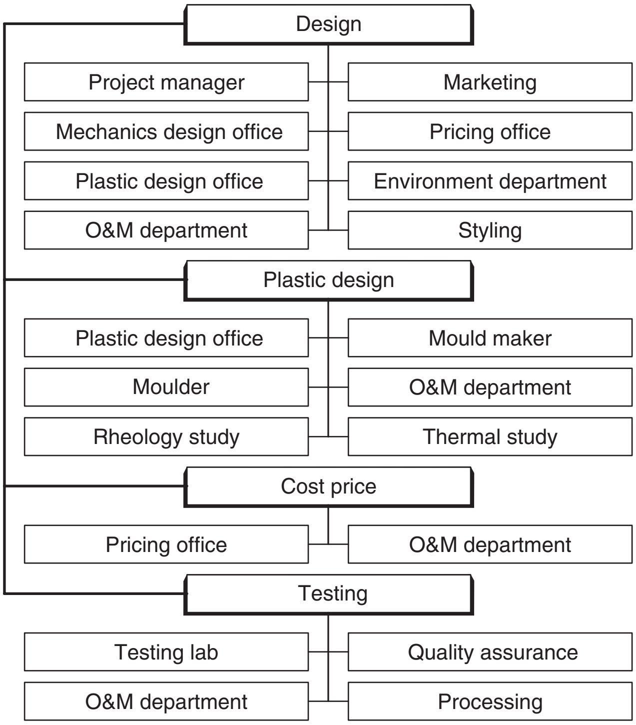


Figure 7.2. *Design diagram*

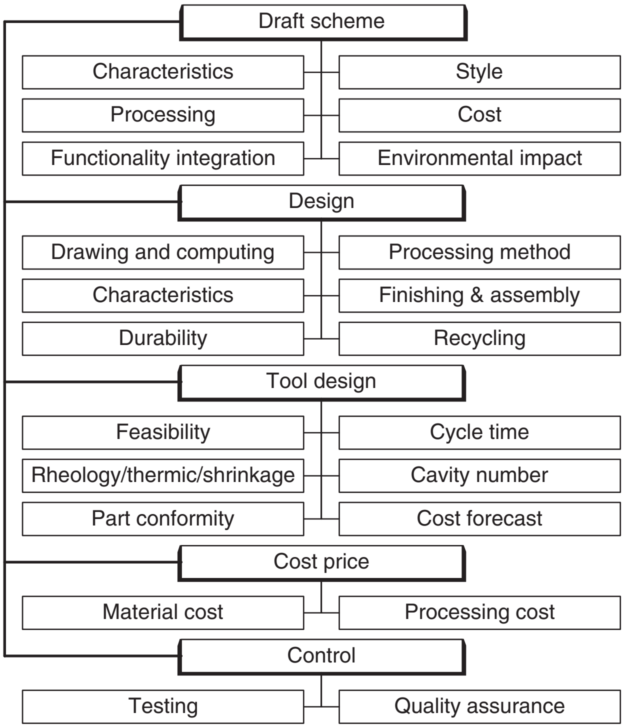


Figure 7.3. *Project diagram*

- The design of the parts that optimizes the thicknesses and reduces weights and cycle times.
- Processing methods that are adapted to the product, and that allow the series to be manufactured with the simplest tools and minimal investment. The combination of several techniques, for example, extrusion or moulding and machining, can bring economic solutions.
- The possibility of bulk colouring and in-mould decoration, which can simplify or avoid the finishing operations.
- The simplest assembly and joining methods. In-mould assembly can significantly reduce or eliminate assembly costs.

At the **manufacturing step** it is necessary to ensure:

- the adequacy of the machines and tools for the parts to be manufactured and the materials to be processed, in order to ensure optimal properties and reduce waste
- good maintenance of the machines and tools to ensure the accuracy of the size and geometry, combined with optimal properties, a minimum of finishing operations and a minimum of waste
- the reasonable use of quality assurance and strict procedures to make the production reliable and to limit wastes.

Provided the design and manufacturing requirements are met, plastic components can offer:

- lower costs that, in certain cases, make it possible to develop new applications
- a light weight involving fuel savings for vehicles, reduced expenses for packaging and transport, and decreased waste at the end of product life
- corrosion resistance, decreasing the maintenance or renovation costs for boardings, roofs, etc. and in composites
- transparency for certain families and grades, such as polycarbonates, PMMA glazings
- better impact resistance than glass
- greater design freedom than many traditional materials such as metals (realization of forms that cannot be achieved with metals)
- reduction and miniaturization of parts by the integration of functions and co-transformation (combination of flexible and rigid parts or compact and cellular parts)
- a faster adaptation of manufactured parts thanks to easier replacement and modification of tools than with metals
- a shortened time for design, development and manufacturing
- aesthetic properties and versatility of surface aspects
- possibility of bulk colouring
- possibility of decoration to obtain traditional material appearances such as wood or metals
- good thermal insulating properties allowing energy savings (buildings) and comfort improvement
- good electrical insulating properties
- damping properties: lower noise, improvements to comfort and safety (polyethylene, polypropylene and other foams)
- ease of handling and installation.

On the other hand, it is necessary to be aware of the ageing, mechanical resistance and thermomechanical behaviour, which are different from those of metals. The recycling of plastics presents some difficulties that are not generally solved in a satisfactory way.

To achieve greater **market penetration**, thermoplastics and thermoplastic composites must enhance prices, performances, characteristics, productivity, ease of processing and recycling.

Among the ways to success we can cite:

- improvement of the cost/performances ratios
- improvement of the immediate and long-term characteristics, after use and ageing, for the conquest of structural parts
- better thermal resistance
- better weathering behaviour
- enhancement of the colouring and surface appearance
- improvement of the surface properties: scratch resistance, dusting, staining, tarnishing, chalking and so on
- adaptability of the grades, which must satisfy the requirements of the market and develop specific properties, for example coefficient of friction, electrical conductivity, better combination of mechanical properties/thermal behaviour/electrical characteristics/ageing
- availability of halogen-free fire-retardant grades
- improvement of the adherence of paints, printing inks, adhesives
- better low-temperature performances: legal requirements are moving towards an increase in the impact resistances at low temperature with a ductile behaviour
- ease of processing: improvement of the flow properties and the aptitude for injection lead to cycle time shortening and better productivity
- improvement of mould productivity: cooling, use of multiple cavities
- automation of the process equipment
- better control of the processes by statistical processing of the recorded parameters (SPC)
- development of new manufacturing methods
- on-line compounding to reduce costs and thermal degradation
- hybrid combinations with non-plastic materials, for example:
- ○ assembly of plastic panels onto a metal structure allowing very large objects to be obtained for extremely low investments
- ○ hollow PVC elements filled with concrete to form rigid structures
- use of wastes and recycled materials to satisfy environmental requirements and lower the costs.
- management of recycling, which starts with the design reducing the diversity of the materials used, improving their compatibility, the marking of the parts and their ease of dismantling. The subsequent waste collection, recycling and outlets require work on economical and technical issues.

7.3 Markets: what drives what? The forces driving development

7.3.1 Consumption trends

In round figures, the consumption of thermoplastics and composites may increase by a few percent per year during the next few years (see Table 7.1).

Environmental regulations and trends favour:

- thermoplastic composites
- sustainable materials
- water-based or powder-based adhesives, coatings and so on.

Table 7.1 Annual growth (%) in major thermoplastics and composite consumption

	Thermoplastics
Polyethylene	4
Polypropylene	10
PVC	4
PS	4
ABS	5
Polyester (thermoplastic)	7
Polyamide	6
Polycarbonate	10
PMMA	4
Polyacetal	5
	Composites
Automotive & transportation	5
Corrosion protection	5
Shipbuilding	5
Electrical & electronics	4
Sports & leisure	4
Railway	4
Medical	4
Aeronautics	3
Building & civil engineering	2
Mechanical & industrial	2

The preference granted to thermoplastics compared to thermosets stems from some inherent advantages such as:

- the predominance of the thermoplastic industry with a very much larger offering of materials, equipment and manufacturers
- the avoidance of the curing step, which consumes time and money
- the shorter processing cycles
- the welding possibilities
- a greater ease in recycling.

7.3.2 Requirements of the main markets

The main expressed requirements are:

- automotive: costs and recycling
- aeronautics: costs and durability
- electrical & electronics: costs, recycling, conductive polymers
- building and public works: durability with a 50-year objective, processing and cost
- shipbuilding: durability, industrialized processing, and costs
- sports & leisure: cost and low weight
- railway: fire behaviour, cost, processing
- medical: performance, biocompatibility, cost, processing
- mechanical & industrial: cost, processing.

For each market there are also underlying demands and the global requirement list can be estimated as follows:

- cost and [cost/performance] ratio
- recycling and outlets

- processing: the objectives depend on the market and cover all situations from fully automated processes for automotive mass production to unitary processes for prostheses
- performance, including manufacturing possibilities from very small to giant parts
- durability including aesthetics. The lifetime requirements vary from a few years to 50 years according to the market
- light weight and [weight/performance] ratio
- fire behaviour: halogen-free fire-retardant behaviour; low smoke emissions of low toxicity
- electrical conductivity: from antistatic to metal conductivity.

7.4 Cost savings

7.4.1 Material costs

There are several ways to cut down material costs:

- Choose a cheaper family with the proviso that the performances are of a sufficient level to satisfy the functions.
- Use a reinforced grade to reduce the wall thickness and consequently the material weight. In ascending order of performance but also of cost, the most-used reinforcements are: natural fibres, glass fibres, aramid fibres, carbon fibres. Carbon fibres, if their development leads to a substantial lowering of their cost, could solve many cost problems.
- Increase the performances (and costs) to lead to a very substantial improvement in performances, particularly in the durability of the finished part, which reduces the overall number of parts to be manufactured and recycled, and the associated costs.

7.4.2 Hybrids

Hybrid materials, as defined and described previously in Chapters 1 and 2, are developing because of the substantial cost cutting they offer due to:

- High function integration thanks to the plastic elements that allow integration of fixings, housings, embossings, eyelets, clips, etc. avoiding:
  - ○ the assembly of the integrated components
  - ○ the accumulation of the dimensional defects of the integrated components
  - ○ later welding operations capable of causing deformations.
- The combination of simple processes from plastic and metal technologies. Each material has its advantages and drawbacks. Hybrids that closely associate two or more families benefit from their best properties and mask their weaknesses.

The polymer can often bring:

- aesthetics and style
- global cohesion of all the components
- damping
- thermal and electrical insulation.

Metals often bring:

- structural properties
- impermeability
- electrical conductivity.

Several producers such as Bayer, Dow (LFT-PP concept), Rhodia (PMA and MOM processes) have developed their own hybrid technologies.

A typical development is the front-end of recently introduced cars such as the Mini Cooper from BMW or Mazda 6 in which long glass fibre reinforced polypropylene is injected onto stamped metal. The weight saving is in the range of 30–35% compared to traditional solutions with a high function integration.

7.4.3 Processing costs

Intensive processing research is based on several routes to reduce costs:

- globalization of processing, from raw materials to finishing
- automation
- industrialization
- simplification.

Some examples are listed below.

7.4.3.1 Example of compounding integrated on the process line

The integration of the compounding of long glass fibre reinforced thermoplastics on the process line is an example of the globalization and automation of the process.

This technique brings cost savings and decreases the thermal and mechanical degradation by avoiding one step involving plasticization and re-heating of the material. In principle, the glass fibres are chopped and added to the thermoplastic in a special extruder/mixer synchronized with the shaping processing equipment to feed it with plasticized, hot material.

The economy is expected to be of the order of €0.30 per kg and mechanical properties are improved.

7.4.3.2 Translation towards other conventional, new or modified processes

There is a plethora of routes:

- roboticization, automation of known processing methods
- improvement of known processes
- translation from conventional methods towards other conventional processing routes more adapted to the run size
- integration of production steps directly in the mould: in-mould decoration, in-mould assembly, in-mould labelling . . .
- new processing methods.

Let us quote some examples:

- Krauss-Maffei is launching a new mould-temperature control technology using two separate mould-cooling circuits that it claims will enable DVD discs to be produced with cycle times of less than three seconds. One cooling circuit maintains mould surface temperature during injection of the polymer at a sufficiently high level to achieve a suitable surface quality. The second circuit, much cooler, rapidly draws thermal energy from the mould.
- A new thermoformable grade of polyamide from Bayer can be extruded into sheets and then thermoformed to deep draw ratios, allowing the production of spoilers for BMW.
- Dow Automotive is developing blow moulding of rear car seats. The prototype uses Dow Automotive's Pulse 220BG, a PC/ABS blend.
- Based on microcellular thermoplastic foam technology, the MuCell process uses a blowing agent (typically CO_2) that in a supercritical state creates foams with evenly distributed and uniformly sized microscopic cells, 5–50 μm for example. This foam

offers improved consistency and homogeneity of cell structures, which can result in excellent properties.
- A special design of injection presses (from Husky) is used to mould hinged, flip-top lids for wet-wipe containers that are folded during mould closure. When compared to conventional systems, this new device can lead to a 10% to 15% increase in output and a 15% to 25% reduction in floorspace.
- Milacron is collaborating with Foboha on the development of a machine that simultaneously moulds two parts in two different materials and snap-fits them during injection of the next parts. A robot removes the finished assembly allowing a cycle time of the order of 6–7 seconds to be achieved.
- In-mould assembly (IMA) of a filter housing saves assembly time and simplifies logistics. Cycle times were halved to under 30 seconds with this technology.
- A 50-tonne rotational moulding machine can produce seamless 75 000-litre capacity tanks in polyethylene. These new tanks are designed to meet the requirements of the chemical, pharmaceutical and food sectors and the huge capacity opens the way to new applications.
- Traditional processes can be modified to better industrialize the manufacturing of medium- or short-run manufacturing. In the thermoplastic composite field, the 'Pressure Diaphorm Process' allows the processing of continuous fibre reinforced thermoplastics with low pressures. The press and the moulds (wood, composite or aluminium) can be about 70% cheaper. The process is convenient for short and medium runs in the range of 1000 up to 100 000 parts.
- Several major hearing aid manufacturers use a prototyping method – stereolithography (SLA) – to manufacture custom hearing aid shells for their 'in the ear' products.
- Powder impression moulding (PIM) can produce large parts such as truck beds (Dodge Dakota) with variable thickness skin and a foamed thermoplastic core, capable of structural performances.

7.4.3.3 Integrating finishing in the process

In-mould decoration (IMD) with films reduces finishing operations. If the process and its operating conditions are suitable, the demoulded parts are finished.

As an example, the composite manufacturer Quadrant Plastics Composites (Lenzburg, Switzerland) is studying three solutions for the decoration of GMT body panels:
- coil-coated aluminium
- PMMA-based films (Senotop) already used for the Smart City Coupé roof.
- PP-based films.

In-mould labelling (IML) used for injection-moulded products and blow-moulded bottles is an alternative to self-adhesive or heat-transfer decoration, eliminating a finishing step.

7.4.3.4 Low-cost tool examples

There are numerous solutions. We cite a selection.
- The RenTooling System uses an aluminium honeycomb and an epoxy paste to produce lightweight and stable tools.
- Water-soluble tooling materials such as Aquacore or Aquapoured can be moulded and machined to make strong cores that are then eliminated by water washing. The machining of the moulds is highly simplified.

7.5 Material upgrading and competition

7.5.1 Carbon nanotubes (CNT)

Carbon nanotubes are hollow carbon cylinders with hemispherical endcaps of less than 1 nm to a few nanometres in diameter and several microns in length. The aspect ratios are of the order of 1000 and more. The elementary nanotubes agglomerate in bundles or ropes that are difficult to disperse.

The main properties are:

- very high modulus of the order of 1000 GPa and more
- very high tensile strength of 50 000 MPa and more
- a low density: 1.33 g/cm^3
- high electrical conductivities with a very high current density of the order of 10^9 A/cm^2
- high thermal conductivities of the order of 6000 W/m.K
- very high cost: €1 million per kg in 2000; €100 000 and more per kg in 2002; €1000 up to €400 000 per kg in 2004; €100 and more per kg expected in 2006.

Production is expected to reach 300 tonnes/year in 2007.

The CNT developments in the polymer field concern:

- polymer reinforcement
- compounding with polymers to obtain extrinsic conductive polymers with nanotube levels lower than 1% to produce ESD and EMI compounds and ultra-flat screens
- high thermally conductive polymers for electronics.

Mitsui Chemicals is launching a new grade of carbon nanotube reinforced thermoplastic polyimide, Aurum CNT, with supplementary specific properties such as dust reduction and antistatic behaviour. Targeted applications are, for example, processing jigs for semiconductor or hard disk manufacturing, and parts for hard disk drives.

Industrialization of these developments is foreseen in a few years.

7.5.2 Molecular reinforcement

The concept of polymer reinforcement by monomolecular fibres is already old but many studies date from the last decade. The interest is particularly the very high aspect ratios and the levels of reinforcement with expected mechanical properties as high as:

- 50 GPa up to more than 400 GPa for the modulus
- 1000 MPa up to more than 40 000 MPa for tensile strength.

This is a difficult technique and today the best laboratory samples reach:

- 100 GPa up to 300 GPa for the modulus
- 1000 MPa up to 3000 MPa for tensile strength.

Industrialization is not currently foreseen.

7.5.3 Polymer nanotubes

The Max Planck Institute has developed a process to manufacture polymer ‘nanotubes’ with submicronic sizes of the order of hundreds of nanometres. The mechanical properties would be expected to be attractive.

Industrialization is not yet in sight.

7.5.4 Nanofillers

The total worldwide market for polymer nanocomposites is evaluated according to a report from BCC Research at:

- 11 100 tonnes valued at €74.5 million in 2003 for an average cost of €6.7 per kg
- 25 600 tonnes valued at €173 million by 2008.

Nanomaterials are expected to play a role in:

- reinforcement
- gas-barrier effect
- flame retardancy
- improvement of the lifetime of external components of cars by preventing soiling and scratching
- reducing reflectance of transparent components such as helmet visors or headlamps
- UV resistance
- conductivity.

The main problem with nanofillers is the need for complete exfoliation. Some special compounding techniques have been developed such as, for example, the ZSK MEGA compounder by Coperion Werner & Pfleiderer with a special screw configuration.

Among the numerous applications and projects, let us quote some of those characterizing the versatility of the nanotechnologies:

- Fiat projects new applications for nanocomposites in the form of PA fuel lines incorporating PA nanocomposite barrier layers from Ube.
- Ube developed the PA nanocomposite named 'Ecobesta' to replace PVDF or other traditional barrier materials. The all-polyamide structure offers recycling advantages compared to traditional multi-material designs. It incorporates:
  - ○ a PA 12 outer layer
  - ○ a PA 6/12 adhesive layer
  - ○ a PA 6/66 barrier layer incorporating 2% nanoclay
  - ○ a PA 6 inner layer in contact with the fuel.

  Ube produces the PA nanocomposites by the *in situ* polymerization route.
- Ultradur HighSpeed nanopolymer modified PBT (BASF) is used to manufacture a telephone socket.
- Voltron (DuPont) is a wire enamel in which nanoparticles of silicates or other inorganic materials are chemically linked to the enamel polymer backbone. Voltron provides a much better corona resistance than enamels merely filled with inorganic ingredients. One of the first ignition coils to use Voltron is for road-course and circle-track racing of modified stock cars.
- DSM Somos has developed a composite stereolithography material incorporating nanoparticle technology – NanoForm™ 15120. It exhibits high mechanical performance including a modulus superior to 5 GPa, and a HDT superior to 132°C.
- A 6% nanoclay-PP composite is used for the structural seat back of the Honda Accura TL 2004 car. This Forte 35CPP091 grade replaces a 30% glass PP compound in the seat back.
- PolyOne and Nanocor have formed an alliance to manufacture and market nanocomposites made from polyolefins, PVC and related polymers, such as EVA, TPE, EPDM and nitriles.
- Degussa will develop composites with nanoparticles to produce wafer-thin plastic film that could be used for light emitting diodes, decorative applications, or to improve the surface properties of skis.

7.5.5 Short fibre reinforced thermoplastics to compete with LFRT

Borealis has developed a high-performance short glass fibre reinforced polypropylene (HPGF) family that has the technological and economical potential to replace long glass fibre (LFRT) in highly stressed parts for technical automotive applications.

The advantages of the LFRT products are offset by requirements to optimize the whole process chain including extruder screw design, processing parameters and mould design, thus needing higher investment and production costs.

By contrast, the processing of HPGF compounds requires no additional investments as it utilizes standard injection moulding machines.

The high performances of HPGF are due to a better coupling of fibre and matrix, and the properties are near those of the LFRT grades with some advantages:

- improved weldability, increased flowline and weldline properties
- better fatigue behaviour
- lower emissions, lower fogging and lower odour than LFRT grades.

Table 7.2 shows the properties of an HPGF (Xmod GB305HP) containing 35% short glass fibres compared to LFRT polypropylene.

Table 7.2 Examples of properties of HPGF and LFRT polypropylene

	HPGF (XMod)	LFRT
Glass fibre weight (%)	35	35
Density (g/cm^3)	1.18	1.18
Tensile strength (MPa)	115	Up to 125
Tensile modulus (GPa)	9	4–8
Notched Charpy impact (kJ/m^2)	12	
HDT A (°C)	152	

The HPGF grade containing 35% glass fibres, compared to a conventional 35% GF reinforced polypropylene, shows:

- a significant improvement of tensile modulus over a range of temperatures tested up to 140°C
- better impact behaviour
- significantly increased tensile strength to 115 MPa.

Compared to LFRT, HPGF brings:

- Retained weldline strength over twice the value for LFRT grades.
- Superior fatigue behaviour, as measured by the fatigue crack growth rate.
- Tensile strength in the 115 MPa range versus 125 MPa for an LFRT.
- Slightly lower impact strength.

These improved properties of HPGF grades make them suitable for use in the automotive industry, with the potential to replace metal or long glass fibre polypropylene:

- Front-end carriers moulded in HPGF grades could be an economically better solution than those using LFRT polymers.
- Dashboard carriers: low emission and fogging values are achievable with HPGF.
- Pedal carriers: HPGF performs better than LFRT in weldline behaviour.
- Air intake manifold applications.
- Fan supports and shrouds, drive belt covers, blower wheel covers, bases for air filters, battery supports, engine covers and parts for the cooling system are further potential applications.

7.5.6 Thermoplastic and thermoset competition

There are numerous examples ranging from mass production, such as automotive applications, to high-tech industry such as aeronautics. We mention three examples:

- The use of glass fibre reinforced polyamide or BMC for engine covers: the two techniques are industrialized. One is predominant in the USA, the other in Europe and Japan. The main characteristics are roughly similar, as shown in Table 7.3.
- The use of glass and carbon fibre reinforced thermoplastics for aircraft elements.
- GMT can be preferred to SMC for small or medium runs in the automotive industry. For example, German fire-fighting equipment manufacturer Rosenbauer is using thermoformed sheet (multilayer ABS/PMMA) instead of hand-laid GRP. The cost of a body panel can be cut by 30% if the number of parts – in ‘three-digit quantities’ – is sufficient to justify the investment in thermoforming tools.

Table 7.3 displays property examples of glass fibre reinforced polyamide and BMC.

Table 7.3 Property examples of glass fibre reinforced polyamide and BMC

	PA	BMC
Glass weight (%)	30–43	10–30
Flexural strength (MPa)	175–210	40–135
Flexural modulus (GPa)	6–9	5–11
HDT A (°C)	248–251	>260
Melt temperature (°C)	255–260	Infusible
Izod notched impact (J/m)	100–250	300–600
Thermal expansion coefficient (10^{-5}/°C)	2–3	1.4–2

There are numerous studies and some industrialization of fibre reinforced engineering thermoplastic uses in aeronautics, for example:

- Airbus A380 structure uses 25% of advanced composites. Carbon fibre reinforced plastics (CFRP) are used for about 22% of the airframe.
- Lockheed F-22: carbon fibre reinforced PEEK and PEI processed by the SuperPlastic Diaphragm Forming (SPDF) technique.
- Fairchild Dornier 328, a regional transport: carbon fibre reinforced PEI for flap ribs.
- Airbus A340–500/600: glass fibre reinforced PPS for 3-metre-long components, carbon fibre reinforced PPS and honeycomb for inboard lower access panels.
- Prototype fuselage panel by Cytec Fiberite: carbon fibre reinforced PEEK and PEI.
- National Aerospace Laboratory: investigations of fibre-reinforced LCPs.

In all these cases, the cost and weight savings are significant.

7.5.7 3D reinforcements compete with 2D

2D reinforced composites have lower performance between the layers of fabrics and other 2D reinforcements. To enhance performances in all directions, numerous 3D reinforcements have been developed. Several concepts are marketed, such as:

- StructurPly I and II by Multi-Axial are thermoplastic matrix resin prepregs used in the construction of primary-load-carrying composite structures. Unlike the few hours typically required by the thermoset resin materials to cure, StructurPly needs a few minutes at 196°C.
- Woven 3D fabrics such as 3Weave Z Advantage by 3Tex.

- Stitched glass reinforcements such as Multimat or Multiaxials by Vetrotex.
- Two glass decklayers bonded together by vertical glass piles such as Parabeam by Parabeam Industrie.

7.5.8 Carbon fibres compete with glass fibres

For many properties carbon fibres have better performances than glass fibres and are also lighter, although more expensive. However, the cost has been decreasing for several years and it is expected that, with their industrial development, this trend will continue. Currently, the average price of a finished part incorporating carbon fibres is 50% higher than that of the finished part made with glass fibres, although the carbon fibre price is far higher than that of glass fibre.

Zoltek anticipates that a price of €12/kg could involve the use of carbon fibres in mass production. This is not unrealistic and the replacement of glass fibres for highly-loaded body components is foreseen. Today, €14/kg appears to be a sustainable prospect and is leading to new developments.

Glass/carbon hybrid lamination is also being investigated.

7.5.9 New special-performance polymers

Launching new polymers of medium-range performance is a difficult operation economically, as proved by the case of the aliphatic polyketones. New polymer families are rarely marketed but there are some examples where they provide improved processing performances, which is a particularly needed property to satisfy economic requirements. Modification of existing polymers is also an interesting route. Let us quote some examples:

- Cyclic polybutylene terephthalates (CBTs) are powders at room temperature. When heated, they melt to a water-like liquid and with the use of a catalyst polymerize into thermoplastic polybutylene terephthalate (PBT). They can be processed by compounding, casting, injection moulding, rotational moulding and composite processing. CBT resin applications under development include wind turbine blades, rotomoulded parts and fuel tanks, tooling blocks, marine composites, and automotive parts. For composite manufacture, CBT resins offer several advantages such as melting into water-like liquids, low moulding pressures, no exotherm and no need to cool the mould to release the parts. Other properties are claimed, such as good surface finish, improved gasoline barrier effect, broad possibilities of fibre reinforcement, and ease of obtaining nanocomposites. The production capacity is:

○ initially 2500 tonnes by 2005
○ 5000 tonnes by early 2006
○ later a world-scale plant is expected to have an annual capacity of 25 000–50 000 tonnes/year.

- New polymer structures allow the control of processability and final characteristics. For example, Mitsui is launching nanostructured metallocene alpha-olefins that have a crystallite size of the order of nanometres instead of microns as for conventional metallocene polyolefins. This yields a better balance of transparency, heat resistance, flexibility and elasticity characteristics. Targeted applications are automotive interior trim, packaging film, construction materials, protective films for electronic and optical parts, sealing products and as polymer modifiers.

Another interesting subject is the development of high-temperature thermoplastics for application in composites. For example:

- Certain polyquinoxalines are thermo-stable with high glass transition temperatures up to 435°C, high decomposition temperatures (510–560°C) and notable oxidative resistance in air, but, on the other hand, they form highly viscous solutions that don't wet reinforcing fibres easily.
- Fluorinated poly(imide-ether-amide)s are readily soluble in organic solvents like dimethylformamide (DMF), N-methylpyrrolidone (NMP), pyridine or tetrahydrofuran (THF) and give flexible films by casting of such solutions. These polymers exhibit decomposition temperatures above 360°C, and glass transition temperatures in the 221–246°C range. The polymer films have a low dielectric constant and tough mechanical properties.

7.6 The immediate future seen through recent patents

Patents published in the year 2004 have been analysed by polymer type, reinforcement type, and material structure and process type: see Figure 7.4 (a) and (b).

The selected patents do not distinguish between polymerization, processing, applications, analysis, etc. For example, polyamides include textile fibres.

7.6.1 Analysis of patents by polymer type

The graph in Figure 7.4(a) positions the number of patents for the main thermoplastics, while Figure 7.4(b) displays the number of patents for each thermoplastic versus its consumption.

Note:

- The above-average activity concerning polyamides (perhaps because of the textile applications), polycarbonates and polypropylene, because of its versatility allowing commodity and engineering applications.
- The below-average activity concerning PVC, perhaps because of environmental pressures.

7.6.2 Analysis of patents by reinforcement type

There are many patents concerning fibres but some relate to applications other than polymer reinforcement, for example, building insulation.

Figure 7.5 shows, for the same period, the relative number of recent patents per fibre type.

Nanotubes and nanocomposites, particularly carbon nanotubes, are generating intense research activity whereas research is definitely weaker for nanofibres. Figure 7.6 shows, for the same period, the recent patents for the different nano-reinforcements.

7.6.3 Analysis of patents by structure and process type

The analysis in this case is dubious because structures are confused with reinforcements and processes. For example, patents on films or other multilayers spoil the analysis for laminates.

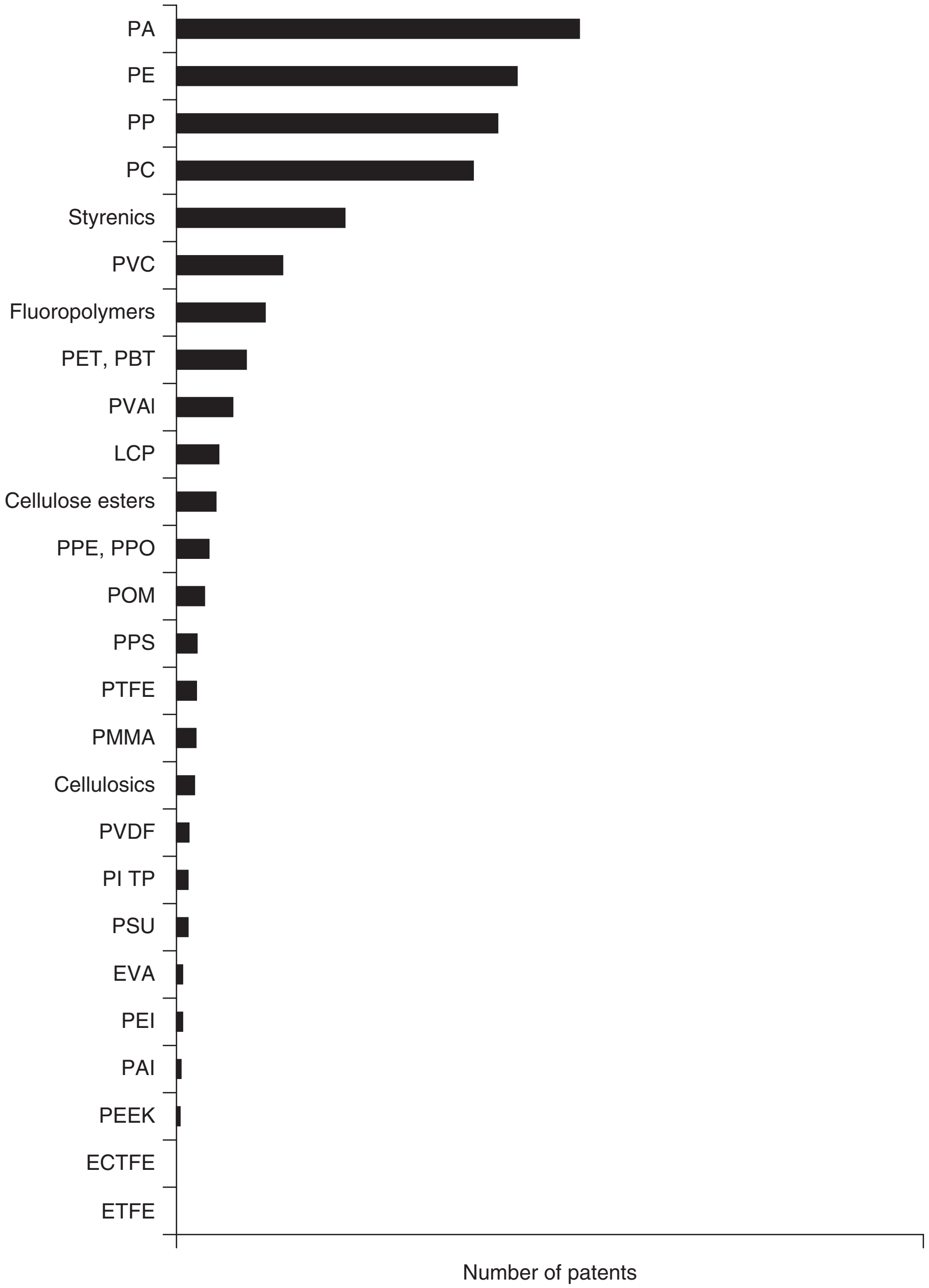


Figure 7.4.(a) Thermoplastic types: recent patents for the same period

However, the high level of patents concerning nanocomposites and prepregs is obvious. On the other hand, the SMC/BMC patent level appears relatively low. The amount of patents concerning laminates, UD composites and filament winding seems to correspond to their level of production.

Figure 7.7 shows recent patents, for the same time period, per composite structure and process.

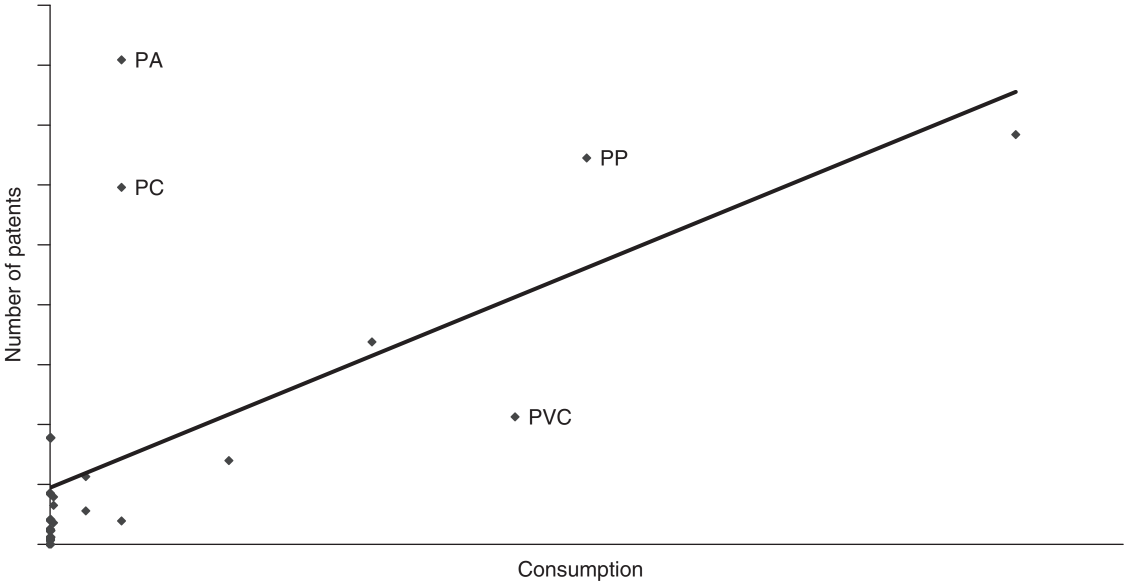


Figure 7.4.(b) *Patents versus consumption for various thermoplastics*

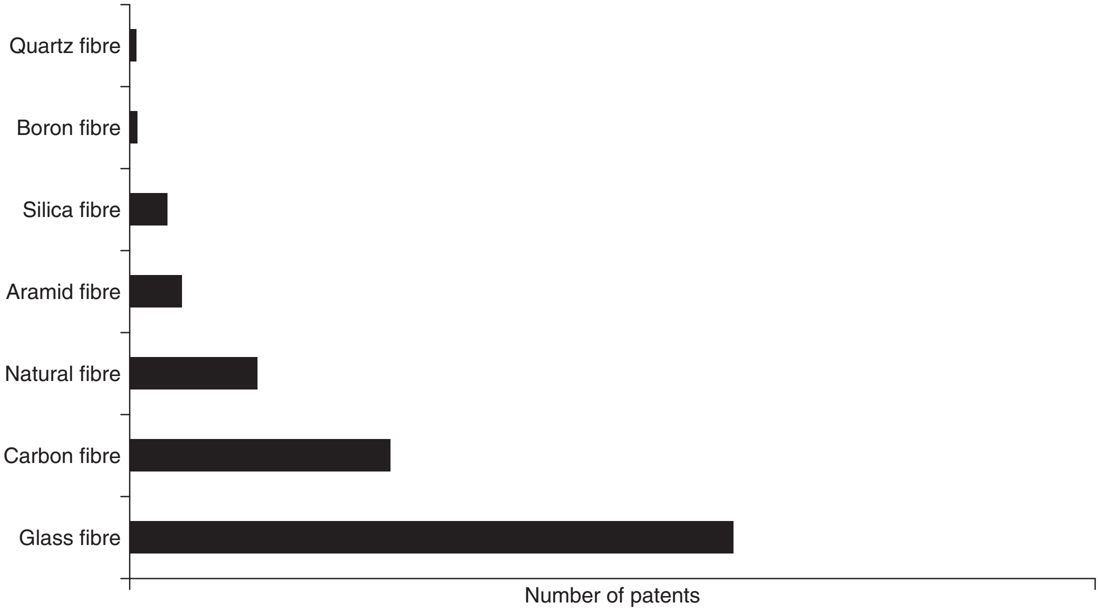


Figure 7.5. *Fibre types: recent patents for the same period*

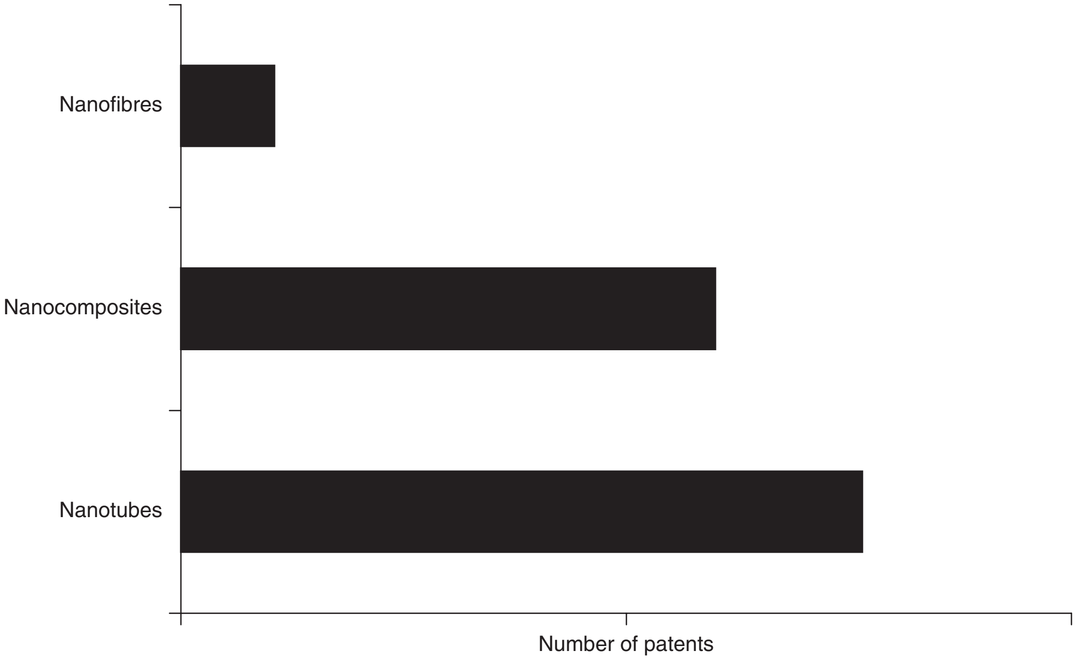


Figure 7.6. *Nano-reinforcements: recent patents*

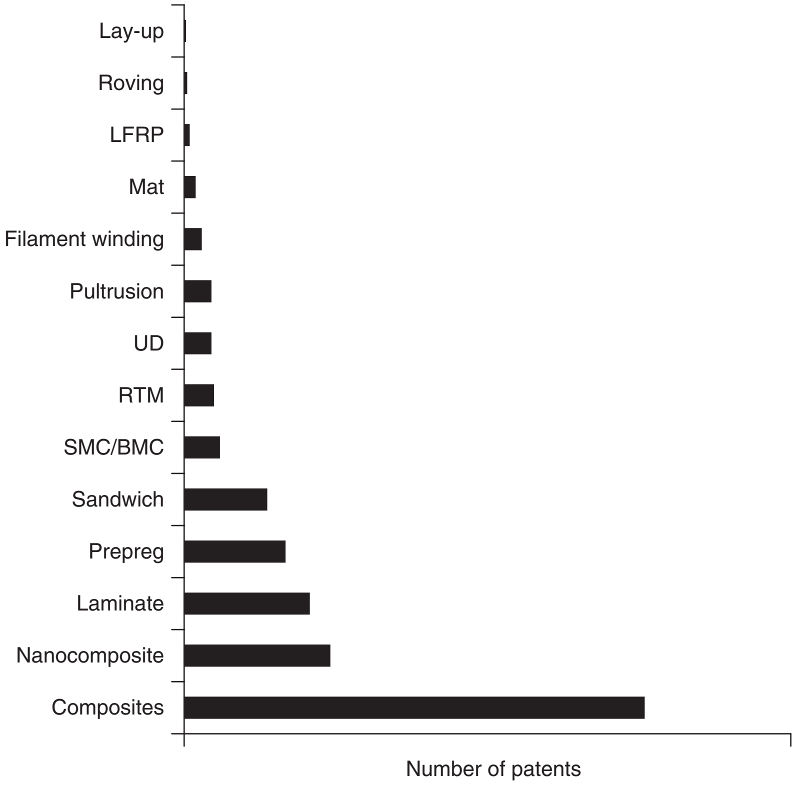


Figure 7.7. *Structures and processes: recent patents*

7.7 The immediate future seen through recent awards

Recent awards from professional organizations, the professional press, engineers' associations and so on reflect the most up-to-date technology. Most awards relate to:

- Processing: new methods, adaptation of conventional processes, translation to other methods unusual for the manufacture of the considered part, that are better adapted to run size.
- Integration of a multitude of functions to decrease the number of parts.
- Use of structural plastics: long fibre reinforced thermoplastics (LFRT), glass mat thermoplastics (GMT), thermoplastic sandwich structures, carbon fibre reinforced thermoplastics.
- Use of hybrids of plastics and metals or other conventional materials.
- Metal replacement.
- Upgrading towards use of a more-sophisticated plastic family: use of more thermostable plastics that can withstand on-line electrostatic coating (e-coating).
- Downgrading to a cheaper plastic family with sufficient performance to satisfy the requirements, possibly thanks to design adaptation.
- Use of TPE to replace rubbers or plastics or to provide new functions.
- Environmental requirements:
  - paint elimination
  - ease of recycling: mono-material concept or compatible material concept
  - decrease in waste and energy consumption.
- Sustainable materials, principally natural fibres . . .

The main goals pursued are:

- cost saving
- weight saving
- compliance with environmental regulations and trends
- durability enhancement
- improvement of custom satisfaction (aesthetics, comfort, ease of use and maintenance . . .).

Among the numerous award-winning developments, we quote the following examples.

Processing: new methods, adaptation of conventional processes, etc.

- The instrument panel (IP) on the Mazda 6 features an extrusion process that enables in-line forming for both ends of parts. The cost savings are more than 10% compared with an extruded/injection-moulded part.
- A two-colour automated injection-moulding machine from Husky allows simultaneous-shot injection moulding of a two-colour instrument panel for the 2005 Ford Mustang. The process reduces squeaks and rattles, equipment costs, production time and scrap, and improves scratch resistance.
- Development of a technology for improved heat transfer (heating/cooling) and process control for slush moulding allowing cost savings: 30–40% cycle time reduction, 50% capital cost reduction and 80% energy reduction.
- Glass-filled PP speaker pods for the Jeep Wrangler are blow moulded with QMC 8590 from Quantum Composites. It is a one-piece housing for the speaker and overhead dome light. Replacing numerous metal parts saves several kilos.

- Process (Top Glass SpA) combining extrusion, pultrusion and moulding to produce threaded rod from Fulcrum.

Use of structural plastics: LFRT, GMT, etc.

- Plastic sealed door module is injection moulded from long-glass fibre polypropylene pellets by Faurecia for the Ford Fiesta.
- The running boards (0.25 × 2 m) for the Ford pickups, Explorer and Mountaineer SUVs are injection moulded from 40% long-glass fibre polypropylene. They weigh about 6–8 kg each. Weight saving is near 50% versus steel. The one-piece board replaces several tens of components and saves about €10 per vehicle. Long-glass fibre compounds can be pellets from StaMax or can be prepared in-line according to processes such as CPI (Composite Products Inc) or LFT-D-ILC (Dieffenbacher).
- All-plastic integrated front-end module for BMW Mini Cooper is injection moulded from StaMax, a LFRT, with no metal support.
- Door carrier panel on 2005 Lancia Y-Epsilon is made of Quadrant GMT and GMTEx 40% GMT polypropylene. Benefits are large functional integration, weight reduction, cost saving.
- SymaLITE™ lightweight reinforced thermoplastic (LWRT) composites are used by BMW on the underbody shields for the new 5 Series passenger cars.
- Tanks (by Covessa) capable of withstanding up to 100 bars made by welding three parts in glass fibre reinforced polypropylene (Twintex).
- HTPC (Hybrid ThermoPlastic Composite) bumper beams made by Plastic Omnium are used by General Motors on the Pontiac Montana, Chevrolet Venture and Oldsmobile Silhouette. Continuous woven fibres are overmoulded with a long or short fibre reinforced polypropylene to save weight (6 kg), enhance impact resistance (20–40%) and integrate numerous functions such as reinforcement ribs. The process is fully automated.
- Composite grid to replace steel reinforcement of precast concrete panels.
- Springs made of glass or carbon fibre reinforced UD thermoplastic composite.

Upgrading to a more-sophisticated plastic family that can withstand on-line e-coating

- A thermoplastic grille-opening reinforcement (GOR) for Ford SUVs is injection moulded from 40% mineral/glass-filled PET that can withstand on-line e-coating (210°C). HDT B (0.46 MPa) is 241°C and HDT A (1.8 MPa) is 212°C. PET GOR allows at least a 10% weight reduction and 15% cost reduction per part.
- Structural Mirror Bracket on 2004 DaimlerChrysler Durango and Dakota made of Rynite 935, a glass fibre reinforced thermoplastic polyester that can withstand e-coating (177°C for one hour), providing an 86% weight reduction and a 45% cost reduction.

Hybrids

- Hybrid GMT/steel used for instrument panel carrier on vehicles from Ford, Volvo and Mazda, reduces weight, provides easier assembly, lowers cost and improves noise/vibration/harshness (NVH) and crash performance.
- Plastic Metal Hybrid Structural Roof Frame on 2005 Audi A6 made of Durethan BKV30 H2.0, a 30% glass fibre reinforced PA 6 from Lanxess, provides a 30% weight saving.

Downgrading to a cheaper plastic family . . .

- Instrument panel lower carrier on General Motors full-size trucks is made of a low-cost filled homopolymer polypropylene replacing a more-expensive filled SMA.
- Low Cost Fan Shrouds on Ford F-150, Expedition, Navigator, Ranger are made of PP-5140-F1, a 40% talc polypropylene replacing glass/mica-filled polyamide fan shrouds.

Metal replacement

- Oil Pan Module on 2004 DaimlerChrysler Actros is injection moulded from Ultramid A3HG7, a 35% glass fibre reinforced PA 66. It allows extension of the oil change intervals by 50%. Design integrates many features and weight saving is about 50% versus an aluminium module.
- Transmission Oil Pan with Integral Filter on 2005 BMW 7 Series is injection moulded from Durethan AKV35 H2.0, a 35% glass fibre reinforced PA 66. Benefits include part consolidation, ease of recycling and improved acoustics, 40% weight savings versus comparable metal designs, and up to 18% cost savings.
- Oil Module with Plastic Housing on 2005 Volkswagen Audi A3/A6 is injection moulded from Durethan AKV35SR1 H2.0 PA. An all-plastic housing replaces die-cast and machined aluminium for significant cost and weight savings. The plastic oil module integrates all the functions and provides an innovative automatic oil drain system.
- Integrated Air Intake Module and Cylinder Head Cover on 2004 Toyota/Daihatsu is injection moulded from Ultramid B3WG6 BGVW, a glass fibre reinforced PA 6. Weight saving is 30% versus aluminium.
- Pi-Pregs (Porcher Industries), balanced or UD composites, are made of glass, aramid or carbon fibre reinforced thermoplastics (PPS, PEI, TPU, PA 12).
- Glass fibre braids impregnated with PEEK for high-performance moulded parts.

Use of TPE to replace rubbers or plastics or to provide new functions

- Charge Air Cooling Duct on 2004 Ford Super Duty F-Series Truck is produced from soft and hard durometer Hytrel (TPEE) grades in sequential co-extrusion process. Three plastic pieces replace seven metal pieces.
- Engine-Mounted Mechanical Fan Shroud on 2004 DaimlerChrysler RAM HD Pick-Up is manufactured from a TPE (NexPrene® 1087A) overmoulded on a plastic ring, leading to a lower cost.
- Jounce Bumper/Coil Spring Isolator Assembly on 2004 General Motors uses TPU elastomer to form the upper and lower coil spring isolators while integrating the jounce bumper cup and jounce contact surface, respectively.

Unpainted parts

- Development of a glossy, aesthetic and unpainted roof module on the Smart Roadster by DaimlerChrysler AG's Smart. The two-piece, removable roof, built by ArvinMeritor, is surfaced with a thermoformable three-layer film (Lexan by GE Plastics) that can be co-moulded with either thermoplastic or thermoset substrates. The film exhibits 95% gloss retention after the equivalent of 10 years of Florida sun exposure. Weight saving is 50% versus a painted steel roof system.

- Other variations of film decoration are, for example, the rocker moulding for General Motors' Chevrolet Trailblazer North Face Edition, a 2-metre-long part thermoformed over injection moulding because of the relatively low volumes (7000 to 8000 vehicles per year) and the short development time required.
- Another non-paint approach is being developed by Mayco and DaimlerChrysler Corp, consisting of the extrusion of a glossy, coloured film. After thermoforming to the part shape, it is placed in an injection mould, and thermoplastic is injected behind it. Cost savings are estimated to be €5 to €12 per fascia.

Custom satisfaction

- Long Life Filtration System on 2005 Ford Focus is injection moulded from HPP30GR20BK, a glass fibre reinforced polypropylene allowing a zero-maintenance engine air filter.

Electronics applications

- A prototype heating and ventilation control panel produced by Bayer and Lumitec using a luminescent plastic film system incorporating a special electroluminescent electrode system. The panel can be produced in a single process step using Bayfol® films and a PC/ABS blend (Bayblend®).
- Project (by Sarnoff Corp with DuPont de Nemours and Co Central Research and Development) to print organic transistors on plastic for electronic displays and circuits. The goal is to develop materials, thin flexible plastic substrates, and methods for continuous high-resolution printing.

Innovative design

- Controlled Energy Management Bumper Isolator (by Ford with LDM Technologies and Concept Analysis Corp) includes a conical geometric design that enhances crash behaviour absorbing more energy in less space than polypropylene foam. Cost, weight, front and rear overhangs are reduced.
- The big underbody panel on the new 5 Series from BMW with variable stiffness and density values within the panel produces a weight saving of 30% compared with a similar glass-reinforced PP compression-moulded or injection-moulded part.

Recycling

- Sheets of recycled fibre-reinforced thermoplastics (Haller Formholz).
- Process to make powertrain throttle bodies with recycled polyamide from carpet (Ford with Visteon and Honeywell).
- Recycled plastic composite railroad crossties can save millions of trees, significantly reduce plastic landfill waste and cut maintenance costs.
- A plastic waste processor (from Carderock Division) has been developed to compress the Navy's plastic wastes into discs, solving the environmental and space problems from 600 kg daily plastic waste (20 m^3) per ship. Seaward International Inc and Carderock Division are developing a marine piling (The SeaPile) in structurally reinforced composite with a core made of these discs.

Sustainable materials

- Sheets of natural fibre reinforced thermoplastics (Haller Formholz).
- Wood-plastic composites (WPC) are used as building material for decking, fencing, siding . . . for the low maintenance constraints. US demand is forecast at €2.5 billion through 2008.

7.8 Environmental concerns

It may be useful to recall some facts concerning the environmental impact of plastics. Sustainability, pollution minimization, recycling and safe elimination of wastes are basic principles of environment policy.

Renewable raw materials are made or derived from short-term renewable sources (one to a few years or a few tens of years) such as plants, trees, wood wastes and other agricultural products. Not all these materials are necessarily biodegradable. Natural rubber, for example, comes from the latex of a tree (*Hevea brasiliensis*) and is not biodegradable. Renewable materials are often considered as opposites to *fossil sources* such as petroleum that are not renewable on a human timescale. On the other hand, some synthesized plastics such as certain polyesters are biodegradable.

Sustainable materials must preserve the potential of future generations and from an ideal point of view must:

- come from a renewable source and incorporate the highest acceptable level of recycled material. In contrast, most plastics come from fossil resources that are not renewable on the human timescale
- consume the lowest possible energy, which decreases pollution and cost, and saves fuel
- emit the lowest levels of gases, fumes and other pollutants, which decreases pollution
- produce the lowest level of wastes, which decreases raw material and energy consumption, reduces pollution, and minimizes the material to be recycled and cost
- have the longest possible lifetime, which reduces raw material consumption, processing energy and pollution and decreases the amount of end-of-life wastes, the more so the longer the lifetime
- be easily recycled and effectively re-used.

Pollution minimization is related to all steps of the product life, from its production to its elimination at the end of life.

Safe elimination of wastes From an environmental point of view, these routes for the end-of-life products are in a decreasing order of interest:

- reprocessing of plastic wastes in the same production or primary recycling. This is the best solution but not always realistic
- re-use in another production that has lower performance, is less demanding and of course less lucrative
- physico-chemical degradability by natural elements
- biodegradability, perhaps the most environment friendly.

Degradable materials can be destroyed by natural environmental elements such as light, oxygen and water.

Biodegradable materials are destroyed by micro-organisms into short molecules that can be assimilated by plants and other living organisms. . .

The degradability is not necessarily satisfactory from the environmental point of view:

- The biodegradation releases CO_2 into the environment.
- The pollutant atoms or chemical functions are not eliminated by the degradation. For example, the chlorine in PVC is included in the low-molecular weight degradation products. Nevertheless, the pollution is globally reduced.
- The skeleton of the non-degradable polymers containing a high percentage of biodegradable additives survive the degradation and pollute the environment.

Figure 7.8 schematizes different routes towards degradation.

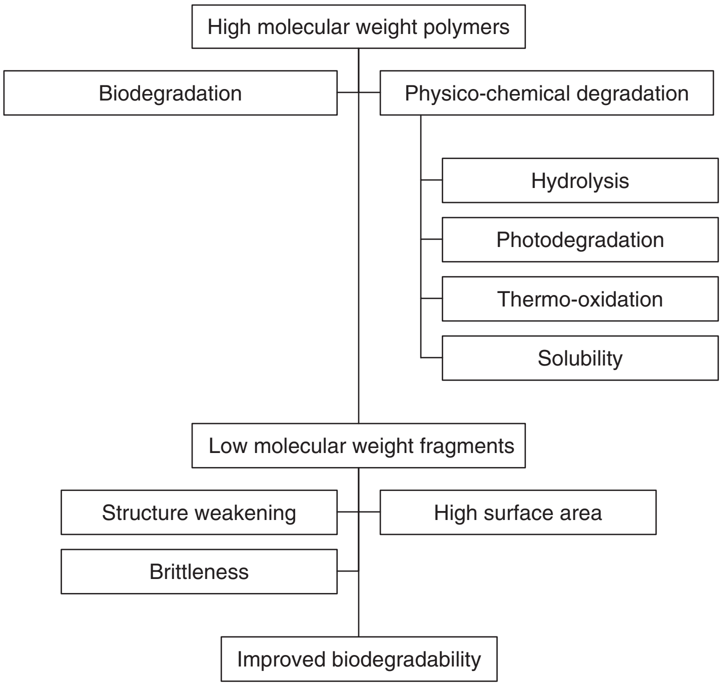


Figure 7.8. Various routes to degradation

7.8.1 Recycling of thermoplastics and thermoplastic composites

From a practical point of view, the recycling of thermoplastics and thermoplastic composites is difficult and is constrained by:

- the technical possibilities: the feasibility for handling mass quantities
- economics: the final cost and the recyclate/virgin polymer cost ratio determine the success or failure of the method
- environmental regulations: recycling must globally decrease the pollution balance versus tipping or landfill.

7.8.1.1 Collection and pretreatment of wastes

The paths differ according to the source of the waste:

- Manufacturing scrap: it is easy to sort and store these wastes separately in good conditions (clean and dry). These wastes are not subjected to ageing and corrosion.

- End-of-life products: this case is more difficult to treat. It is necessary to collect the products, dismantle (if necessary) or shred them before recycling. These pretreatments are expensive. These wastes have been subjected to ageing and corrosion for several years and are often polluted.
- Plastics incorporated into municipal solid wastes: these are burnt without special treatment.

Figure 7.9 shows schematically the main paths leading to the recycling step.

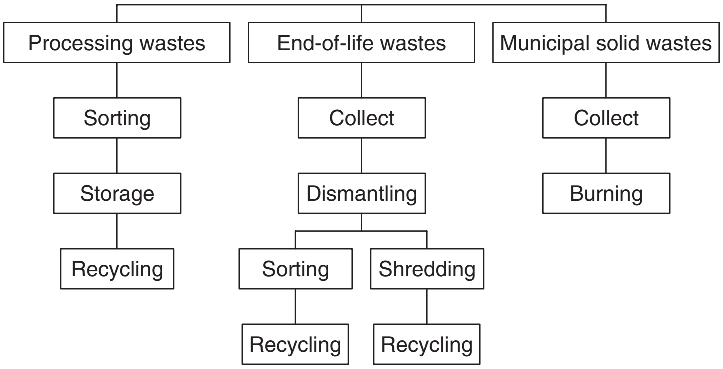


Figure 7.9. Waste collection and pretreatment

7.8.1.2 The main recycling routes

The main recycling routes utilize the following

- Mechanical recycling, the most realistic way used by almost all the plastic manufacturers: shredding and grinding of polymer scraps allow a partial re-use in the original application but the recyclate level is low because of the decrease in performance. An extension of this principle is obtained by manufacturing other parts of lower performance, sometimes in another industry.
- Chemolysis: certain polymer families such as polyurethane are chemically depolymerized. This is theoretically the best recycling solution if the performances of the original material are to be recovered and if the recyclate is used in the same application. This is, technically and economically, a difficult method that is industrialized in few cases.
- Solvent extraction of the polymer from shredder residue is only suitable for soluble thermoplastics.
- Thermolysis: gasification, pyrolysis . . . to produce petrochemical feedstocks for steam-cracking or alternative fuels.
- Co-combustion with municipal solid wastes.

7.8.1.3 Composite specifics

The presence of fibres or other reinforcements is an additional obstacle for waste recycling because it makes it impossible to:

- recover the original size of the reinforcements for all composites. The processing and/or the mechanical treatments involved in recycling break the fibres, foams, honeycombs, etc.
- return to the original properties

If we make the assumption that the difficulties of collecting, sorting and cleaning are solved, some examples of mechanical recycling methods (shredding and grinding) are listed below:

- Micronized powders are added at the 5–15% level in new adapted formulations to replace mineral fillers. The density is slightly inferior and the performances are in a similar range.
- Short fibre (few millimetres or less) recyclates used to reinforce polymers or concrete.
- Long fibre (10 mm and more) recyclates used to reinforce polymers.

7.8.1.4 *Thermoplastics and thermoplastic composite recyclates: mechanical and calorific properties*

The recycling treatments and the possible presence of pollutants, paints or other surface products cause a reduction in the mechanical properties of recyclates, notably the impact strength and the ultimate characteristics. On the other hand, it is possible to upgrade the recyclate using additives or compatibilizing surface treatments.

Table 7.4 (after figures from Bayer, NRC of Italy, Owens Corning) shows the retention of certain properties versus the recycling conditions.

Table 7.4 Processing scraps and end-of-life wastes of polypropylene and ABS: property retentions versus the recycling conditions

	Retention (%)			
Number of recycling cycles	Tensile strength	Tensile modulus	Notched impact	Fibre length
	Glass fibre reinforced polypropylene: processing scraps			
0	100	100	100	100
1	87	95	78	91
2	79	90	72	84
4	65	79	58	75
PP from bumpers	Recycled end-of-life (10 years old) bumpers made of glass fibre reinforced polypropylene			
New	100	100	100	
Old	94	90	29	
Recycled old	82	87	20	
Recycled and upgraded old	91	90	74	
ABS from vehicles	ABS from recycled end-of-life vehicles			
New	100	100	100	
100% recyclate	95	98	57	
50% recyclate	98	100	64	
20% recyclate	98	100	86	

For a high-performance glass fibre reinforced thermoplastic such as PEEK, the retention of modulus and strength after two and four recycling cycles are in the ranges of 79–87% and 76–84%, respectively.

Some plastic producers market recycled thermoplastics such as polyamides. Table 7.5 (after BASF) shows examples of properties for recycled and virgin polyamides.

Table 7.5 Neat and reinforced polyamide 6 based on post-consumer recyclate: examples of properties

	Recycled Impact modified (Wet)	PA 6 Virgin (Wet)	30% GF PA Recycled (Dry)	30% GF PA Virgin (Dry)
Miscellaneous properties				
Density (g/cm^3)	1.06	1.13	1.36	1.36
Shrinkage (%)		1	0.3	0.4
Absorption of water (%)		1.7	1.1	0.95
Mechanical properties				
Stress at yield (MPa)	40	45		190
Elongation at yield (%)	15			4
Tensile strength (MPa)		45	155	190
Elongation at break (%)	>100	250	3	5
Tensile modulus (GPa)		1.4	8	9
Flexural modulus (GPa)	1.1	1.4	8.5	10
Notched impact strength ASTM D256 (J/m)	210	300	85	145
Thermal properties				
HDT B (0.46 MPa) (°C)		170		217
HDT A (1.8 MPa) (°C)		70	205	205
Melting temperature (°C)	220	220	220	220
Coefficient of thermal expansion (10^{-5}/°C)		7	3.8	3.5
Relative Temperature Index (RTI)				
Electrical (°C)			140	
Mechanical without impact (°C)			140	
Mechanical with impact (°C)			115	
Fire behaviour				
UL94 fire rating			HB	HB

UL (Underwriters Laboratories) accepts:

- no regrind for thermoplastic elastomers and recycled materials
- regrind up to a maximum of 25% by weight with the same grade of virgin thermoplastic at the same moulder facility without further testing
- for regrind levels exceeding 25% in the same virgin thermoplastic, UL requires a special evaluation of relevant performance tests such as mechanical, flammability and ageing tests.

Table 7.6 (after Neste) displays some calorific properties of plastic wastes compared to coal. The laminates and sandwich composites are handicapped by the low heat value and carbon content. Moreover, the laminates have a high ash content.

Table 7.6 Comparison of the calorific properties of coal and plastic waste fuels

	Coal	Polyethylene	Mixed plastics	Laminate	Sandwich
LHV (low heat value)	25	40	32	17	19
Carbon	64	81	65	39	52
Ash	16	3	18	43	21

7.8.1.5 Recycling costs

In the most unfavourable case, the cost of recycling is a combination of the operations of collecting, dismantling, sorting, treatment and recycling.

From an economic point of view, the cost assessment of the recyclate depends primarily on the price retained for the waste. The recycling cost is in the range of:
- €0 per kg for a recyclate of processing scrap whose grinding cost balances the cost it would have been necessary to pay to dispose of it
- to more than €1.3 per kg if the combined costs of collecting, dismantling, sorting, grinding and recycling treatment have to be taken into account.

To decrease the dismantling and sorting costs of plastic parts it is necessary to anticipate these steps at the design stage:
- to consider methods of assembly to make dismantling easier
- to standardize the plastics used. The monomaterial concept is the most attractive but is sometimes unrealistic for technical and economical reasons. The compatible material concept is more realistic but less attractive.

As examples:
- for a certain part with volumes of 3000 t/year, it was shown that the economic equilibrium was between €0.6 and €0.7 per kg for the recyclate
- for various methods and end-of-life products, the claimed costs vary in the range of €0.5 to €1 per kg
- for the solvent process, Wieteck – a commercial operator of a 4000 t facility – estimates that the process is economically viable for a polymer price exceeding €1 per kg.

7.8.2 Sustainable and biodegradable thermoplastics

Like the synthetic polymers, natural and biodegradable matrices are principally thermoplastics. Now there are few inherently biodegradable polymers but biodegradability, for the non-biodegradable polymers, can be obtained by using high levels of biodegradable additives. These are sources of nutrients for microorganisms but the conventional polymer, polyethylene particularly, is not biodegraded; only the biodegradable additives are completely biodegraded:
- the skeleton of conventional polymer becomes weak and brittle and can disintegrate more easily
- the surface area is highly increased and promotes chemical and bacterial attacks.

One of the most-commercialized routes is the addition of starch-based materials but other biodegradable additives are used. Marketed solutions are numerous, for example, without claiming to be exhaustive.
- starch-loaded polyethylene (PE)
- starch-loaded PEAA (PE/acrylic acid)
- alloys of cellulose or starch acetates with polyethylene, polypropylene, polystyrene
- biopol at 30% into PE, PVC.

The choice of biodegradable polymers coming from synthesis or bacterial fermentation is wide. For example:
- alginates
- bacterial celluloses
- cellulose
- chitin and chitosa
- lignin
- microbial poly(amino-acids)
- polyaspartates

- polylactic acid (PLA)
- polyglycolic acid (PGA)
- polycaprolactone (PCL)
- polyhydroxyalkanoate (PHA)
- polyhydroxybutyrate (PHB)
- polysuccinates
- polyesteramides
- starch and other natural derivates of uncertain formula
- mixtures of the previous items such as polyester/PLA and so on . . .

These thermoplastics can be processed in nanocomposites and fibre-reinforced composites.

Degradability of the polymers is expensive, particularly biodegradability. Let us quote some examples:

- For alloys of:
  - ○ 40–60% of biodegradable polyester
  - ○ 20–40% of starch
  - ○ 11–16% of PCL

  The material cost is in a range from $27–$30/kg.
- Biopol: in 1995 Zeneca Bioproducts plc produced 75 tonnes at DM13.5/kg (c. €6.9/kg). This is:
  - ○ 5–7 times the cost of commodities such as PE, PP, PS or PVC
  - ○ 1.5–2 times the PA price.

The cost is expected to decrease to DM3/kg (c. €1.53/kg).

- Starch-based polyester copolymer (Mater-Bi) is marketed of the order of €1.25–€4/kg.
- The cost of PLA is expected to come down to nearly €2/kg.

Costs of environment-friendly plastics in a mass-production scenario are forecast between €1 per kg up to €4 per kg and more.

Applications

Consumption

Data vary widely between sources, depending on the concept of environment-friendly plastics, a certain confusion between consumption and production capacity, and the optimism of the forecaster. In any case, biodegradable polymers are speciality materials that currently represent less than 0.1% of the total plastics, reaching, perhaps, 1% by about 2020.

Major application sectors are packaging, disposable goods, horticulture and agriculture, for example:

- blown-films, cling films to replace vinyl in vegetable, fruit and meat wraps; moisture-barrier films; nappy films; agricultural films; films for lawn and garden; breathable films; optically enhanced films; films and liners for protecting metals and other industrial goods; loose fill foils; covering films; mulching films; tying films for agriculture; stretch films; industrial stretch-wrap films used to protect automobiles during shipment and disposable by hot washing and flushing . . .
- candy wraps; flexible sandwich wraps for fast-food chains; fresh produce and meat wraps; packages for poultry . . .
- commodity bags; yard waste bags; seedling bags; shopping bags; lawn and garden bags; organic-waste sacks . . .

- disposable food-service market including plates, hinged clamshells, hot and cold cups; crockery, cutlery, straws, beakers, plates, bowls, waffles; disposable hot- and cold-drink cups to replace EPS . . .
- industrial trays; food trays; fresh produce and meat trays; thermoformed trays; replacement for EPS foam trays . . .
- diaper backing; oversized bin liners used for animal feed and composting; paper coatings . . .
- sealant layers in form-fill-seal co-extrusions . . .
- personal hygiene products . . .
- bottles; hollow bodies; single-serve drink bottles; thermoformed cups . . .
- crimped staple fibres . . .
- blisterpacks . . .
- labels and caps; shrink labels . . .
- erosion-control uses . . .
- plant pots, underlays, peat sacks, seed/fertilizer tapes, flower pots, seed mats . . .
- hairbrush handles . . .
- implants; operation materials; oral hygiene; medical gloves; lower-cost biohazard or medical-waste containers and devices; medical products; disposable wipes . . .
- moisture barrier on natural-composite . . .
- netting . . .
- traffic cones . . .
- clothing, technical textiles, fabrics . . .
- toys, craft materials, bricks and blocks, golf tees . . .
- writing implements . . .

Properties

According to the chosen options (nature and ratio of components, compounding, crystallinity, etc.) properties can be tailored to mimic:

- polyethylene: low modulus, clarity . . .
- polypropylene: medium modulus . . .
- polystyrene: higher stiffness . . .

Elongations at break range from near 5% up to 1000% and melting temperatures are roughly between 100°C and 195°C.

Trade name examples

BAK, Bioceta, Biomax, Bionelle, Biopol, Cortec, CPLA, Easter Bio, Ecoflex, Mater-Bi, Metabolix, NatureWorks PLA, Nodax, PEC (polyester carbonate), PLA, Sky Green BDP.

7.8.3 Sustainable standard and high-performance reinforcements

Natural reinforcements have been used for a very long time:

- wood flour was one of the first fillers used with phenolic resin
- wood shavings are used in wood particleboards
- short cotton and other cellulose fibres are commonly used in phenolic and melamine resins.

The renewed interest in natural reinforcements may continue because:

- ecology is a sustainable policy
- the growing consumption of plastics uses more and more glass fibres that natural fibres can partly replace in general-purpose composites
- other industries processing natural fibres, such as the paper or flax industries, are seeking outlets for their by-products
- natural fibres can bring specific properties
- the development of new processing methods opens new applications such as the extrusion of 'wood'
- biosynthesis allows the production of high-tech reinforcements such as BioSteel.

Natural fibres were considered in previous sections of Chapters 2 and 6 above, and we will only examine two prospective aspects of sustainable reinforcements here.

'Extruded (or injected) wood'

Unlike the well-known phenolic resins reinforced with a low level of wood flour, 'extruded or injected wood' is composed of a majority of cellulose (60% up to 90%, or even 95%) and a small amount of polymer as binder. This binder can be synthetic or partially to totally natural. The US natural fibre and wood composite market was estimated at 340 000 tonnes in 2001 growing to just over 450 000 t in 2003, that is, roughly 1% of the total plastic consumption. According to *Plastics Additives & Compounding*, the market is predicted to grow to 635 000 t in 2006 or a 12% annual growth rate – dramatically higher than the average annual growth of plastics.

Europe is a less-important market than the USA because of the lack of available wood by-products and the lack of end uses.

Table 7.7 displays some properties of different 'extruded or injected woods' compared to PVC. The value ranges are broad according to the various marketed techniques.

Table 7.7 Examples of properties of 'extruded or injected woods' compared to PVC

	PVC	Extruded or injected wood		
Density (g/cm^3)	1.4	1.2–1.4	1.3–1.4	0.96–1
Tensile strength (MPa)	35–50	17–25	10–22	26–38
Tensile modulus (GPa)	2.4–4	4–8	1–5	1.9–2.2
Flexural strength (MPa)		30–50		58–69
Flexural modulus (GPa)	2.1–3.5	4–6		3
Elongation at break (%)	2–30	0.5–1	0.3–0.7	
Charpy impact strength (kJ/m^2)		3–7	2–5	
Izod notched impact (J/m)	20–110			24–57

As an example, for an extruded wood grade with a PVC binder, a cost of €1 per kg is claimed.

BioSteel high-performance fibres

Nexia Biotechnology is developing and producing these fibres made out of silk proteins secreted by transgenic goats. 25% lighter than Kevlar, the failure energy would be much higher.

The targeted applications are:

- medical devices
- industrial or sports ropes, fishing lines and nets
- polymer reinforcement for ballistic protection such as soft body armour, competing with Kevlar fibres.

7.8.4 Examples of sustainable composites

Here we outline just a few examples of sustainable composites:

- Polylactic acid (PLA) reinforced with kenaf fibres developed by NEC for personal computer housings. With a 20% level of kenaf fibres, the main properties compete with glass fibre reinforced ABS but the cost is 50% higher. The flexural modulus is more than 4.5 GPa and the HDT reaches 120°C.
- PLA/montmorillonite nanocomposites with a better heat resistance, a doubled modulus and an easier processing than neat PLA.
- VTT, a Finnish research centre, is developing fully biodegradable composites based on PLA reinforced with flax and other natural fibres. These composites can be used indoors in a dry environment. Outdoors there is a risk of degradation but this is sometimes an advantage, as for agricultural products; using biodegradable composites reduces disposal costs. The tensile strengths are in the 70–80 MPa range for a 40% by weight level of flax fibres.
- Earthshell composite is made of biodegradable polyester, paper wastes and ground limestone.

References

Technical guides, newsletters, websites

3Tex, BASF, Bayer, BCC Research, Biodegradable Plastics Society, Borealis, Business Wire, Ciba, CPI, Dieffenbacher, Dow, DSM, EPG, JEC Composites, Menzolit, Multi-Axial, NASA, Naval Research Laboratory, NCL, Neste, Novamont, PRW, Owens Corning, Parabeam Ind., Quadrant, Sekundanten, SMC, SPE, Symalit, Techniwatch, Tektran, TISTR, Tubulam, Valcor, Vetrotex, VTT, Zoltek . . .

Reviews

[1] *Plastics Additives & Compounding* (Elsevier Science)
[2] Plastics Technology on-line
[3] *PRW Newsletter* (PRW.com & *European Plastics News*)
[4] *Reinforced Plastics* (Elsevier Science)
[5] *Techniwatch* (CRIF)

Papers

[1] Zoltek User's Guide for Short Carbon Fiber Composites, (June 2000), Zoltek Companies, Inc, St Louis, MO 63044, USA, www.zoltek.com
[2] L.L. Madyuskina *et al.*, *International Polymer Science and Technology*, 27, 5, (2000), p. T/80)

Conclusion

Today, plastics are an industrial and economic reality competing with traditional materials and in particular metals, among which steel is the most important.

Global consumption of plastics is roughly 170 million tonnes per annum, which is:

- intermediate between steel and aluminium consumption in weight, that is, roughly a sixth of the consumption of steel and six times the consumption of aluminium for recent years
- higher than steel and aluminium consumption in volume in recent years: roughly 1.4 times the consumption of steel and 16 times that of aluminium
- lower than steel and aluminium consumption if we reason in terms of equal rigidity: equivalent to roughly 1% of the consumption of steel and half that of aluminium

The growth of plastics is significantly higher than that of steel.

No engineer or designer can be ignorant of plastics, but the decision to use a new material is difficult and important. It has both technical and economic consequences. It is essential to consider:

- the actual penetration of the material category in the industrial area
- the functionalities of the device to be designed
- the characteristics of the competing materials
- the abundance or scarcity of the material and the process targeted
- the cost
- the processing possibilities
- the environmental constraints.

The intrinsic mechanical properties of plastics and composites are different from those of conventional materials:

- Expressed in the same units, the hardnesses of engineering materials cover a vast range broader than 1 to 100. Plastics are at the bottom end of the range but are of a wide diversity and offer decisive advantages compared to metals, glass, ceramics, wood and others.
- The properties of unidirectional composites in the fibre direction can compete with those of current metals and alloys. The highest-performance engineering plastics compete with magnesium and aluminium alloys.
- Polymers are electrical and thermal insulators but have high coefficients of thermal expansion.
- Polymers are not sensitive to rust but are sensitive to thermo-oxidation and, for some, to moisture degradation.
- Polymers present a more or less plastic behaviour under stresses, leading to lower modulus and ultimate strength retentions, and higher long-term creep or relaxation when the temperatures rise.
- Many polymers, including the commodities, are resistant to the chemicals usually met in industry or at home and displace the metals previously used for applications such as domestic implements, gas and water pipes, factory chimneys, containers for acids and other chemicals.

To compensate for their handicaps in terms of properties compared to traditional materials, polymers have effective weapons:

- design freedom
- manufacturing in small quantities or large series of parts of all shapes and all sizes, integrating multiple functions, which is unfeasible with metals or wood
- possibility of selective reinforcement in the stress direction

- weight savings, lightening of structures, miniaturization
- reduction of the costs of finishing, construction, assembling and handling
- ease and reduction of maintenance operations
- damping properties
- aesthetics, the possibilities of bulk colouring or in-mould decoration to take the appearance of wood, metal or stone, which avoids or reduces finishing operations
- durability, absence of rust and corrosion (but beware of ageing)
- transparency, insulation and other properties inaccessible for metals.

Plastics and polymer composites are much more expensive than metals, even more-specialized ones such as nickel. As for the specific mechanical properties, the high densities of metals modify the classification of the various materials. According to the cost per volume, plastics are competitive. Only the very high performance plastics or composites are more expensive than metals.

The freedom of the chains of the thermoplastics increases their mobility and possibilities of relative displacement, which brings certain advantages and disadvantages:

- easier processing
- quicker processing cycles
- suitability for welding
- repair possibilities
- easier recycling
- fusibility
- lower modulus retention when the temperature rises
- tendency to creep.

The main advantages of polymer composites are:

- high mechanical properties
- the possibility of laying out the reinforcements to obtain the best properties in the direction of the highest stresses
- the possibilities of repair: a significant advantage of composites.

The development of composites is hindered by the difficulties in recycling, attenuated in the case of the thermoplastic matrices.

Hybrid materials are often a good solution to take advantage of plastics and one or several other conventional materials. This principle, in more or less complex versions, is applied to the front-ends of recent cars, footbrake pedals, aircraft wheels, car doors, etc.

The final choice of the design team may result from many iterations concerning the functional properties, the environmental constraints, the possibilities to produce the part in the required quantities and the price. The price considered may just be the part cost but can also include assembling, delivery, set up and end-of-life costs, taking account of durability, the savings in maintenance, etc.

The future of plastics is promising thanks to research and development efforts, with significant new patents.

The goals for future development are diverse:

- improvement of the cost/performance ratios
- improvement of the immediate- and long-term characteristics, to win structural parts
- better thermal resistance
- better weathering behaviour
- enhancement of the colouring and surface aspect
- improvement of the surface properties

- adaptability of the grades, which must satisfy the requirements of the market and develop specific properties and better combinations of properties
- halogen-free fire-retardant grades
- improvement of the adherence of paints, printing inks, adhesives
- better performance, particularly impact resistances, at low temperature
- improved ease of processing
- improvement of the mould productivity
- automation of the process equipment
- better control of the processes by SPC (statistical process control)
- development of new manufacturing methods
- on-line compounding to reduce costs and thermal degradation
- hybrid associations with non-plastic materials
- use of wastes and recycled materials to satisfy environmental requirements and lower the costs
- management of recycling, starting with the design.

All the developmental routes are being investigated:

- New materials are being introduced, including:
    - new polymers, for example, Dow is starting to market cyclic resins developed by Cyclics Corp.
    - new reinforcements ranging from the more-or-less conventional to the highly sophisticated, such as carbon nanotubes.
- Evolution of processing: globalization, automation, industrialization, simplification, low-cost tools.
- Popularization of high-performance products such as carbon fibres and 3D reinforcements to compete with their 2D counterparts.
- Sustainable standard and high-performance reinforcements, sustainable and biodegradable components for matrices, sustainable composites.
- New combinations of known products or techniques such as the low weight reinforced thermoplastics (LWRT).

The above comments are only a superficial overview of the immense possibilities of these young polymer materials, which could be ‘The Materials of the 21st Century’.

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