

POLYMERS FROM BIOBASED MATERIALS

Edited by

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Foreword

Polymers from biobased materials are polymers derived from renewable resources by chemical or combined chemical and mechanical methods, or produced directly in biological processes. Combinations of renewable and conventional fossil-fuel-derived plastics are also biobased materials. This assessment reviews materials from renewable resources and their properties including major biopolymers produced by plants and selected animal sources.

A major goal of biobased materials research is the manufacture of new materials which perform as well as fossil-fuel-derived plastics, and which also exhibit high strength, light weight, corrosion resistance and biodegradability, and/or which could be used to replace certain metals.

Examples discussed are wood, its polymeric components such as cellulose and lignin, related polymers such as chitin, and other carbohydrate polymers such as starch, which when combined with plastics can impart environmental degradability to the resulting material. The conventional role of inexpensive wood flour as a filler is reviewed, as well as the future research necessary to bring this material into a higher value use as a reinforcing material for composites. Automotive, building, and packaging materials applications are considered. Bioproduction of materials is reviewed for selected polymers such as cellulose, other plant cell wall polymers, and protein, with emphasis on silk and wool. These biobased polymeric materials can be produced with specific environmentally significant properties such as biodegradability (e.g., polyhydroxybutyrate and valerate copolymers, polylactide polymers) or with specific mechanical properties (e.g., high tensile properties for cellulose for specific uses).

The book is presented in two parts. Part I describes materials from renewable resources and their properties. Part II reviews bioproduction of materials. An appendix provides examples of recent Japanese research activities.

The information in the book is from *Assessment of Biobased Materials*, edited by Helena L. Chum of the Solar Energy Research Institute for the U.S. Department of Energy, December 1989.

The table of contents is organized in such a way as to serve as a subject index and provides easy access to the information contained in the book.

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Executive Summary

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INTRODUCTION

Since 1980, the Energy Conversion and Utilization Technologies (ECUT) Division of the U.S. Department of Energy (DOE) has supported generic, high-risk applied research and exploratory development pertaining to energy conservation. These activities, which have long-, mid-, and near-term elements, are ones that private enterprise cannot or will not undertake. Innovative concepts from basic research and other fields of technology are identified and brought to a stage at which other end-use government programs or industry will carry them into more advanced technology and engineering development (Carpenter 1984). The major objective of ECUT R&D is to develop generic technologies enabling energy conversion and utilization concepts. Key to the ECUT activities is ECUT's role as a **bridge** between basic research (such as sponsored by the National Science Foundation or DOE Basic Energy Sciences) and end-use applied research that uncovers a wide range of concepts that, if further developed, could be used in many applications. These applications serve a variety of end-use sectors such as transportation; industry; buildings and community systems; and power generation, storage, and transport.

The need for this type of government program in the DOE Office of Conservation and Renewable Energy was recognized by both the Research and Development Coordination Council in 1979 and the Energy Research Advisory Board in 1983. To bridge the gap, for instance, between materials research and materials engineering, it is necessary to a) monitor and evaluate U.S. and international basic research and exploit it for energy conservation purposes; b) expand the generic technology base, common to many end-use sectors, through the understanding of techniques, processes, and materials relevant to energy conservation; c) identify potentially revolutionary materials conservation technologies and establish concept feasibility; and d) transfer the technology to DOE end-use programs and/or to private industry. Over the years, in many technologies, this approach has been successfully implemented, for instance, by Japanese researchers, in programs that have significant contributions from government agencies.

One area identified by the ECUT Materials Program is biobased materials--polymers derived from renewable resources by chemical or combined chemical and mechanical methods, or produced directly in biological processes. Combinations of renewable and conventional fossil-fuel-derived plastics are also biobased materials. One example of a biobased material is a phenolic resin made with a feedstock derived from fast pyrolysis of renewable wood or bark wastes, followed by simple chemical fractionation. This feedstock replaces conventional petroleum-derived phenol. An example of a biologically produced biobased material is microbial cellulose, known since 1886 when Adrian Brown described that it could be produced from the bacterium *Acetobacter xylinum* (Brown, Jr. Chapter 9). Significant basic research in

this area has been carried out at the University of Texas, with some funding from government and U.S. industry. An example of an industrial product emerging from this research is high-tensile-strength microbially produced cellulosic fibers that have superior acoustic performance and, therefore, are being used by Ajinomoto Co., Inc. in Japan to produce acoustic diaphragm materials. Also, films of bacterial cellulose with extremely good properties such as an effective barrier to growth of pathogenic microbes and close adhesion to the wound are being marketed in Brazil for the treatment of severe burns and other wounds (Fontana et al. 1989). The United States still leads in the basic research area, but the development of new markets and applications, albeit in high-value, low-volume, specialty areas, is primarily in foreign countries. A well established pathway for the development of innovative technologies is to focus initially on the highest value products, and then, as the technologies mature and their cost decreases, expand them into low-value, high-volume markets of interest to the program because they have the highest impact on energy conservation. This approach is being used by industrial consortia described in Chapter 4.

In September 1986, SERI began the technical assessment of biobased materials for the ECUT Materials Program. The assessment included literature reviews; discussions with researchers from universities, research institutes, and industry; and participation in relevant meetings. After its announcement in *Commerce Business Daily* (May 20, 1987), a Letter of Interest (LOI) was distributed to 250 members of the technical community. Nineteen proposals were received and reviewed by a panel. Five proposals were selected for funding (September 1987), and work started on four subcontracts in January-July 1988. These ongoing subcontracts support the area of biomass-derived plastics: lightweight biobased composites and biobased packaging plastics.

This report consists of a series of contributions from North American researchers in areas of their expertise. The authors were asked to review the topics and to present their views on directions of R&D in both the United States and other countries. They were also asked to identify "gap" areas in the R&D of biobased materials. These contributions have two companion volumes that emerged from the symposia sponsored, in part, by the ECUT Biobased Materials project, a number of industries, and the American Chemical Society, Division of Cellulose, Paper and Textile. These symposia took place at the 3rd North American Chemical Congress, Toronto, April 1988, and covered the topics: "Lignin: Properties and Materials" and "Biosynthesis and Biodegradation of Plant Cell Wall Polymers." They were organized by W. G. Glasser/S. Sarkanen and N. G. Lewis/M. G. Paice, respectively; full papers representing the bulk of the contributions to the meeting were published in 1989 as ACS Symposium Series volumes 397 and 399, respectively. These two volumes complement the present assessment and summarize the state of these fields internationally. Chapters 4 and 10 summarize these symposia and research directions worldwide.

ECUT BIOBASED MATERIALS GOALS

The ECUT Biobased Materials R&D goal is the identification of new materials, or combinations of renewable and synthetic ones, that have the same level of performance as metals and plastics used in key industries such as automotive and packaging plastics. These materials can be made to have special properties. Environmental degradability, biodegradability, and photodegradability can be imparted to packaging plastics. New composites can have high strength, light weight, corrosion resistance, and sound deadening effects for the automotive and buildings industries. The R&D aims to identify new materials that are inexpensive and not energy-intensive to manufacture. To help select options that will lead to cost-effective technologies and guide limited research funds, the R&D includes techno-economic evaluations of the key concepts investigated by an

independent process engineer (Mr. Arthur Power, A. J. Power and Associates, Boulder, Colorado). In these assessments, performed with contributions from project participants and the SERI field program manager, mass and energy balances for selected processes are prepared; equipment is sized and the associated capital costs are estimated; operating costs are evaluated; and, finally, overall costs are calculated as a function of the return on investment, to provide industry with a realistic economic assessment of the routes chosen. In addition, sensitivity analyses are performed. These assessments indicate process areas in which research improvement would have the highest impact on the materials cost and process energy use. These evaluations are performed on a case-by-case basis instead of on a global, or in principle, basis. As will be clearly seen with biobased materials, such a variety of concepts and chemical and engineering options is involved that global assessments may not be useful.

Many of the lightweight biobased composites developed can also be used in more traditional applications such as materials of construction, insulation, and other applications in buildings and community systems. The ECUT Biobased Materials R&D supports the overall conservation goal to replace plastics currently derived from fossil fuel and natural gas with renewable materials of similar or improved properties, while providing materials that are environmentally acceptable and designed for reuse or degradation. Energy is conserved directly by the reduction in energy and feedstocks derived from fossil resources, and indirectly, in various ways. For instance, for transportation applications, indirect energy savings are accrued because automobile weight reductions can increase fuel economy on the order of 0.7 mpg for every 100 pounds saved in the weight of the vehicle. Considering that in the United States in 1986, 169 million vehicles consumed roughly 124 billion gallons of motor fuels, the impact of weight reduction on overall fuel consumption can be very high indeed. Between 1978 and 1984, approximately 16% of the total 36% increase in fleet fuel economy could be attributed to automobile weight reductions (Kulkarni 1984). Strategies employed included downsizing, weight reduction by materials substitution, improved aerodynamics, and improved power train efficiencies.

Plastics are not inherently environmentally degradable. In fact, polymer scientists historically have concentrated on making plastics more and more durable and reproducible. Plastics are resistant to biological degradation for many reasons. Microorganisms have not yet had time enough to adapt and synthesize polymer-specific enzymes capable of degrading and using these man-made synthetic polymers of recent origin. The hydrophobic character of the plastics inhibits enzyme activity and the low surface area of the plastics with its inherent high molecular weights compounds the problem further. The permanence of plastics in the environment has resulted in increasing concerns over their disposal. There is also evidence that plastic wastes present a hazard to wildlife, particularly in the marine environment (Office of Technology Assessment 1989). Hence, Congress and state legislatures are addressing mandated plastics degradability--a move that can affect significantly the plastics packaging business, mostly for consumer products, institutional products, and packaging. Overall, 4.8 billion pounds of plastics were used in 1988 to produce 38.6 billion units (Society of the Plastics Industry 1989). As many as 15 states have banned or proposed bans on nondegradable plastic products ranging from egg cartons, disposable food service items, and clam shell packaging used by fast food restaurants, to plastic grocery bags, liquor bottles, and beverage rings that keep 6-packs together. On the federal level, 10 degradable plastics bills and a concurrent resolution are pending before Congress. Biobased packaging plastics introduce environmental degradability into conventional plastics, such that at least the volume is reduced, thereby decreasing harm to wildlife. Usually, the current concepts impart environmental degradability but do not maintain the level of performance of conventional plastics. ECUT-identified concepts strive to make combinations

of plastics and renewable polymers, such as those derived from starch, compatible through the design of specific graft copolymers of both entities. These copolymers would permit common plastics processing practices of making alloys between incompatible polymers possible in a cost-effective way.

ASSESSMENT OF BIOBASED MATERIALS

The assessment addresses two areas:

I. Materials from Renewable Resources and Their Properties

This area discusses major biopolymers produced by plants and selected animal sources. Figure 1 shows a simplified schematic of the flows of these materials in the industry today, and Figure 2 presents chemical formulae of the typical renewable polymers discussed in this assessment. The various chapters address the following topics:

Biobased materials can contribute to materials substitution by offering low-cost options in polymer composites. Advantages of polymer composites include light weight with reasonable strength properties and cost; ease of manufacture in continuous processes that achieve parts consolidation and, therefore, lower capital cost than conventional multiple metal stamping operations; higher corrosion resistance compared to metals; increased durability; and sound deadening properties. The disadvantages of these materials are lower shatter resistance than steel for some applications; the difficulty of attaining a high-quality surface finish for some types of composites; the higher temperature sensitivity of the composites; and the difficulty of attaching the composites to other materials, principally steel. Chapter 1 reviews composites in the industry, with emphasis on automotive applications for conventional and emerging biobased materials. Recognizing the importance of the composites area, General Motors, Chrysler, and Ford formed the Automotive Composites Consortium to address synthetic plastics and plastics/metals composites, not biobased materials (Alper and Nelson 1989) and to conduct further research on how these materials can be incorporated into automotive design in the years ahead. Industrial efforts in the biobased materials area for automotive composites were sponsored by General Motors through Cadillac ASA; these efforts terminated soon after the formation of the consortium.

Wood is the oldest composite material. Wood and other lignocellulosic materials consist of flexible cellulose fibers assembled in an amorphous matrix of lignin with the hemicellulosic polymer. These polymers make up the cell wall and are responsible for most of the physical and chemical properties of these materials. They have been used as engineering materials because they are low cost, renewable, and strong, and require low processing energy. However, they have undesirable properties such as dimensional instability caused by moisture sorption with varying moisture contents; biodegradability; flammability; and degradability by ultraviolet light, acids, and bases. These feedstocks and their modifications that allow improvement of mechanical and chemical properties are discussed in Chapter 2 by Drs. R. Rowell (U.S. Forest Products Laboratory) and R. Young (University of Wisconsin). Inexpensive lignocellulosics such as wood flour and a number of lignocellulosic materials have been used as cheap fillers in many applications both in thermosets and thermoplastics. The properties of the renewable feedstock used are cost and availability. However, to use the fiber properties as reinforcements has not been successfully achieved, mainly for lack of compatibility between cellulosic fibers that are hydrophilic and the hydrophobic thermoplastic matrices (Zadorecki and Michell 1989). Increasing the compatibility between these types of polymers would greatly facilitate their incorporation

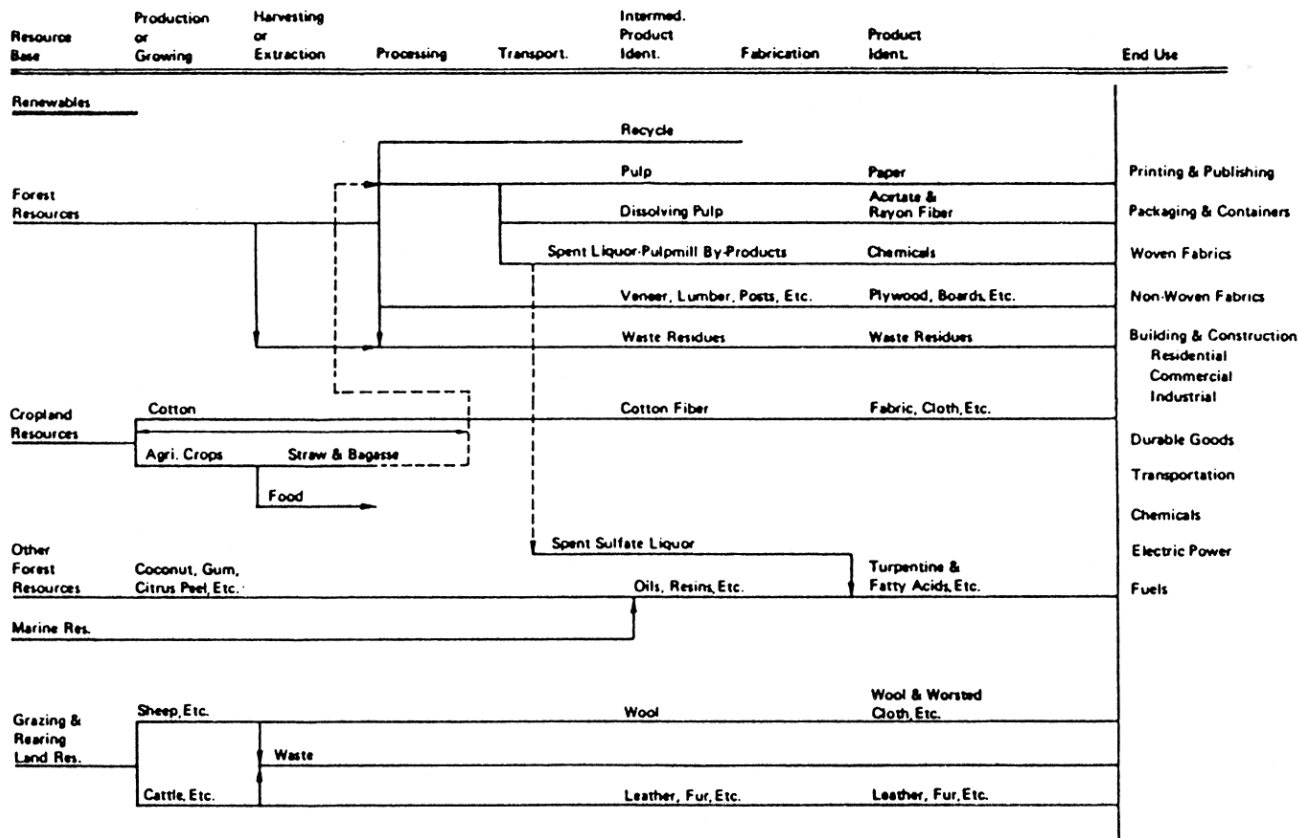


Figure 1. Simplified reference materials system

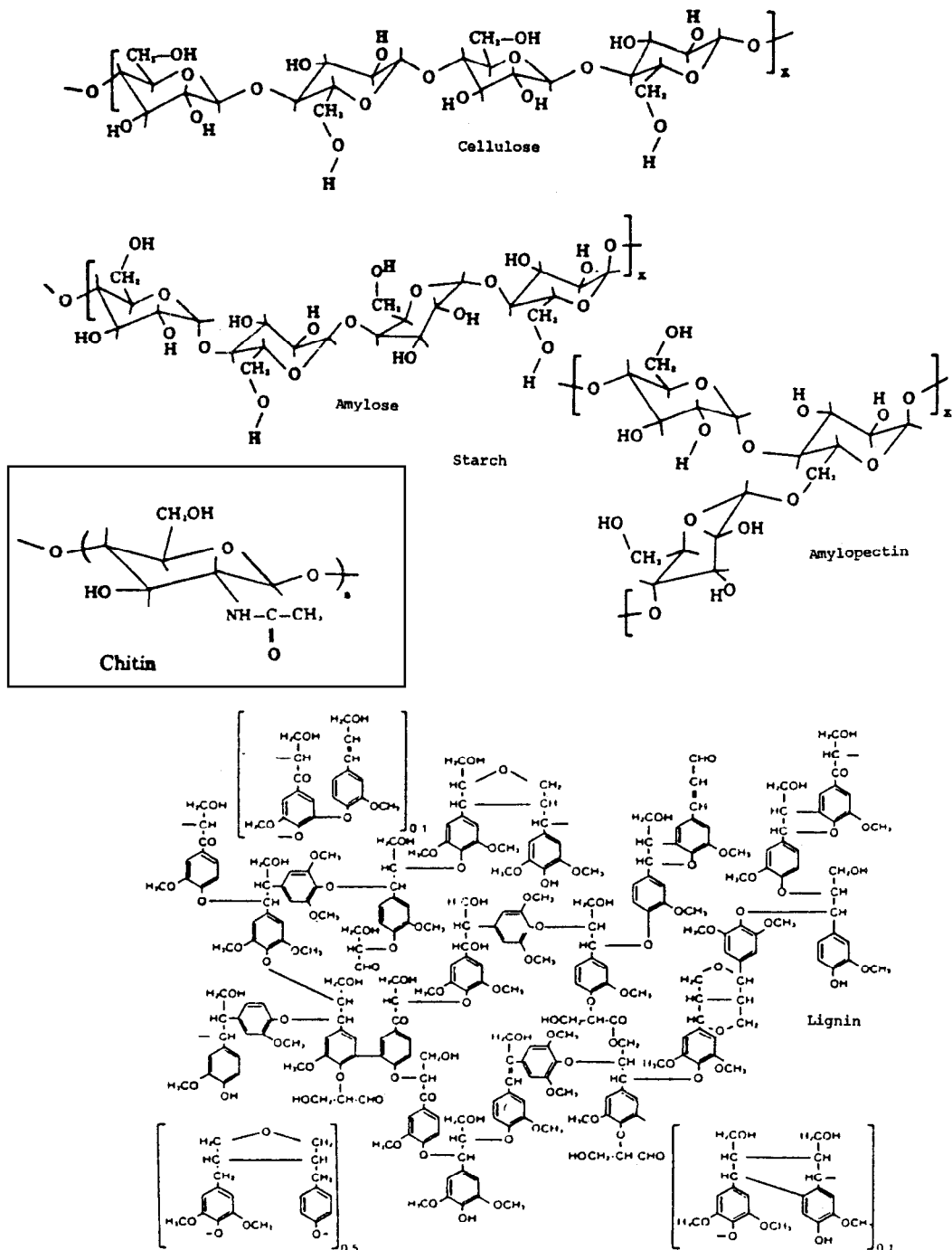


Figure 2. Examples of chemical formulae of selected biobased materials

into a number of applications. This type of R&D is conducted in industry worldwide to increase the compatibility of glass fibers with polymer matrices (Toensmeier 1987).

Isolated components from wood and lignocellulosics in general, such as cellulose and derivatives, are discussed in Chapter 3 by Professor V. T. Stannett, North Carolina State University, who reviews past work and future directions in cellulose grafting. The bulk of the grafting R&D has been carried out based on free-radical approaches, but more controlled ionic polymerization methods are evolving that can yield grafts of better defined structures. These chemical derivations add cost to the starting inexpensive feedstocks and also increase substantially the required process energy. Thus approaches that could accomplish the desired chemical derivations at low cost and high energy efficiency would be highly desirable.

In Chapter 4, Professor W. G. Glasser of Virginia Tech reviews the symposium "Lignin: Properties and Materials," which gathered the international community working in this area. Although these feedstocks are abundant, the key application today is combustion for process energy and chemicals recovery in conventional pulping processes. The main polymeric application is as an inexpensive surfactant; lignosulfonates are less expensive than petroleum sulfonates (Lin 1983, Chum et al. 1985). Other polymeric applications are evolving. Two consortia with industries are currently trying to introduce lignin-derived products into the plastics industry. One is mentioned above for the production of phenol replacements for phenol-formaldehyde thermosetting resins (Chum et al. 1989), and the other is emerging from the structure-property-performance data gathered by Glasser and coworkers at Virginia Tech on epoxylated and propoxylated lignins for use in polyurethanes.

Professor D. Goring was invited to review biobased materials opportunities, based on his extensive experience with the pulp and paper industry and his outstanding vision of the field. His comments are incorporated as Chapter 5. A key remark is the following:

It should be noted that research in this area has been done mostly with pulps produced for papermaking, where much effort is put into making the fibers flexible with hydrophilic surfaces. In the case of mechanical pulps, a large expenditure of energy is required. It is possible to produce mechanically stiff fibers coated with lignin at much lower energy consumption than is currently used. Such pulps would be **useless for papermaking** but might prove to be the ideal fiber component for a composite. . . .

Goring highlights a common problem of the area. The research and development carried out for the traditional applications of pulp and paper, as well as conventional construction materials, is not what is required if these materials are to fit other market areas such as the automotive industry with the development of high tensile properties fibers, of low density and low cost. The elastic modulus of bulk wood is 10 GPa. Cellulose fibers with moduli up to 40 GPa can be separated from wood by chemical pulping processes. Such fibers may be further separated by hydrolysis and comminution into microfibrils with modulus of 70-80 GPa. Theoretical calculations of the Young's modulus of elasticity for cellulose crystallites give a value of 250 GPa (Jeronimidis 1980), comparable to Kevlar and to some carbon fibers (see Chapter 1). Figure 3 illustrates the evolution of structure-process-modulus envisioned for cellulose materials compared to those of synthetic fibers. We do not have technologies at present that can achieve the theoretical values. Materials of this type could compete favorably with other reinforcing fibers of excellent properties, principally when




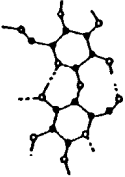
Structure	Process	Component	Young's Modulus	Young's Modulus	Component
		Wood	10 GPa		
	Pulping	Single Pulp fiber	40 GPa		
	Hydrolysis followed by mechanical disintegration	Microfibrils	70 GPa	34-55	Rayon carbon fiber
	New Technologies: o Bacterial Cellulose o Non pulp/paper technology	Crystallites	250 GPa	70-85	Glass Fiber
				60-200	Aramid fiber, Kevlar
				190	Silicon carbide
				230-490	Polyacrylonitrile carbon fiber

Figure 3. Comparison of fiber properties

cost and density are considered together. Actually, even now, some wood fibers (1.5 g/ml density and under \$1/lb) compete quite favorably with E-glass, with its density of 2.5 g/ml and \$1.5-\$5/lb (Matsuda 1988).

Chitin (see Figure 2), poly(2-amino-2-deoxy-D-glucose), is one of the most ubiquitous natural polymers, isolated where crustacean shells are collected in large quantities. Crustacean shells are natural composites of chitin, polypeptides or proteins, and an inorganic filler, calcium carbonate. Chitin has been found in shells of hundreds of mollusk species. Chitin is present in tendons and other stress-bearing fibrous portions of marine animals, where the chitin molecules adopt a highly oriented structure. Professor W. Daly (Louisiana State University) reviews in Chapter 6 the research activities, occurring primarily outside the United States, related to the many high value uses of these interesting materials.

Starch is a polymer of anhydroglucose units linked by α -D-1,4-glycosidic bonds. Two distinct structural classes exist: linear and branched (see Figure 2). Amylose, the linear component, is the lower molecular weight polymer, having an average molecular weight of about one-half million. Amylose makes up approximately one-fourth of the weight of starch for some species. The preponderant polysaccharide is amylopectin, consisting, like amylose, of mostly 1,4-linked α -D-glucopyranosyl units, but with branched chains, with a molecular weight of up to 10 million. The abundant hydroxyl groups on the starch molecules impart the characteristic hydrophilic properties. The polymer attracts water and itself through hydrogen bonding. The self-attraction and crystallization tendencies are most readily apparent for the amylose. The association between the polymer chains results in the formation of an intermolecular network that traps water and forms gels. Precipitation is particularly evident for amylose. Amylopectin association is interrupted because of amylopectin's highly branched character. However, at low temperatures, even amylopectin will associate, resulting in decreased water binding and gel formation. As would be expected from their differences in structure, amylose and amylopectin exhibit different properties. Amylose forms strong flexible films and has value as a coating agent. The branched component forms films with poor properties but finds wide usage as a thickening agent, especially in food and paper applications. Dr. R. Narayan (Michigan Biotechnology Institute) reviews in Chapter 7 work originated from the Northern Regional Research Center of the U.S. Department of Agriculture, the commercial technologies practiced through January 1989, and the technology he and coworkers developed while at Purdue University. Starch can introduce environmental degradability into plastics. The higher the proportion of the natural polymer present in the resulting plastic, the more true biodegradability is expected to be achievable. However, starch and thermoplastic matrices are incompatible. Thermoplastic amylose alone can form films for packaging applications (Lacourse and Altieri 1989), which are currently being pursued by industry.

In Chapter 8, Dr. C. Rivard and coworkers review the biodegradation of plastics. This is an area of intense research today since test methods are not yet standardized, while legislation is being created mandating biodegradation without clear definitions of parameters.

II. Bioproduction of Materials

This section addresses bioproduction of selected polymers such as cellulose, other plant cell wall polymers, and proteins, with emphasis on silk and wool. These materials can be produced with specific properties such as biodegradability (e.g., polyhydroxy-butyrate and valerate copolymers, polylactide polymers --see also Chapter 8), or specific mechanical properties. The following topics are addressed.

Microbial cellulose production is reviewed in Chapter 9 by Professor M. Brown, Jr., of the University of Texas. It is intriguing that bacterial cellulose can have high modulus as produced or perhaps can be genetically manipulated to have very high modulus. Bacterial cellulose has several unique features not found in trees or cotton: (a) *Acetobacter* can synthesize pure cellulose, devoid of lignin and other polymers; (b) bacterial cellulose has a very marked hydrophilicity; (c) microbial cellulose is capable of being directly synthesized into articles of virtually any shape or size; (d) bacterial cellulose has outstanding shape retention and dimensional stability; (e) bacterial cellulose can be synthesized from a variety of inexpensive substrates; (f) the physical properties of microbial cellulose can be controlled during synthesis; and (g) expected high rates of pure cellulose synthesis could lead to efficient scale up. Outstanding microbial cellulose synthesis and genetic engineering can also help the understanding of the more complex cellulose synthesis in higher plants.

An authoritative review of the biogenesis and the biodegradation of plant cell wall polymers constitutes Chapter 10, written by Professor N. Lewis of Virginia Tech. This chapter is complemented by the ACS Symposium Series Volume 399, in which many outstanding worldwide contributions to these fields are made. Research and development in the United States is concentrating by far on biodegradation aspects, with major emphasis on lignin model compounds and cellulose biodegradation. Very little emphasis, by comparison, is being given to the biosynthetic work. Worldwide, more balanced research portfolios have been achieved. This trend parallels increased emphasis in other countries in emerging industries using biosynthesized polymers.

Another set of interesting polymers are proteins. In fact, silk proteins have extremely high tensile properties. Drs. K. Grohmann and M. Himmel review in Chapter 11 the properties and syntheses of these materials. They also present approaches that could be undertaken to design protein fibers.

The Appendix provides Examples of Research Activities in Japan through excerpts of the exposition guide distributed at the Cellucon '88 meeting in Japan. Current Japanese industry efforts are given for the various areas addressed by this assessment.

CONCLUSIONS

The use of the wood natural composite material is energy efficient. For instance, the production of most solid-wood products uses only 5-10 million Btu/ton (Bider et al. 1985, Gaines and Shen 1983, McRae et al. 1977). Wood, however, has limited thermoplasticity, though it can be bent under steam and chemical treatment. Ways of improving whole-wood thermoplasticity that lend themselves to heat molding, an important way of shaping materials for high-speed composite production, are key for cost-effective penetration of biobased materials into the composites markets. The low energy requirements for wood products and for the simple fractionation of the wood into its component polymers suggest that it would be possible to produce materials conserving energy from renewable resources. Fiber reinforcements for inexpensive composites for the automotive

industry are an attractive area; one pound of a material introduced in an automobile represents a potential 10 million pounds market opportunity. Most plastics used today consume between 30-90 million Btu/ton (Bider et al. 1985, Gaines and Shen 1983, McRae et al. 1977), but the plastics have very low density and thus a low-energy-per-unit product is achieved. The products formed are very reproducible. But they are derived from fossil resources that are finite and obtained partially from foreign sources, subject to political vulnerability in their exclusive use. Another important rationale for government programs in this area is the improved international competitiveness that could accrue to many segments of U.S. industries, primarily small businesses, in an area currently addressed by programs in other countries. In fact, the United States is currently importing biobased materials and technologies for their production from other countries (see Chapter 1).

The use of starch is appealing. The feedstock is readily available; if the 1986-1987 surplus of about 5 billion bushels of corn were used to produce starch, 195 billion pounds would be available as a feedstock (Rutenberg 1988), a number very close to the total top fifty organic compounds produced in 1986 in the United States (Anon. 1987). Cost-effective strategies that increase the compatibility between starch and thermoplastic materials could lead to the development of new materials with mechanical properties that rival those of the plastics and include environmental degradation or biodegradation.

A large industry based on renewable sources of materials exists; small business industries dedicated to these technical areas are striving to survive. They can take new materials developed by government-sponsored programs into the marketplace. The R&D carried out by the large renewable resources industries is necessarily oriented toward high-value products and established product lines. There is a large gap between the current product-oriented industrial research and government programs, which consist of basic research (National Science Foundation, Biological DOE/Basic Energy Sciences) and applied end-use programs (Biofuels and Municipal Waste Technology Division, Office of Industrial Programs, and U.S. Department of Agriculture). There is also a large gap between government programs that is partially addressed by the ECUT program. There is a need to explore potential innovations that can emerge from the systematic exploration of the properties of renewable materials, which can play a major role in the future when our traditional feedstocks are depleted or when the relevant developed technologies become cost-competitive. Examples are already emerging of cost-effective biobased materials technologies. If these industries are to remain profitable and internationally competitive, there is a need for government involvement in planning and implementing such research programs, with input from industry. These government programs must be initiated and continued. The development of the necessary data base is a long-term effort. The ability to bring together the relevant disciplines that will lead to cost-effective and energy-efficient products from the most successful concepts in biobased materials requires a sustained effort. Developments are ongoing worldwide with major emphasis centered in Japan, Canada, and Sweden. Significant efforts also continue in other countries.

Many strategies are identified in this report to expand biobased materials beyond the current areas. They are based on a better understanding of the starting materials and end-use applications. In the composites area, technologies developed for pulp and paper are not likely to be the best for the development of inexpensive fibers for reinforcement of composites; in fact, materials not suited for current conventional applications are likely to be best and will use less energy in their manufacture than kraft pulp and some high yield pulps (chemomechanical processes). Developing compatibility between hydrophilic renewable polymers and hydrophobic synthetic polymers is a theme

throughout many chapters of this assessment. It is one of the high-priority areas of the ECUT Biobased Materials project. Designing compatible polymers and understanding the resulting properties can bring about the increased use of biobased materials into various markets--lightweight composites and packaging plastics, which will serve the transportation, buildings, and many industrial sectors.

ACKNOWLEDGEMENTS

Discussions with many researchers from industry, universities, and research institutions are gratefully acknowledged. In particular, thanks to H. M. Chang, B. Gunnesin, M. Hearon, H. Hergert, J. Hyatt, E. Malcolm, A. Power, M. Rutenberg, K. Sarkanen, and S. Shoemaker for profitable discussions from the industrial point of view. Thanks are due to all contributors to the assessment; their enthusiasm for the area and encouragement are greatly appreciated. Finally, thanks are due to Drs. J. Eberhardt and Stanley Wolf of ECUT for their support and guidance.

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Part I

Materials from Renewable Resources and Their Properties

1. Structural Materials for the Automobile of the Future: Composite Materials

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INTRODUCTION

A composite is broadly defined as a material consisting of a large number of fibers (fine filaments) embedded in a continuous phase or matrix, which gives it a definite shape and a durable surface (Phillips 1987). Matrices may consist of inorganic glasses or cements, metals, and other materials, but in this chapter they will be restricted to synthetic resins or polymers, which can be readily shaped or hardened by many different methods. Once the shaping/hardening process has taken place, the remaining function of the matrix is to distribute evenly between the fibers any structural loads imposed on the composite. The matrix can be a thermoset material such as polyester, vinylester, or epoxy, which cure (or chemically crosslink) by means of heat or catalytic hardening. Alternatively, the matrix can be of a thermoplastic material, in which case there is no cure (chemical crosslinking). Typical examples of thermoplastic are nylon, polycarbonate, polysulfone, polyethersulfone, and polyether ether ketone. (Phillips 1987). These composites can be heat reformed.

The percentage of fiber (vol %) in the composite is a function of the preparation process. Many processes have been developed over the past 20 years. They range from fiber impregnation with the appropriate matrix (soaking, brushing, spraying, etc.), followed by proper fiber reinforcement orientation and lay-up against the surface of an accurate mold. Finally, heat treatment (or pressure, or the action of chemical hardeners) converts the matrix from liquid to solid, which is resistant to further softening. Such processes will yield composites with 25%-45% fiber volume. Autoclave or vacuum can increase the fiber volume substantially so that the excess resin and entrapped air are removed. More than 60% fiber volume can be achieved.

In advanced composites (Fishman 1988), resin-based composites with continuous or discontinuous fibrous reinforcements are oriented in an organized pattern; the reinforcing fibers constitute at least 60% by volume of the composition. Reinforcing fibers are high-modulus inorganic or organic materials such as carbon fibers, aramids, and glass fibers. Table 1 presents some examples of conventional fibers and their properties, along with a few properties for some biomass-derived fibers, not necessarily optimized for composites.

These materials penetrate three major markets--aerospace, automotive, and industrial/commercial, which cover respectively high, low, and intermediate raw materials and fabrication costs, as shown in Figure 1. A few customers in the **aerospace industry** buy high-performance materials, and therefore, high-value products, from many suppliers in a highly competitive business environment. The recreational/sports equipment manufacturer can easily afford the very costly advanced composites because of the performance needed. A few customers in the **automotive industry** (24 companies--155 car lines worldwide) would like to have high-performance materials, but usually have no or very little tolerance for cost premium in passenger cars or trucks. They need high-volume low-cost composites, in many areas of the vehicles, such as components, structures, and frames, where

TABLE 1
REINFORCING FIBER PROPERTIES

Material	Density g/cm ³	Tensile strength GPa	Specific strength 10 ⁶ cm	Tensile modulus GPa	Specific modulus 10 ⁶ cm	Elongation %	Price \$/lb
Glass Fiber E-Type	2.5	3.4-4.5 1.7	18-19	70-85 72	2.8-3.4	4.8-5.4	1.5
Polyacrylonitrile carbon fiber	1.7-1.9	2.3-7.1	12-39	230-490	13-26	1.5-2.4	30-150
Pitch carbon fiber	1.6-2.2	0.8-2.3	5-10	38-820	2.3-38	2.1-2.4	6-1200
Rayon carbon fiber	1.4-1.5	0.7-1.2	7	34-55	2.3		30
Aramid fiber Poly(p-phenylene- terrephthalamide) (PPT) (Kevlar)	1.4	2.4-2.8	17-19	60-200	4.2-14	3.8	30-60
Super-drawn Polyethylene fiber	1.0	3.0	32	175	1.8	3	
Boron fiber	2.8	3.6	12	400	14		300
Si carbide fiber	2.6	2.8	10	190	7.3		600
Alumina fiber	2.7-3.9	1.4-1.7	3.6-6.3	120-380	4.4-9.7		
Whisker	2.3-3.2	14-21	43-91	380-1000	12-43		90
Wood fiber ^a	1.5	0.5-1.5	10	20-80	1.3-6		<<1
Ramie, flax ^b	1.5	.67		22.5-27		1.5-3	

Matsuda, 1988; ^aWoodhams, et al., 1984; ^bAmin et al., 1985 (See Chapter 11 for additional data.)

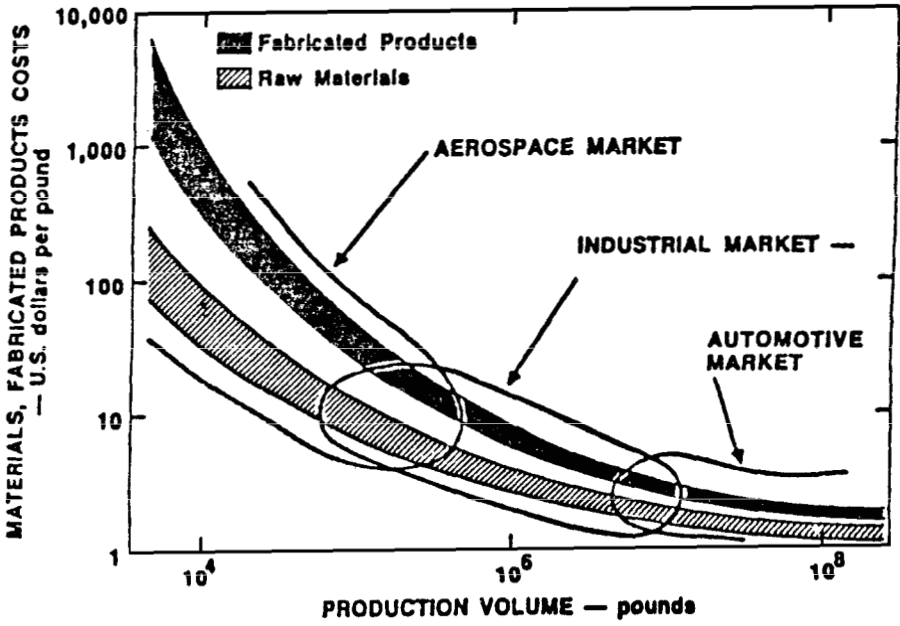


Figure 1. Major markets for structural composites (Fishman 1988)

corrosion resistance, improved damage resistance, sound-deadening effects, and reduced weight are necessary. Military vehicles, on the other hand, can afford performance-driven increased costs (Loud 1988, Beardmore, 1988). The **industrial/commercial market** is highly fragmented and embryonic. It is characterized by a multitude of small-to-intermediate specific applications. The costs range from the high-value, low-volume aerospace industry to the low-value, high-volume automotive industry (Rasmussen 1988). Examples include equipment for process, agricultural and forestry, mills, mining, and medical industries (see Table 2).

The world market size and projected growth of fabricated composites is shown in Table 3 (Fishman 1988). The curves that describe the volume of a product versus the time it takes for such products to become developed commodities are usually "S" shaped. The time necessary to achieve commodity status was 150 years for steel, 100 years for aluminum, and 75 years for plastics. Advanced composites have had approximately 25 years of development with roughly 64 million pounds production (see Table 3), quite far from the projected potential of these products as commodities (billion pound range). Because technological progress can occur faster now as we move into the late 1980's, compared to early 1980's, Rasmussen suggests that 25 additional years will see advanced composites become commodity materials.

This chapter addresses composites for the automobile industry in more detail. Industry trends and areas of R&D that the industry is pursuing will be identified. The role for federal government R&D, complementary to the industrial needs, will be discussed. Key references used to prepare this chapter are by Beardmore (1988); Matsuda (1988); Fatsch and Eckert (1988); and Wright, Hamblin, and Rader (1988). In addition, materials presented by W. Surber and S. H. W. Brooks of General Motors, Corp. and Cadillac/ASA, respectively, in October 1988 at the Forest Products Research Conference on Opportunities for Combining Wood with Nonwood Materials (Madison, Wisconsin), were employed. The American Chemical Society Division of Chemical Marketing and Economics held a Symposium on Marketing and Economic Aspects of Advanced Composites in Los Angeles (September 1988). Talks by Norman Fishman (SRI International), S. N. Loud, Jr. (Composite Market Reports, Inc.), and B. M. Rasmussen (BMR Associates) provided invaluable materials. General computer searches revealed hundreds of specific references for more detailed information.

AUTOMOBILE INDUSTRY

The U. S. automobile industry has begun to change its materials radically in response to energy crises, fuel economy legislation, and safety and emissions requirements since the 1970's. There were four key methods used to improve fuel economy: downsizing, weight reduction by materials substitution, improved aerodynamics, and improved power train efficiencies. In fact, the average weight of the American car decreased from about 3800 lb in 1976 to approximately 2800 lb in 1986 (Beardmore 1988).

Automobile weight reduction alone can lead to an increase in fuel economy of **0.0068 km/L per kilogram saved** (0.0073 mpg/lb--in a range of 0.0002-0.05 km/L/kg or 0.0021-0.053 mpg/lb). Considering that in 1986, **169 million automobiles**, buses, and trucks consumed roughly **124 billion gallons of motor fuels** (1986 U.S. statistics from the Federal Highway Administration: National Transportation and Safety Board), the impact of weight reduction on overall fuel consumption can be very high indeed. Between 1978 and 1984, approximately 16% of the total 36% increase in fleet fuel economy could be attributed to automobile weight reductions (Kulkarni 1984).

TABLE 2
PARTIAL LIST OF INDUSTRIAL APPLICATIONS BASED ON
ADVANCED COMPOSITE MATERIALS

<u>Category</u>	<u>Applications</u>
Process Industry Equipment	<ul style="list-style-type: none"> - Drive Shafts for Pumping Stations, Cooling Towers, & Chemical Mixers - High Speed Print Rollers - Grinding Wheels, Repler Sticks, Picks & Shuttle Cocks for Weaving Equip. - Shaft Couplings
Heavy Vehicle Rigging	<ul style="list-style-type: none"> - Drive Shafts & Brake Linings for Garbage, Fire, Dump, & Transit Mixers - Railroad Hopper Cars
Agricultural/Forestry Equip.	<ul style="list-style-type: none"> - Tractor ROP's, Light Weight Parts for Sprayers, Planters, & Harvesters - Forest Flumes
Mill Equipment	<ul style="list-style-type: none"> - Drive Shafts for Rubber, Steel, Textile, & Lumber Mills
Medical/Scientific/Office	<ul style="list-style-type: none"> - X-Ray Table Tops, Alignment Fixtures, Copy Machine Base, Ultracentrifuge Rotor - Artificial Braces & Limbs, Implants
Electronic/Electrical	<ul style="list-style-type: none"> - Lamp Poles, Ladders & Antennas - Satellite Dish Antennas, Fiber Optic Cable - Circuit Breaker Tubes, Circuit Boards - Windmill Blades, Electromagnetic/Radio-Frequency/Electrostatic Distortion Shielding
Construction	<ul style="list-style-type: none"> - Bridges, Decks, Highways, Buildings, & Office Walls - Cranes, Backhoes, & Forklifts
Mining/Oil Field	<ul style="list-style-type: none"> - Well Logging Tubes, Mine Props, Off Shore Riser Pipe, Sucker Rods, Sucker Ribbons, Pump & Valve Packing, Pump Impellers, Undersea Exploration Capsules - Drive Shafts for Logging & Drilling Equip.
Material Handling	<ul style="list-style-type: none"> - Robotic Arms for Point & Pick Operations
Musical	<ul style="list-style-type: none"> - Drum Sticks, Speaker Boxes, Violin Frames, Drum Wall
Marine	<ul style="list-style-type: none"> - Drive Shafts for Tug Boats & Barges - Shipboard Handling Cranes
Other	<ul style="list-style-type: none"> - Walking Canes, Wheel Chairs, Cryogenic Pressure Vessels, Ballistic Protection Garments, Flag Poles, Handles for Brooms and Window Cleaning Equipment

From B. Rasmussen, BMR Associates, N.J., 1988

TABLE 3

WORLD MARKET SIZE AND ESTIMATED GROWTH -
FABRICATED COMPOSITES
(in 1985 U.S. Dollars)

Composite Parts Based on:	1985		1995		Average Annual Growth Rate in \$ value, %/y 1985-1995
	Consumption, Millions of Pounds	Dollar Value Millions of Dollars	Consumption, Millions of Pounds	Dollar Value Millions of Dollars	
Carbon fiber, advanced	5.4	1,620	12.3	3,075	6.6%
Aramids, advanced	2.2	440	7.2	1,225	11%
E-glass fiber, advanced	10	50	290	1,160	37%
E-glass fiber, structural pultrusions	46	92	138	280	12%
Total	63.6	2,200	447.5	5,740	10%

Assumptions:

Reinforcing fibers in advanced composites constitute 65% of the composites.
Average prices of fabricated composite parts are:

Carbon	\$300/pound (1985)	\$250/pound (1995)
Aramids, advanced	\$200/pound (1985)	\$170/pound (1995)
E-glass, fiber, advanced	\$5/pound (1985)	\$4/pound (1995)
E-glass, fiber, structural pultrusions	\$2/pound (1985)	\$2/pound (1995)

Total dollar values include all other products, such as hybrids and high-strength glass fiber composites.

From N. Fishman, SRI International, 1988

The demand for lighter vehicles is expected to continue (Beardmore 1988). Though decreases in vehicle weight will also result from the development of new engine materials, the discussion in this chapter will center primarily on body structure and components, more germane to biobased materials applications. The automobile body structure is composed of a body shell (Figure 2A) and the corresponding closure panels--hood, deck lid, doors, and front fenders (Figure 2B). The body shell sustains all the durability loads through the suspension and the energy absorption loads. The body shell also provides the overall vehicle stiffness and dynamics for comfortable performance. The outer panels, on the other hand, provide dent resistance and should have a high surface quality so that attractive finishes can be accomplished. Reindl (1986) reviewed materials and requirements for these structural parts extensively.

As expected, steel and plastics currently compete for use in the outer skin panels. The steel-derived panels (mild steel or low-carbon) generally have a high-quality surface finish for their cost; weight and less damage resistance are the disadvantages of these metal parts. While the steel itself is relatively inexpensive on a weight basis (about \$0.35/lb), the cost of the fabricated part usually involves so many operations that a true cost comparison must be done on the cost of a unit weight of the finished part (Surber 1988). Technical developments in steel manufacture are to produce higher yield strength steel (15,000 psi) such that thinner (and therefore lighter) parts can be made at the same performance. The competing materials for the outer skin panels are plastics of many different types. For instance, for the bumper systems and vertical panels, unreinforced injection-molded thermoplastics have been developed, which have comparable surface quality to steel. However, because these unreinforced materials have low stiffness and a high expansion coefficient, they are not suitable for the horizontal panel applications such as hoods, roofs, and deck lids. For these parts, the sheet-molding compounds (SMC) are preferred, though the surface quality is inferior to that of steel and the price needs to decrease for widespread use. However, the advantages are lower weight and improved damage resistance (Beardmore 1988).

Thus, inexpensive materials and manufacturing technology may well be the key to success of large-scale implementation of composites in the automobile industry. Examples of process technologies employed for the fabrication of composites are: Compression molding is used for bodies and panels as illustrated in Figure 3 for sheet-molding compound (SMC). Fiber-reinforced plastics are fabricated in the form of sheets and then compression molded to the final shape.

Injection molding is used for mass-produced parts; these parts are stronger and stiffer than unreinforced polymers at a reduced coefficient of shrinkage.

Pultrusion produces continuous lengths of composite materials with uniform cross section; the fibers with the matrix are drawn into the die and the matrix cures.

Filament winding involves the winding of the tow and resin simultaneously onto a former--shaped as a solid of revolution--by means of a lathe-like machine. The fiber is led from a creel (adapted from the textile industry), through a resin bath via a comb fitted with a swiveling head to direct the former or mandrel. After the winding process, the resin is hot cured. It is possible to make simple shapes of great size with this technology (e.g., rocket bodies). Tape laying and braiding are also used.

Reaction injection molding (RIM) involves polymerization of the monomers or pre-polymers during the process of molding the finished parts. Reinforcement is obtained by adding suitable milled glass or other fibers (RRIM). These materials have lower strength and stiffness compared to SMC. To obtain similar properties

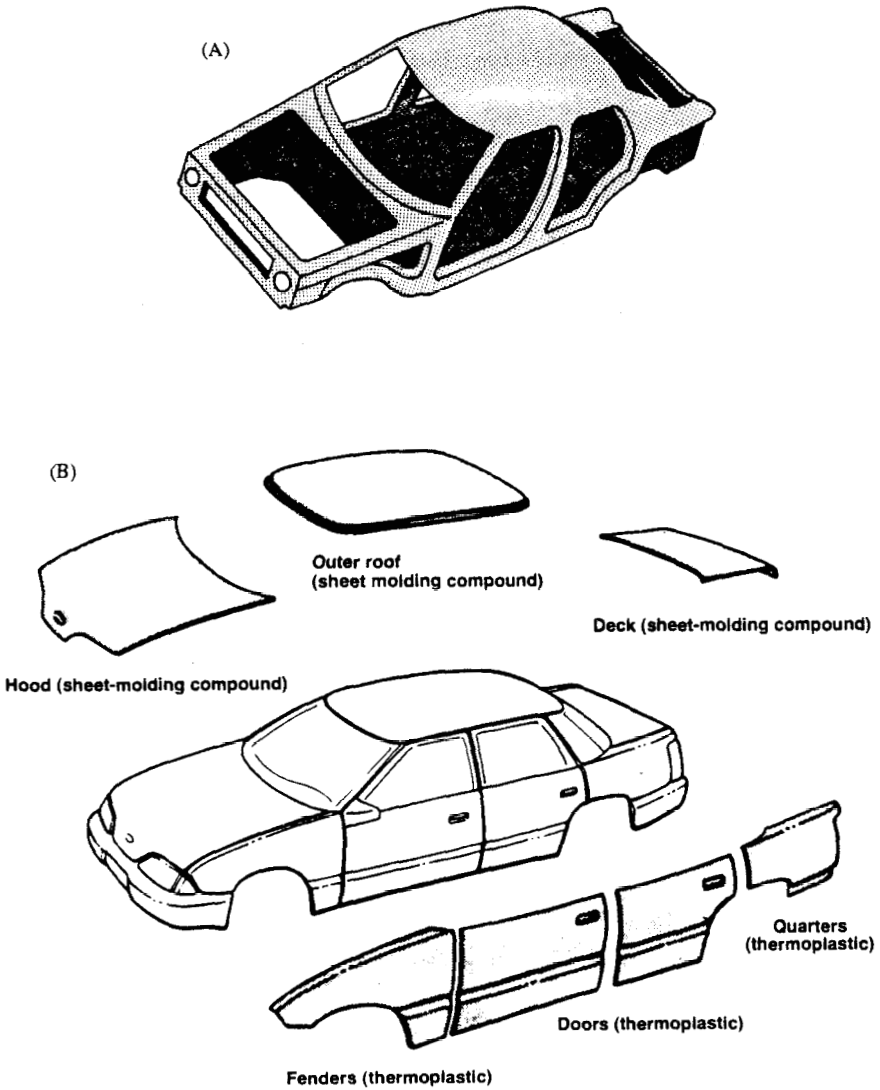


Figure 2. (A) Body shell; (B) Outer skin panel (Beardmore 1988)

to SMC, fibers are placed in the mold for reinforcement before injection and reaction of the matrix (structural RRIM), and

High speed processes are resin transfer molding (RTM) and high-speed resin transfer molding (HSRTM) (illustrated in Figure 4). It is estimated that with HSRTM large-scale structures could be fabricated in the form of complete front ends and complete body tubs, in which substantial parts consolidation can be achieved.

In manufacturing technologies, teams of designers and manufacturers will use the best features of the composites to optimize the manufacture of parts having the appropriate strength and appearance properties. Automation and robotics can be used fully as well as computer-aided design, manufacturing, and engineering (CAD/CAM/CAE), after the scant data base that now exists is developed further. As with any new area, standards, test methods, and data bases will be necessary. Phillips (1987) points out that mechanical property tests are crucial, but not only this short-term testing (usually carried out by the companies) is important. Long-term testing that pays particular attention to fatigue (repeated stresses), creep (continuous loading), thermal cycles, long-term weathering, water absorption, and chemical resistance is crucial to aerospace composites. The automotive industry needs some of the same testing and the corresponding data base but the tests should be performed on different composites. Phillips (1987) stresses the role of government agencies in ensuring that such a data base exists and is maintained.

Because every pound of a new material introduced into an American vehicle can represent a 10-million-lb market opportunity, tailoring products to vehicle applications is a justifiable investment. But the raw material and fabrication costs have to come down for substantial penetration into the market (Fatsch and Eckert 1988). Excellent opportunities exist for new materials--carbon fibers of reasonable quality in the \$5 - \$8/lb range, with a minimum of 200 GPa (30 M psi) modulus. Inexpensive fibers under \$2/lb are highly desirable. In summary, total system cost with acceptable performance is a key, as opposed to the performance-driven systems of the advanced aerospace, electronics, recreational, and selected industrial composites.

The advantages of advanced composites include the relatively low capital investment necessary to implement many of the fabrication processes--this increases the manufacturer's **flexibility of product design**. The industry would like to produce complex-shaped parts for many reasons including aesthetics and aerodynamics. In addition, advanced composites offer increased **flexibility in manufacturing** -- large moldings can consolidate a number of parts and operations such as metal stampings into a few operations. For instance, two one-piece moldings made with a high-speed resin transfer process can make 90 steel stamping operations unnecessary and reduce weight by more than 33% in the front structure of the Ford Escort (Beardmore 1988). Ultimately, these advantages translate into savings in assembly costs. **Increased durability** is another characteristic of advanced composites. The corrosion-resistance of these parts relative to metals provides this key property.

The main limitations of advanced composites are lower shatter resistance than steel for some applications; the difficulty of attaining high-quality surface finish for some types of composites; the higher temperature sensitivity of the composites; and the difficulty of attaching the composites to other materials, principally steel. Thus adhesives becomes a major area of activity, bonding composites to steel and other materials, rather than welding or mechanical fastening.

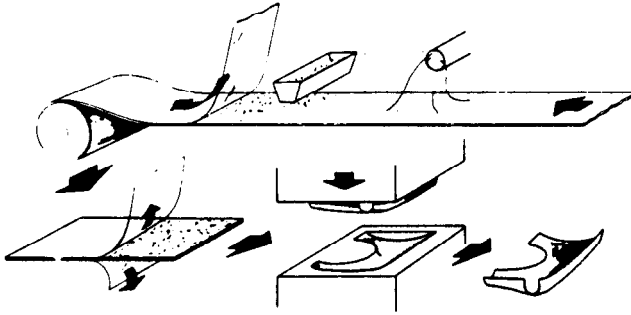


Figure 3. Schematic of sheet molding (Beardmore 1988)

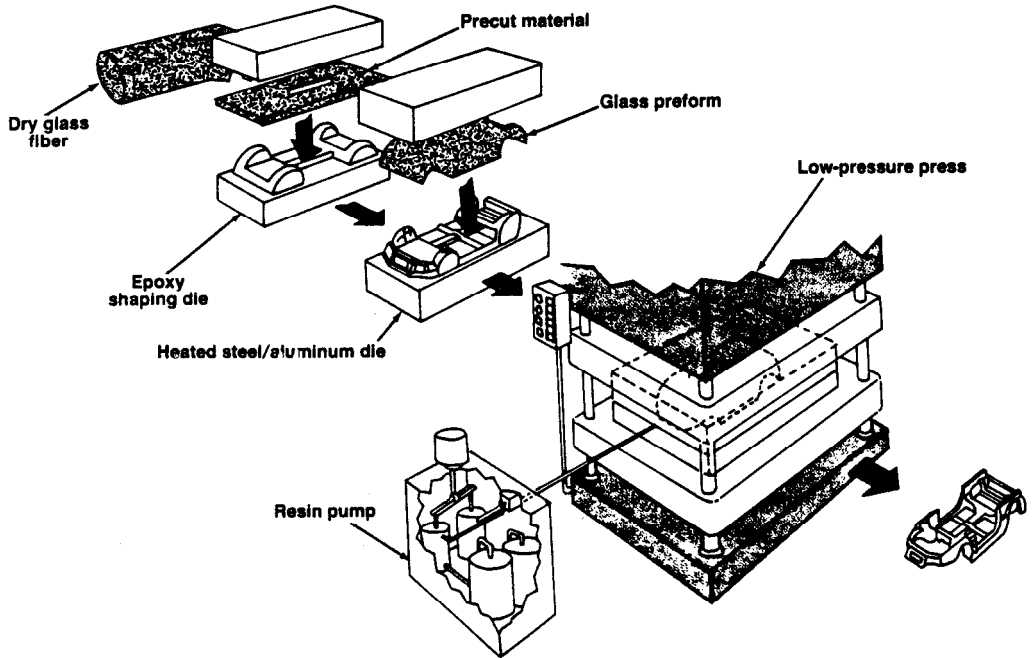


Figure 4. Schematic of high speed resin transfer molding (Beardmore 1988)

Common types of reinforcements are glasses (E-, R-, S-, and T-), carbon fibers based on polyacrylonitrile and pitch, Aramid fibers, silicon carbide fibers, whiskers, particles (see Table 1), and other organic fibers. To date for automobiles, the more inexpensive E-glass fibers appear to have the highest potential, whereas the higher cost carbon and aramid fibers can find only specialized applications. Note, however, that wood-fiber materials have a low density and can be made with reasonable strength properties. Mixed fiber reinforcements using properties and cost as parameters are practiced (Phillips 1987). The resin systems are dominated by low-cost polyesters and vinyl esters to form the thermoset structural matrices (versus the epoxy matrices often employed in the aerospace industry). In the thermoplastics area, stampable polypropylenes are very useful as well as thermoplastic elastomers (TPE). TPE can be blow molded faster than thermoset rubbers. TPE and thermoplastic olefins offer design flexibility in automotive applications (Wright, Hamblin, and Rader 1988). Other combinations such as metal matrix composites and ceramic matrix composites are being developed (see Milberg 1987, Ishikawa 1989). Again, the development of low-cost resin materials could provide the advanced composite suppliers with ways to reduce overall cost and penetrate additional automotive markets.

The General Motors, Ford, and Chrysler Composites Consortium was announced on September 9, 1988. It is a 12-year agreement, with chair and secretary to rotate annually, starting with GM. It includes polymer-based and metal-plastics composites (not biobased materials) for structural uses. It will stimulate technological communication in the generic area of advanced composites to establish a network of information and protect the technological edge of U.S. companies (Loud 1988).

BIOBASED MATERIALS IN THE AUTOMOTIVE INDUSTRY

Lightweight biobased composites are based on very inexpensive renewable materials such as wood (~\$0.04/lb) and wood fibers (~\$0.1-0.2/lb depending on the process). Wood costs have been declining over the years (discounting the abnormal oil crisis period) and this trend is expected to continue (Comstock 1988). Wood flour has been and continues to be used as an inexpensive filler for automobiles and in thermoplastic conglomerates in general (Savonuzzi 1988). Trunk liners, mats and many other products have been made, tailored to the specific needs. Usually the thermoplastic is polypropylene because it shows good moldability, and retains its thermoplasticity, even at 50% wood incorporation. The additional advantage of the product is recyclability. Japan leads the research, development, and commercialization of such products (see Appendix on the Cellucon 88 meeting). For instance, Mitsubishi Corp. in Japan has introduced PapiTM, a polypropylene composite containing 50% of reclaimed newspaper fibers for injection molding and thermoforming of automotive components (Woodhams et al. 1984). These uses begin to take advantage of the fiber properties of cellulose, reinforced by the hemicellulose/lignin matrix or other biobased fibers.

In Canada, Woodhams et al. (1984) have made extensive measurements of the reinforcing properties of various wood fibers in polyolefins. Woodhams et al. concluded that wood pulp fibers possessed strength and modulus properties which compared favorably with E fiber glass when the differences in fiber densities were considered. Dispersion of the fibers was accomplished with the aid of dispersing agents (carboxylic acids) leading to 50% wood fiber mixtures that could be injection molded. The best way to compatibilize wood fibers with the polyolefins has not been reached. Similar mechanical properties were obtained for kraft mechanical and chemo-mechanical fibers, as well as recycle newsprint. The wood fibers imparted equal or higher stiffness/weight compared to glass fibers, steel, or aluminum. The strength properties were not as good because of voids created in processing due to volatiles formation. The wood fibers were not abrasive such that machining was easier even at 50% loading compared to a

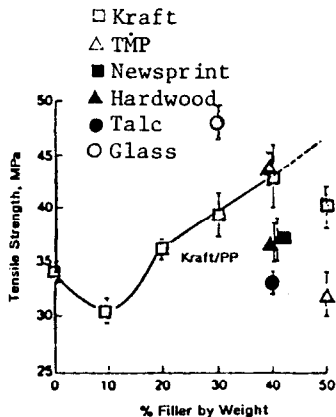
lower level of glass fiber addition. Examples of selected properties are shown in Figure 5.

There are many different materials to be developed for specific automotive applications that require moderately high-temperature performance with low cost and with other specific properties such as low brittleness, high stiffness, high strength, low weight, and easy processing. Ease of processing can be achieved from simple moldings made by RIM, RTM (or HSRTM), or SRIM, or from textile-derived methods such as web technologies, which lend themselves to easy manufacturability, automation and robotic control. Processing needs to lead to a surface that can be finished as metal parts can, which has been a difficult task for composites.

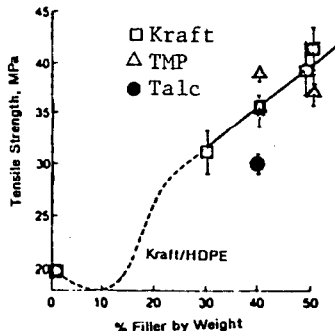
For the past five years, GM, through the Cadillac/ASA Industries, has been involved in investigating such composites using a variety of biomass-derived fibers such as thermally processed wood from the batch steam explosion process (Figure 6) or one of its continuous versions, such as the Stake digester (Figure 7), which maintains good dimensional stability (see Chornet and Overend 1986). Hammer-milled kenaf fibers, which have good sound-deadening properties have also been investigated. Using web technologies, wood-glass fiber composites have been made for the automobile panels with thermoset resins (phenolic novolaks and polyesters). Innovative approaches were used to spin the novolak fibers so that blends of the various components could be made into webs (inch thick mats). The resulting air-laid mats can be heat molded (Brooks 1988). These developments evolved from the self-supporting moldable fiber mats and processes patented by Brooks (1982) for use in automotive applications, such as dashboards and interior door panels. An example of the flow sheet for this processing shown in Figure 8. Cadillac/ASA Industries have produced a number of car parts and have achieved some successes in parts consolidation. The major success of these experiments has been in meeting the strength properties required for the same surface area of material, such that lightweight biobased composites have been made that exhibit acceptable properties for several car applications. Complete crash testing has not been performed. Cost reductions are necessary in all areas, but especially in the phenolic resins. Performance improvements of the starting materials will open up new applications in this very interesting high-volume low-price materials area. These materials can have a major impact on future petroleum savings both in transportation and in materials production. General Motors terminated the effort in 1989.

Cadillac/ASA Industries have collaborated with several government institutions such as the United States Department of Agriculture (USDA) Forest Products Laboratory (FPL) (Dr. Roger Rowell), the University of Wisconsin (Professor Ray Young, Energy Conversion and Utilization Technologies [ECUT] subcontractor), and SERI. A donation of a 12-in. Rando Forming line to the FPL, to which ECUT subcontractors have access, has been instrumental in the development of new composites for testing. It is extremely important to develop these composites so that during the service life (about 10 years), mechanical properties are good, dimensional stability exists, and the composites resist biological, chemical, and photochemical degradation. However, after the useful life, easy reclaim of these parts, either through recycling or reuse of the parts, or degradation into safe degradable and biodegradable components is highly desirable.

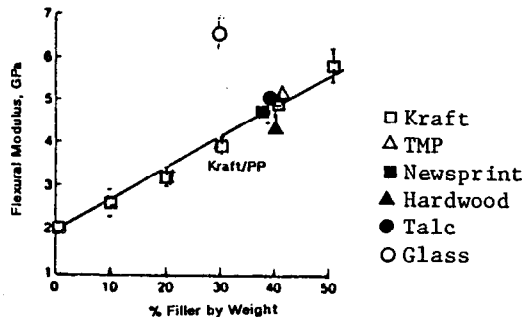
A joint venture between Magna International Inc. and the General Financing Society of Quebec (Quebec government, Canada) has been formed to produce wood fiber components for automotive application and other industries. The plant will use West German technology for mat production; mats will be shipped to the USA for use in the Nashville, IL plant to be molded into interior door, roof and instrument panels for cars and trucks (Globe & Mail, Toronto, March 9, 1989)!



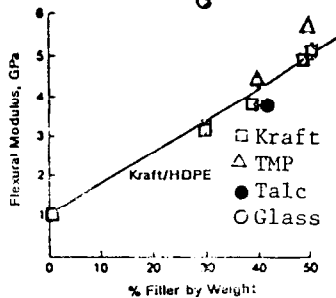
a. Effect of Filler Level on Tensile Strength of Polypropylene.



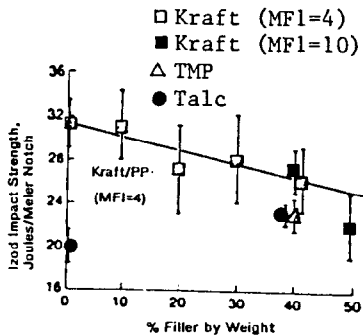
b. Effect of Filler Level on Tensile Strength of High Density Polyethylene



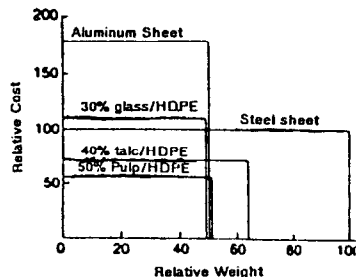
c. Effect of Filler Level on Flexural Modulus of Polypropylene



d. Effect of Filler Level on Flexural Modulus of High Density Polyethylene



e. Effect of Filler Level on Impact Strength of Polypropylene



f. Cost versus Weight of Equivalent-Stiffness Materials

Figure 5. Physical properties of polyolefins with wood fibers as reinforcing fillers and comparative costs and weights (Woodhams et al. 1984)

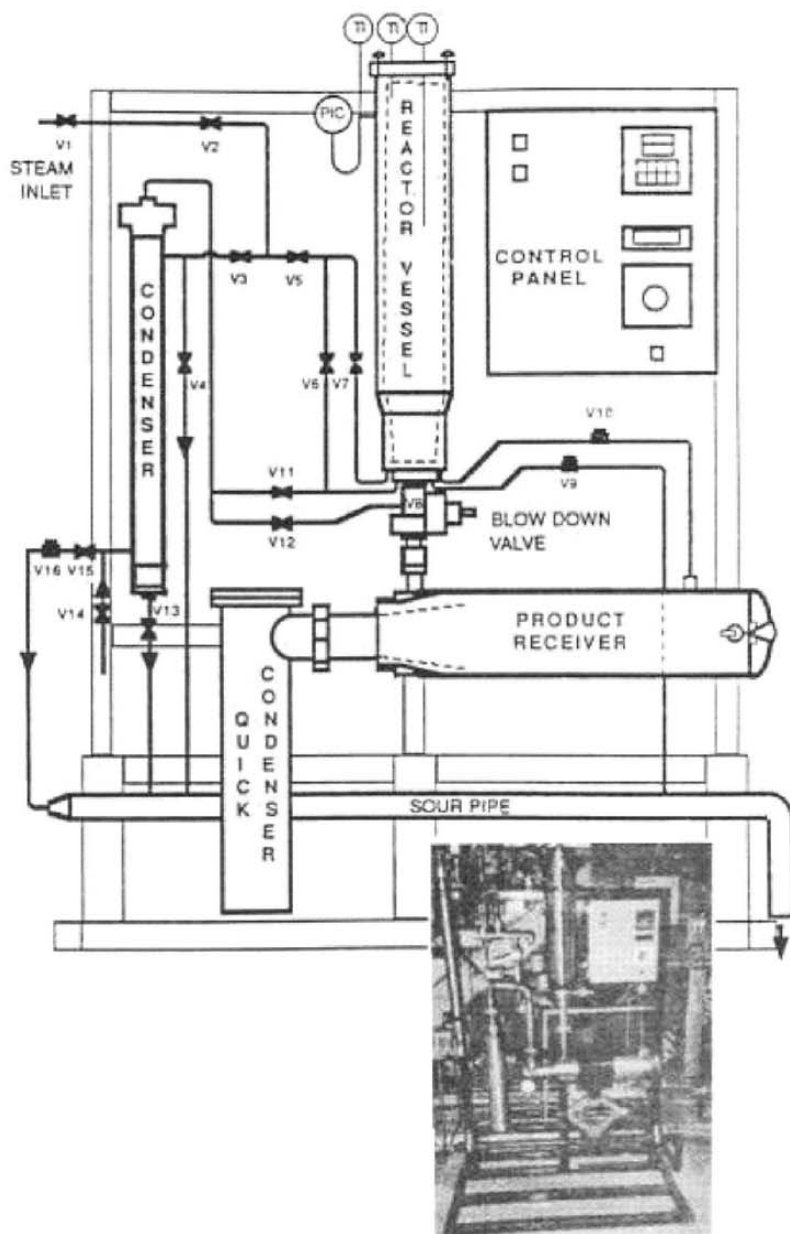


Figure 6. Schematic diagram of a steam explosion unit (Chornet and Overend 1985)

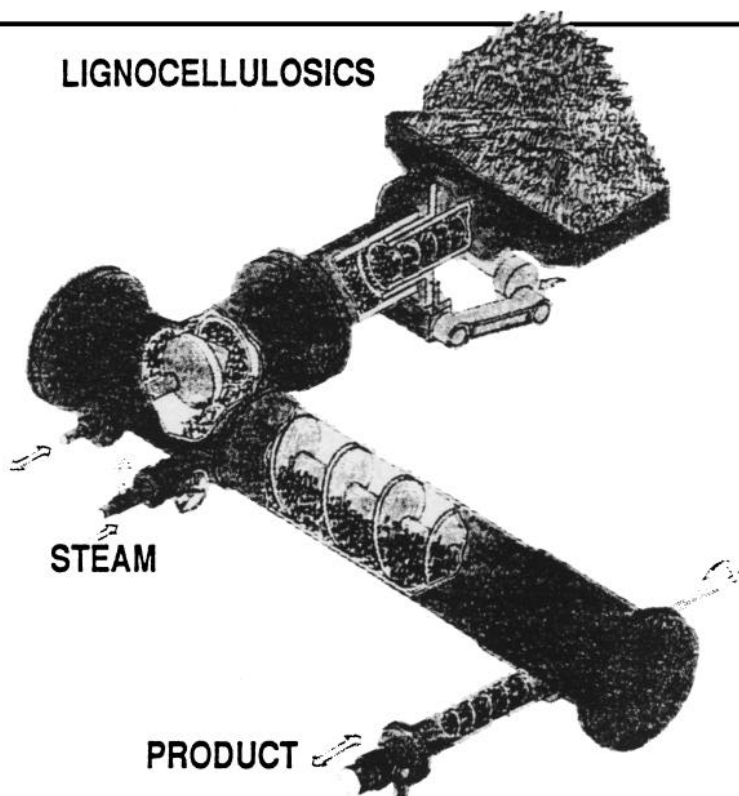


Figure 7. Configuration of the STAKE system (Chornet and Overend 1986)

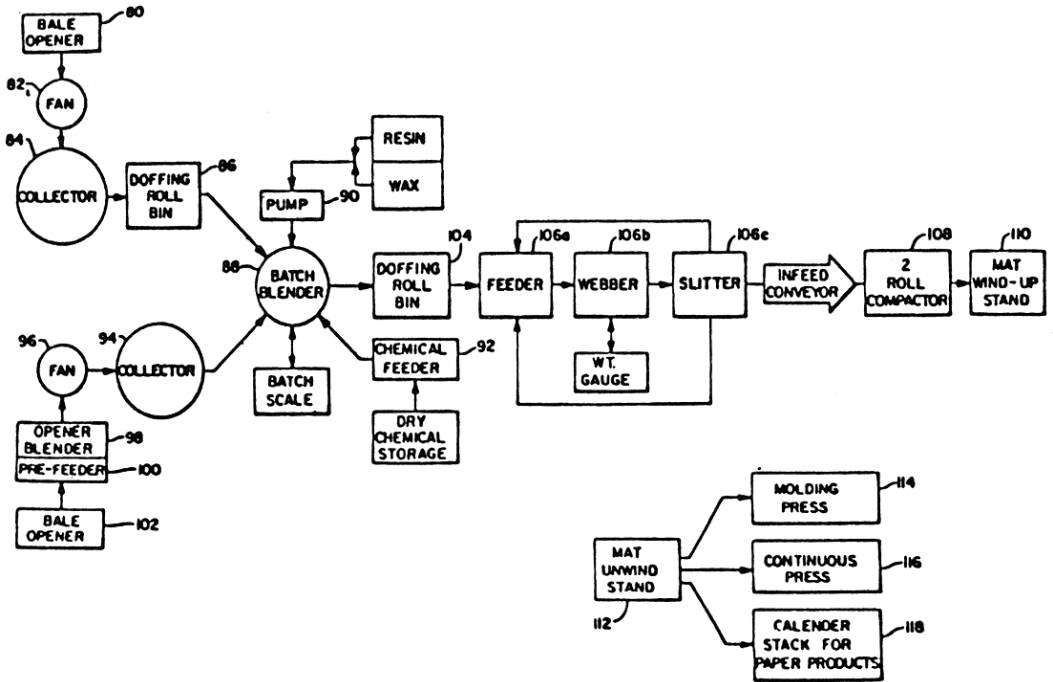


Figure 8. The moldable fiber mat is formed of cellulosic fibers, a small percentage of textile fibers, and a binder. Wood chips (or bark or refuse) are abraded and heated to about 260° to 370°C to melt the lignin in the material, depolymerize and redistribute the lignin through the fiber surfaces. The lignocellulosic material has 75%-85% solids before the heating stage. Blending the lignocellulosic fibers with the textile ones with the binder is accomplished batchwise (88). The mat is passed through a compactor (108). The mat can then be formed into a variety of products from paper products to rigid fiberboards.

To develop successfully these characteristics in materials, researchers need a data base of properties of the lightweight biobased composites that includes: modulus of elasticity; tensile, compression, and impact strength; brittleness; and processability. The data base must include data on chemical and biological degradation; dimensional stability as a function of moisture and heat; and thermal cycling. With this information, researchers from academia and industry can develop new materials that will reach the automotive industries with a host of special properties and have a major impact on vehicle weight reduction and thus fuel savings and cost. The federal government has a major role in this area. The conventional composites with all plastics components are being investigated by the U.S. industry; much less effort is currently dedicated to the biobased materials role in composites. Thus, funding in this area allows a host of new materials that are inexpensive to produce to be made available for industry testing.

One example of inexpensive materials soon to be available for industrial testing stems from research at SERI in the area of waste wood and bark utilization through fast pyrolysis coupled to solvent extraction to isolate mixtures of phenolic compounds. These mixtures are likely to replace at least 50% of phenol in phenol-formaldehyde thermosetting resins in the near future. These mixtures are produced in a very simple process for which the pay back is expected to be one year (maintaining the current \$0.20 difference between the highest production cost of the substitute (\$0.27) and the current price of phenol (Chum et al., 1989)). A consortium of industries has been formed and will help the U. S. Department of Energy through the Office of Industrial Programs to explore this 2.5-year-old process. Because the risk of these new processes and of new materials production is very high, companies will not undertake their development alone. The high pay off in terms of short pay back, independence from petroleum feedstocks, and suitable property development are not enough to allow most of U.S. industry today to dedicate a sizable fraction of its resources to this area without continued government and SERI involvement.

Government-sponsored programs can indeed lead to new technologies, economic development through the creation of new industries, and ultimately to energy conservation. Note that use of biobased materials provides one of the best solutions to the greenhouse effect and conservation of carbon dioxide in a material that can be used for a short or long period of time, depending on its function. Use of these materials is at least neutral (carbon dioxide fixed by plants will be eventually released in a controlled way) or very positive if strategies are made that will incorporate these products and recycle them in long-term uses. New enabling materials technologies will be generated, along with extensive data bases of properties of these new materials, so that industry can continue to develop these attractive options. Industry involvement is a key to the success of these new technologies through review boards, joint work, and true collaboration.

ACKNOWLEDGMENTS

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2. Recent Advances in Lignocellulosic-Derived Composites

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Wood and other lignocellulosic materials are three-dimensional, polymeric composites made up primarily of cellulose, hemicelluloses, and lignin. These polymers make up the cell wall and are responsible for most of the physical and chemical properties of these materials. Wood and other lignocellulosic materials have been used as engineering materials because they are economical, low in processing energy, renewable, and strong. However, they have several undesirable properties such as dimensional instability caused by moisture sorption with varying moisture contents, biodegradability, flammability, and degradability by ultraviolet light, acids, and bases.

Because of the undesirable properties and susceptibility to environmental degradation of lignocellulosic materials, most composites made from them have a limited service life. Most lignocellulosic composite markets are price driven; i.e., sales depend on the price of the composite. The markets for other composite materials such as metals, plastic, and glass are generally performance driven; i.e., sales depend on the way the material performs in service.

Lignocellulosics are now part of multi-material composites. But in most cases, the lignocellulosics are there as filler to reduce the cost of the material, not to improve the properties of the composite. Lignocellulosic materials could be part of a performance driven composite if their undesirable properties could be improved.

The undesirable properties of lignocellulosics all result from chemical reactions involving degradative environmental agents (Figure 1). Because these types of degradation are chemical in nature, it is possible to eliminate them or decrease their rate by modifying the basic chemistry of the lignocellulosic cell wall polymers (Figure 2).

The majority of research on chemical modification of lignocellulosic materials has been done on wood; this research has mainly dealt with improving either dimensional instability or biological resistance.

This chapter will review the chemical modification of lignocellulosic materials, improvements in properties of lignocellulosic materials resulting from chemical modification, the combination of lignocellulosics with other materials, and opportunities for future composites using modified lignocellulosics in combination with other materials.

- Biological Degradation — Fungi, Bacteria, Insects, Termites
- Enzymatic Reactions — Oxidation, Hydrolysis, Reduction
- Chemical Reactions — Oxidation, Hydrolysis, Reduction
- Mechanical — Chewing
- Fire Degradation — Lightning, Sun, Man
- Pyrolysis Reactions — Dehydration, Hydrolysis, Oxidation
- Water Degradation — Rain, Sea, Ice
- Wood-Water Interactions — Swelling, Shrinking, Freezing, Cracking
- Weathering Degradation — Sun, Water, Heat, Wind
- Chemical Reactions — Oxidation, Hydrolysis
- Mechanical — Erosion
- Chemical Degradation — Acids, Bases, Salts
- Chemical Reactions — Oxidation, Reduction, Dehydration, Hydrolysis, Acid Rain
- Mechanical Degradation — Storms (Wind, Rain, Hail, Snow), Loads
- Mechanical — Stress, Cracks, Fracture, Abrasion

Figure 1. Degradation reactions that occur when lignocellulosics are exposed to nature

Biological Degradation

Hemicelluloses > > > Accessible Cellulose > Non Crystalline Cellulose > > > > Crystalline Cellulose > > > > Lignin

Moisture Sorption

Hemicelluloses > > Accessible Cellulose > > > Non Crystalline Cellulose > Lignin > > > Crystalline Cellulose

Ultraviolet Degradation

Lignin > > > > > Hemicelluloses > Accessible Cellulose > Non Crystalline Cellulose > > > Crystalline Cellulose

Thermal Degradation

Hemicelluloses > Cellulose > > > > > Lignin

Strength

Crystalline Cellulose > > Non Crystalline Cellulose + Hemicelluloses + Lignin > Lignin

Figure 2. Lignocellulosic cell wall polymers responsible for properties

CHEMICAL MODIFICATION OF LIGNOCELLULOSIC MATERIALS

Reactive organic chemicals can be bonded onto hydroxyl groups on cellulose, hemicelluloses, and lignin in the lignocellulosic cell wall. Simple epoxies (Rowell, Tillman, and Liu 1986; Tillman [in press]) and water-soluble phenol formaldehyde resins (Brown, Kenaga, and Gooch 1966) have been reacted with wood flakes to improve dimensional stability in composites. By far the most research on the chemical modification of lignocellulosic materials, however, has been done using acetylation techniques. Acetylation reactions have been done on wood furnish to produce fiber boards (Bekere, Shvalbe, and Ozolinya 1978; Bristow and Black 1969), hardboards (Sudo 1979; Klinga and Tarkow 1966; Zhang et al. 1981; Ozolinya et al. 1974; Shvalbe 1974), particle boards (Rowell 1985; Tillman, Simonson, and Rowell 1985; Nishimoto and Imamura 1985; Yoshida et al. 1986; Rowell, Simonson, and Tillman 1986a; Imamura et al. 1986; Rowell et al. 1989; Kiguchi and Suzuki 1985; Imamura and Nishimoto 1987), and flake boards (Youngquist, Krzysik, and Rowell 1986; Youngquist, Rowell, and Krzysik 1986; Rowell and Plackett [in press]), using vapor phase acetylation (Klinka and Tarkow 1966; Arora, Rajawat, and Gupta 1981; Rowell, Tillman, and Simonson 1986a,b), liquid phase acetylation (Rowell, Tillman, and Liu 1986; Rowell, Tillman, and Simonson 1986b), or reaction with ketene (Rowell, Wang, and Hyatt 1986).

If the acetylation system does not include a strong catalyst or cosolvent, only the easily accessible hydroxyl groups will be acetylated. Some of us developed an acetylation system that uses no strong catalyst or cosolvent and probably acetylates only easily accessible hydroxyl groups (Rowell, Tillman, and Simonson 1986b).

Several lignocellulosic fibers were acetylated using this procedure using reaction times varying from 15 min to 4 h with southern pine, aspen, bamboo (Rowell and Norimoto 1987), bagasse (Rowell and Keany [in press]), jute (Rowell, Simonson, and Tillman 1985), pennywort, and water hyacinth (Rowell and Rowell [in press]).

All the lignocellulosic materials were easily acetylated. Plotting acetyl content resulting from the acetylation the above fibers as a function of time shows all data points fitting a common curve (Figure 3). A maximum weight percent gain (WPG) of about 18 was reached in a 2-h reaction time, and an additional 2 h increased the weight gain only by about 2% to 3%. Without a strong catalyst, acetylation using acetic anhydride alone levels off at approximately 20 WPG for the softwoods, hardwoods, grasses, and water plants.

IMPROVEMENTS IN PROPERTIES OF LIGNOCELLULOSIC MATERIALS

Moisture Sorption

Sorption of moisture is mainly due to hydrogen bonding of water molecules to the hydroxyl groups in the cell wall polymers. By replacing some of the hydroxyl groups on the cell wall polymers with acetyl groups, the hygroscopicity of the lignocellulosic material is reduced.

Table 1 shows the equilibrium moisture content (EMC) of several lignocellulosic materials at 65% relative humidity (RH). A plot of the reductions in EMC at 65% RH of acetylated fiber referenced to unacetylated fiber as a function of the bonded acetyl content is a straight line plot (Figure 4). Even though the points shown in Figure 4 come from many different lignocellulosic materials, they all fit a common line. A maximum reduction in EMC is achieved at about 20% bonded acetyl. Extrapolation of the plot to 100% reduction in EMC would occur at about

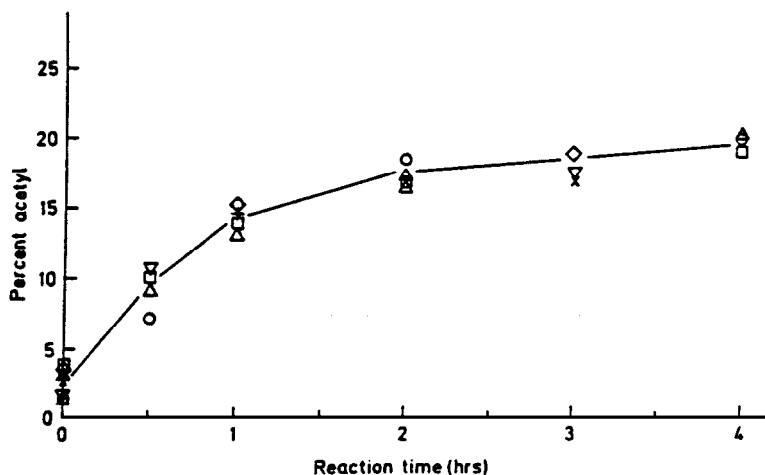


Figure 3. Rate of acetylation of various lignocellulosic materials. \circ , southern pine; \square , aspen; Δ , bamboo; \diamond , bagasse; \times , jute; $+$, pennywort; ∇ , water hyacinth

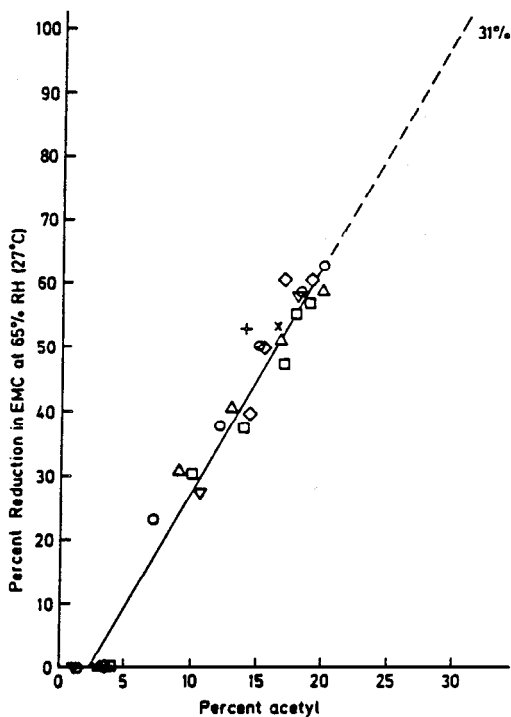


Figure 4. Reduction in equilibrium moisture content (EMC) as a function of bonded acetyl content for various acetylated lignocellulosic materials. \circ , southern pine; \square , aspen; Δ , bamboo; \diamond , bagasse; \times , jute; $+$, pennywort; ∇ , water hyacinth

30% bonded acetyl. Because the acetate group is larger than the water molecule, not all hygroscopic hydrogen-bonding sites are covered.

The fact that EMC reduction as a function of acetyl content is the same for many different lignocellulosic materials indicates that reducing moisture sorption and, therefore, achieving cell wall stability are controlled by a common factor. The lignin, hemicelluloses, and cellulose contents of all the materials plotted in Figure 4 are different (Table 2). Earlier results showed that the bonded acetate was mainly in the lignin and hemicelluloses (Rowell 1982) and that isolated wood cellulose does not react with uncatalyzed acetic anhydride (Rowell, n.d.).

Because these materials vary widely in their lignin, hemicelluloses, and cellulose content, because acetate is found mainly in the lignin and hemicelluloses polymer, and because isolated cellulose does not acetylate by the procedure used, acetylation may be controlling the moisture sensitivity caused by the lignin and hemicellulosic polymers in the cell wall but not reducing the sorption of moisture in the cellulose polymer.

Dimensional Stability

Dimensional instability, especially in the thickness direction, is a great problem in lignocellulosic composites because they exhibit not only reversible swelling, but also swelling caused by the release of residual compressive stresses imparted to the board during the composite pressing process (irreversible swelling). Water sorption causes both reversible and irreversible swelling with some of the reversible shrinkage occurring when the board dries. Dimensional instability of lignocellulosic composites has been the major reason for their restricted use.

The rate of swelling in liquid water of an aspen flake board made from acetylated flakes and phenolic resin (Rowell, Tillman, and Simonson 1986b) is shown in Figure 5. During the first 60 min, control boards swelled 55% in thickness; the board made from flakes acetylated to 17.9 WPG swelled less than 2%. During 5 days of water soaking, the control boards swelled over 66%; the 17.9 WPG board swelled about 6%.

Control boards made from bamboo particles using a phenolic adhesive swelled about 10% after 1 h, 15% after 6 h, and 20% after 5 days. Particle boards made from acetylated bamboo particles swelled about 2% after 1 h and only 3% after 5 days (Rowell and Norimoto 1988). Thickness changes in a six-cycle water-soaking/ovendrying test for an acetylated aspen flake board are shown in Figure 6 (Rowell, Tillman, and Simonson 1986b). Control boards swelled over 70% in thickness during the 6 cycles as compared to less than 15% for a board made from acetylated flakes. Acetylation greatly reduced both irreversible and reversible swelling. In a similar five-cycle water-soaking/oven-drying test on bamboo particle boards, control boards swelled over 30%; boards made from acetylated particles swelled about 10%.

Biological Resistance

Chemical modification of wood composite furnish for biological resistance is based on the theory that the potentially degrading enzymes must directly contact the substrate, and the substrate must have a specific chemical configuration and molecular conformation. Reacting chemicals with the hydroxyl groups on cell wall polymers chemically changes the substrate so that the highly selective enzymatic reactions cannot take place. Chemical modification also reduces the moisture

TABLE 1. Equilibrium Moisture Content (EMC) of Various Acetylated Lignocellulosic Materials (65% RH, 27°C)

Material	Reaction weight gain (%)	Acetyl content (%)	EMC (%)
Southern Pine	0	1.4	12.0
	6.0	7.0	9.2
	14.8	15.1	6.0
	21.1	20.1	4.3
Aspen	0	3.9	11.1
	7.3	10.1	7.8
	14.2	16.9	5.9
	17.9	19.1	4.8
Bamboo	0	3.2	8.9
	10.8	13.1	5.3
	14.1	16.6	4.4
	17.0	20.2	3.7
Bagasse	0	3.4	8.8
	9.4	14.4	5.3
	12.2	15.3	4.4
	17.6	19.0	3.4
Jute	0	3.0	9.9
	15.6	16.5	4.8
Pennywort	0	1.3	18.3
	10.1	14.0	8.6
Water hyacinth	0	1.2	1.7
	8.3	10.8	1.2
	18.6	17.8	0.7

TABLE 2. Chemical Composition of Some Lignocellulosic Materials

Material	Lig ^a nin	Cellu- lose	Sugars					Uronic acids	Extrac- tives ^b	Ash	Acetyl
			Glucose	Xylose	Galac- tose	Arabi- nose	Mannose				
Southern Pine	26.6	45	49.0	5.4	2.4	--	19.2	1.6	6.9	0.3	1.4
Aspen	18.5	49	53.3	18.5	1.0	--	1.4	2.5	4.3	0.4	4.1
Bamboo	24.2	42	52.0	21.7	--	0.8	--	0.8	11.0	0.4	3.2
Bagasse	21.1	45	47.4	27.6	--	1.7	--	1.0	8.4	1.4	3.4
Jute	13.7	58	63.8	13.1	1.2	--	0.6	3.2	3.7	1.0	3.0
Pennywort	10.3	49	39.0	3.5	2.8	0.8	2.9	9.8	38.3	11.2	1.3
Water hyacinth	8.5	58	37.2	8.7	5.0	11.4	1.4	7.1	20.5	7.9	1.2

^aKlason.^b6 h of reflux, benzene ethanol.

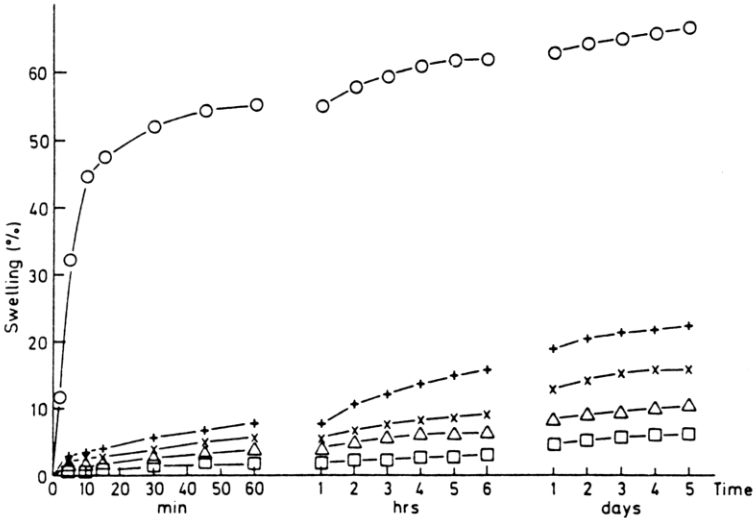


Figure 5. Rate of swelling in liquid water of aspen flakeboard made from acetylated flakes. O, control; +, 7.3 WPG; x, 11.5 WPG; Δ, 14.2 WPG; □, 17.9 WPG

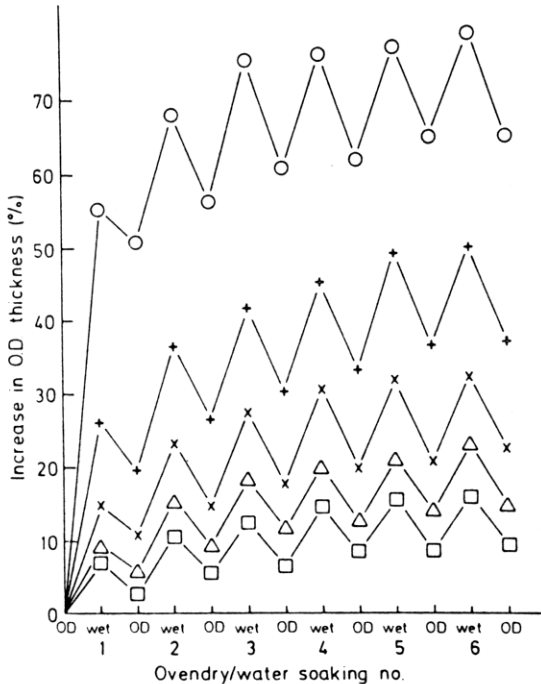


Figure 6. Changes in ovendry (O.D.) thickness in repeated water soaking test of aspen flakeboard made from acetylated flakes. O, control; +, 7.3 WPG; x, 11.5 WPG; Δ, 14.2 WPG; □, 17.9 WPG

content of the cell wall polymers to a point where biological degradation cannot take place.

Particle boards and flake boards made from acetylated flakes have been tested for resistance to several different types of organisms. In a 4-week termite test using Reticulitermes flavipes (subterranean termites), boards acetylated to 16-17 WPG were very resistant to attack, but not completely so (Imamura et al. 1986; Rowell et al. 1987; Rowell et al. 1988). This may be attributed to the severity of the test. However, because termites can live on acetic acid and decompose cellulose to mainly acetic acid, perhaps it is not surprising that acetylated wood is not completely resistant to termite attack.

Chemically modified wood composites have been tested to decay fungi in several ways. Untreated aspen and pine particle boards and flake boards exposed to white-, soft-, and brown-rot fungi and tunneling bacteria in a fungal cellar were destroyed in less than 6 months; particle boards and flake boards made from acetylated furnish above 16% acetyl weight gain showed no attack after 1 yr (Table 3) (Rowell et al. 1987; Rowell et al. 1988; Nilsson et al. 1988). In a standard 12-week single-culture soil-block test, control aspen flake boards exposed to the white-rot fungus Trametes versicolor lost 34% weight; acetylated flake boards (17% acetyl weight gain) lost no weight (Rowell et al. 1987; Rowell et al. 1988; Nilsson et al. 1988). Using the brown-rot Tyromyces palustris, control aspen flake boards lost only 2% weight when a phenol-formaldehyde adhesive was used but lost 30% weight when an isocyanate adhesive was used. If the flake boards are water leached before the soil-block test is run, control boards made with phenol-formaldehyde adhesive lose 44% weight with the brown rot fungus Gloeophyllum trabeum (Rowell n.d.; Rowell et al. 1987; Rowell et al. 1988). This shows that the adhesive can influence results of fungal toxicity, especially in a small, closed test container.

Weight loss resulting from fungal attack is the method most used to determine the effectiveness of a preservative treatment to protect wood composites from decaying. In some cases, especially for brown-rot fungal attack, strength loss may be a more important measure of attack because large strength losses are known to occur in solid wood at very low wood weight loss (Cowling 1961). A dynamic bending-creep test has been developed to determine strength losses when wood composites are exposed to a brown- or white-rot fungus (Imamura and Nishimoto 1985).

Using this bending-creep test on aspen flake boards, control boards made with phenol-formaldehyde adhesive failed in an average of 71 days with T. palustris and 212 days with T. versicolor (Rowell, Youngquist, and Imamura 1988). At failure, weight losses averaged 8% for T. palustris and 32% for T. versicolor. Isocyanate-bonded control flake boards failed in an average of 20 days with T. palustris and 118 days with T. versicolor, with an average weight loss at failure of 6% and 34%, respectively (Rowell, Youngquist, and Imamura 1988). Very little or no weight loss occurred with both fungi in flake boards made using either phenol-formaldehyde or isocyanate adhesive with acetylated flakes. None of these specimens failed during the test period.

Mycelium fully covered the surfaces of isocyanate-bonded control flake boards within 1 week, but mycelial development was significantly slower in phenol-formaldehyde-bonded control flake boards. Both isocyanate- and phenol-formaldehyde-bonded acetylated flake boards showed surface mycelium colonization during the test time, but the fungus did not attack the acetylated flakes, so little strength was lost.

TABLE 3. Fungal Cellar Tests on Aspen Flakeboards Made from Control and Acetylated Flakes^{a,b}

Acetyl WPG ^c	Rating at intervals ^d					
	2 mo	3 mo	4 mo	5 mo	6 mo	12 mo
0	S/2	S/3	S/3	S/3	S/4	--
7.3	S/0	S/1	S/1	S/2	S/3	S/4
11.5	0	0	S/0	S/1	S/2	S/3
13.6	0	0	0	0	S/0	S/1
16.3	0	0	0	0	0	0
17.9	0	0	0	0	0	0

^aNonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria.

^bFlakeboards bonded with 5% phenol-formaldehyde adhesive.

^cWeight percent gain.

^dRating system: 0 = no attack; 1 = slight attack; 2 = moderate attack; 3 = heavy attack; 4 = destroyed; S = swollen.

In similar bending-creep tests, both control and acetylated pine particle boards made using melamine-urea-formaldehyde adhesive failed because T. palustris attacked the adhesive in the glue-line (Imamura et al. [in press]). Mycelium invaded the inner part of all boards, colonizing in both wood and glue-line in control boards but only in the glue-line in acetylated boards.

After a 16-week exposure to T. palustris, the internal bond strength of control aspen flake boards made with phenol-formaldehyde adhesive was reduced more than 90% and that of flake boards made with isocyanate adhesive was reduced 85% (Imamura, Nishimoto, and Rowell 1987). After 6 months of exposure in moist unsterile soil, the same control flake boards made with phenol-formaldehyde adhesive lost 65% of their internal bond strength and those made with isocyanate adhesive lost 64% internal bond strength. Failure was due mainly to great strength reductions in the wood caused by fungal attack. Acetylated aspen flake boards lost much less internal bond strength during the 16-week exposure to T. palustris or 6-month soil burial. The isocyanate adhesive was somewhat more resistant to fungal attack than the phenol-formaldehyde adhesive. In the case of acetylated composites, loss in internal bond strength was mainly due to fungal attack in the adhesive and moisture, which caused a small amount of swelling in the boards.

Acetylated pine flake boards have also been shown to be resistant to attack in a marine environment (Johnson and Rowell 1988). Control flake boards were destroyed in 6 months to 1 year, mainly because of attack by Limnoria tri-punctata, while acetylated boards showed no attack after 2 years.

All laboratory tests for biological resistance conducted to this point show that acetylation is an effective means of reducing or eliminating attack by soft-, white-, and brown-rot fungi, tunneling bacteria and subterranean termites. Tests are presently under way on several lignocellulosic composites in outdoor environments.

Ultraviolet Resistance

There are other properties of lignocellulosic composites that can be improved by changing the basic chemistry of the furnish (Rowell 1984). Acetylation also improves the ultraviolet (UV) resistance of flake boards (Feist, Rowell, and Ellis [in press]). Table 4 shows the weight loss, erosion rate, and depth of penetration resulting from 800 h of accelerated weathering. Control specimens erode at about 0.12 $\mu\text{m}/\text{h}$ or about 0.02 %/h. The depth of the effects of weathering is about 200 μm into the wood surface. Acetylation reduces erosion by 50%. Table 5 shows the acetyl content of the outer 0.5 mm surface before and after accelerated weathering and of the remaining specimen after the surface had been removed. In all specimens, the acetyl content was reduced about 50%.

UV radiation does not remove all of the blocking acetyl group, so some stabilizing effect to photochemical degradation is still in effect. The loss of acetate is confined to the outer 0.5 mm because the remaining wood has the same acetyl content before and after accelerated weathering.

Table 6 shows that the surface layer is richer in glucose, xylose, and mannose and lower in lignin content after photochemical degradation resulting from accelerated weathering. This shows that both the cellulose and hemicelluloses are much more stable to photochemical degradation.

In outdoor tests, flake boards made from acetylated pine flakes are still light yellow in color while control boards have turned dark orange to light gray during this time.

TABLE 4. Weight Loss and Erosion of Modified Aspen After 800 Hours of Accelerated Weathering

Specimen	Before weathering		After weathering	
	Surface	Remainder	Surface	Remainder
	-----%			
Control	4.5	4.5	1.9	3.9
Acetylated	17.5	18.5	12.8	18.3

TABLE 5. Acetyl Analysis Before and After 800 Hours of Accelerated Weathering of Modified Aspen

Specimen	Weight loss	Erosion	Reduction in erosion ^a	Depth of penetration ^b of weathering
	%/hr	μ /hr	%	μ m
Control	0.0194	0.121	-	189-210
Acetylated	.0095	.059	51	84-105

^aCompared to control^bMeasured in cross section

TABLE 6. Chemical Analysis of Modified Aspen After 800 Hours of Accelerated Weathering

Specimen	Klason lignin	Soluble lignin	Sugars				
			Glucose	Xylose	Galactose	Arabinose	Mannose
----- % -----							
Control (before weathering)							
Surface	19.8	2.9	50.9	24.5	-	0.1	3.3
Remainder	20.5	2.7	49.8	23.3	-	-	4.2
(after weathering)							
Surface	1.9	1.6	82.2	10.1	-	0.5	1.6
Remainder	17.9	1.6	52.8	22.9	-	-	4.0
Acetylated							
Surface	4.7	3.2	56.4	17.1	-	-	1.6
Remainder	15.3	3.2	41.8	17.9	-	-	2.3

Pyrolysis Properties

Acetylation does not change the fire properties of lignocellulosic materials. In thermogravimetric analysis, acetylated and control pine sawdust pyrolyze at the same temperature and rate (Rowell et al. 1984). The heat of combustion and rate of oxygen consumption are also the same for control and acetylated specimens, showing that the acetyl group added to the cell wall has approximately the same carbon, hydrogen, and oxygen content as the cell wall polymers. Reactive fire retardants can be bonded to the cell wall hydroxyl groups. The effect would be an improvement in dimensional stability, and biological resistance as well as fire retardancy.

Property Enhanced Lignocellulosics

In recent advancements, technology has been developed to form acetylated high yield whole lignocellulosic fiber into flexible mats using either a non-woven needling technique or a thermoplastic fiber welding technique. These fiber mats can be impregnated with an adhesive (such as a phenolic resin) at the time the mat is formed and pressed into many different shapes. This fiber mat technology allows the formation of a final product all of uniform density directly from the wood fiber.

Products made thus far from this acetylation fiber technology show (1) high dimensional stability both in the thickness and lineal directions; (2) a high level of rot resistance; (3) a low degree of thermal expansion; (4) smooth surfaces that do not require further sanding; (5) a uniform density throughout the product wall; (6) no increase in toxicity of the wood; (7) high strength--both wet and dry; (8) a high degree of UV radiation stability; and, (9) no change in flammability.

Acetylated veneers can be pressed along with the acetylated fiber mat to yield veneer-faced fiber-backed products (Rowell et al. 1989). Other face materials can also be used, such as metals, plastics, glass, or synthetic fibers.

Preliminary economic analysis of producing acetylated fiber shows a cost of about \$0.15 to \$0.18/lb (which includes low raw fiber cost) versus \$0.05 to \$0.07/lb for the fiber. The cost of the acetylated fiber mat adds about \$0.05/lb. The cost of the acetylated fiber is roughly triple the price of unacetylated fiber. This technology directs this technology into value-added products where markets are driven by improved performance rather than cost alone. In considering cost, it must be remembered that it is possible to produce the final product from the fiber mat technology, so the price already includes part of the secondary manufacturing cost.

COMBINATION OF LIGNOCELLULOSICS WITH OTHER MATERIALS

Early work on wood fiber--synthetic fiber composites concentrated on laminate structures. For example, Michell, Vaughan, and Willis (1976) prepared laminates containing 67% by weight of cellulose fibers by hot-pressing paper sheets coated with low-density polyethylene. The flexural properties of the laminates at low relative humidities compared favorably with those of glass filled high-density polyethylene and of paper-phenolic resin laminates; however, at higher humidities the flexural properties for the cellulose fiber laminates were diminished.

Prud'homme (1977) also prepared polymer-paper laminates by hot-pressing a sandwich of paper between polymeric films. The polymer matrices were polymethacrylate and polyethylene. The mechanical properties of Whatman paper laminates were significantly higher than those predicted from the laws of mixtures. This

indicates that the polymer increases the strength of the fiber-to-fiber bonds. Prud'homme noticed, like Michell, Vaughan, and Willis (1977), that there was a considerable decline in properties of the laminates at high moisture levels.

Grafting of vinyl monomers to wood pulp has been used to create new composite materials with lignocellulosic fibers. A summary of the properties of grafted pulp and papers has been made by Phillips et al. (1972). The effect of the grafted polymer on the sheet properties is specific to each vinyl polymer-fiber substrate system. In many cases, simple admixing of the synthetic polymer with the wood pulp gave similar properties to the grafted product. However, both Young and Nguyen (1979) and Kokta, Daneault, and Sean (1986) found that grafting of pulps with polyacrylamide gave improved dry and wet strength values, probably because of the ability of polyacrylamide to form hydrogen bonds with cellulose. Young and Nguyen (1979) found that post-treated, hot-pressed grafted mechanical pulps, heated above the glass transition temperature of the grafted polymer, resulted in considerable increases in the dry and wet strength of the composite. Thus, to take advantage of the unique physical properties of graft copolymerized pulps, a high temperature treatment is probably necessary. Similar conclusions were reached by Kokta, Daneault, and Sean (1986) in a later study of grafted hardwood pulps in thermoplastic composites.

A wide variety of other natural fibers have been incorporated into polymer composites. Paramasivan and Kalam (1974) incorporated sisal fibers in an epoxy matrix and found that the tensile strength of the composites were 250-300 MN/m², which is about one-half that of a fiberglass-epoxy composite, but the specific strengths were roughly equivalent. Jute fiber has been extensively evaluated in composites because of the higher strength of this fiber. Jute has been incorporated into epoxy, polyester, epoxy/polyester, and phenol-formaldehyde resins. Up to 40% by weight of the jute has been incorporated into epoxy or polyester resins. Generally, strength improvement is realized with about a 25% by weight addition of the fiber. Exposure to moisture and temperature results in decreases in tensile strength of the composites. Sridhar et al. (1982) found that the moisture absorption of the composites can be reduced by coating the jute fibers with lignin and ethylene-diamine solutions.

Satyanarayana and coworkers in India (1981) evaluated the properties of composites of coir fibers (coconut husks) with polyester resins. Several types of molded articles were produced from the composites, such as helmets and mailboxes. The products held up well to weathering. However, it was noted that the incorporation of the coir fiber into the polyester resin adversely affected the mechanical properties of the polyester, roughly proportional to the amount of fiber in the matrix. It was suggested that this was due to poor compatibility and therefore limited bonding between the fiber and the resin. To improve compatibility, several different treatments were applied to the fibers. Copper coating of the fibers was found to considerably increase the tensile and flexural strength of the composites, while simple alkali treatment of the fibers resulted in a 40% increase in the mechanical properties of the polyester-fiber composite (Prasad, Pavithran, and Rohatgi 1983).

Wheat straw has also been tested as the fiber component in polyester resin composites. White and Ansell (1983) incorporated up to 50% straw fiber into polyester resins and prepared molded products. Small percentages of fiber improved the properties of the resin and mechanical pretreatment of the fiber gave better performance for the composite. The stiffness of the product was 2.5 times greater than that of pure polyester but one-half a softwood fiber or glass fiber reinforced plastic material. These investigators also recognized the compatibility problems associated with composite structures.

Currently, research is active on compounding of wood fibers with polyethylene to produce a composite for molding and extrusion. Selke, Yam, and Lai (1988) incorporated aspen fibers with recycled high density polyethylene (HDPE) using a co-rotating intermeshing twin-screw extruder. Mechanical properties and dimensional stability were studied as a function of fiber properties and process variables. Inadequate compounding was found to produce poor dispersion and poor wetting of the fibers, while excessive compounding caused severe fiber damage, both of which lead to reduced mechanical properties.

Kokta and coworkers in Canada (Kokta, Daneault, and Beshay 1986; Beshay, Kokta, and Daneault 1985; Raj et al. 1987) have also carried out extensive studies on incorporation of wood fibers into polyethylene composites. These investigators evaluated the use of chemithermomechanical pulp (CTMP) and modified CTMP mixed with polyethylene at 160°C and molded into shoulder type test specimens. It was found that the wood-filled composites gave decreased mechanical properties compared to unfilled polyethylene. To improve the poor interface between the wood fibers and polyethylene, several different chemical treatments of the wood fibers were explored. Surprisingly, a silane treated wood pulp did not give significant improvement of the mechanical properties of the composite. Incorporation of isocyanates was found to significantly enhance the adhesion at the fiber-matrix interface as demonstrated by the improvement in the mechanical properties (Raj et al. 1987). The stress and modulus increased 60% and 90%, respectively, in HDPE and LDPE composites depending on the type of isocyanate treatment.

Raj and Kokta (1988) also studied the mechanical properties of polyvinylchloride-wood fiber composites. In this work, polyvinylchloride (PVC) was reinforced/filled with CTMP, wood flour, and steam explosion pulp. The variables were evaluated as to the effect on the mechanical properties of the composites and included the weight fraction of filler, the addition of coupling agents, and the effect of fiber length. Composites from PVC filled with isocyanate-treated steam explosion pulp (30%) exhibited a 45% increase in tensile strength and an 11% increase in modulus compared with composites prepared with unmodified pulp fiber. A higher fiber aspect ratio resulted in an increase in tensile modulus. Impact strength generally decreased as the concentration of the fiber increased in the samples. Comparison of tensile properties of PVC-wood fiber, glass fiber, and mica composites demonstrated the advantage of wood fiber as a filler in terms of relative cost and performance.

Another fiber treatment evaluated by Kokta, Daneault, and Beshay (1986) was modification of the CTMP fibers through grafting with polyethylene by the xanthate method. This resulted in considerable improvement in the compatibility with unmodified polyethylene in the composite. The energy to break was improved by 100%, the modulus by 160%, and the stress by 133%, compared with a composite of unmodified CTMP and polyethylene. The grafted CTMP-polyethylene composites were superior to both mica and glass filled polyethylene in stress (Figure 7) and better than glass in modulus (Figure 8).

The cost comparisons performed in 1986 are also worth noting. Grafted CTMP fibers were estimated to cost \$250-\$300/ton; the price of mica was \$700/ton and glass \$2900/ton. The overall mechanical properties as well as the favorable price comparisons show good promise for use of grafted wood fibers as reinforcers in polyethylene composites. Kokta et al. are currently evaluating the use of modified sawdust as a filler (Kokta, Daneault, and Beshay 1986) which would drop the price to about \$100/ton.

In recent work in Japan, composites of polypropylene with refiner mechanical pulp (*Pinus radiata*) were prepared by Takase, Shiraishi, and Takahama (1988). The mixture was kneaded at 180°C at 50 rpm for 10 min. The kneaded samples were then

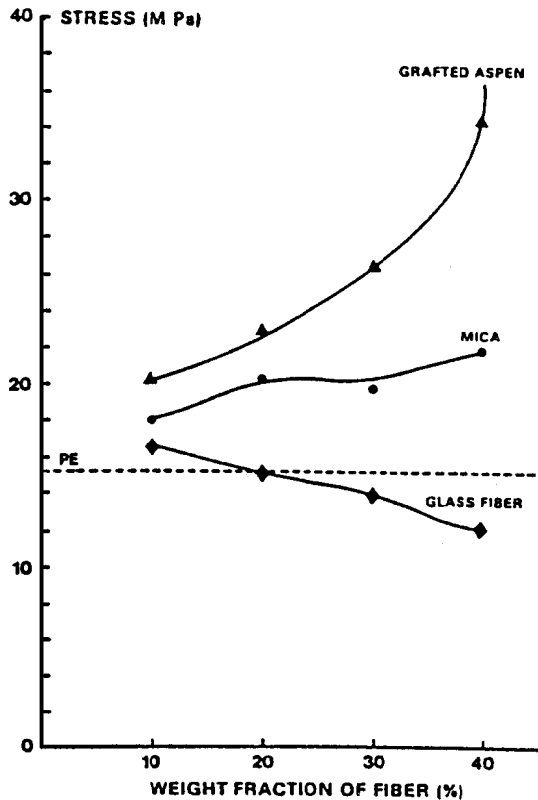


Figure 7. Dependence of stress on weight fraction of filler

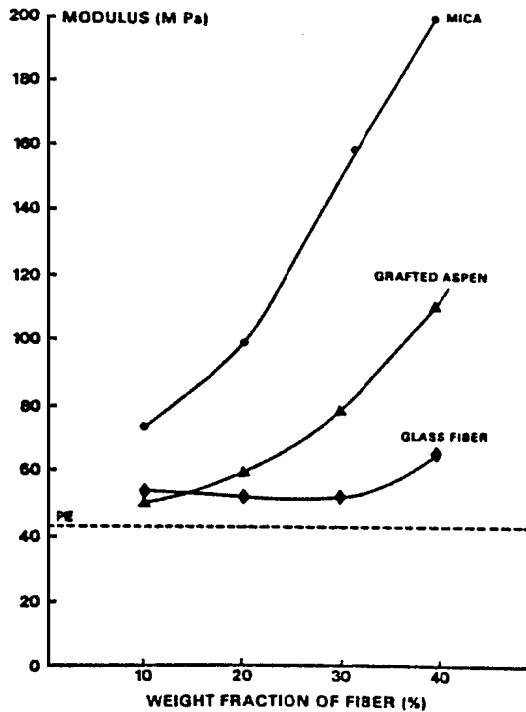


Figure 8. Dependence of modulus on weight fraction of filler

molded into films by hot-pressing. Strips taken from the samples were tested for tensile strength. To achieve good strength, it was necessary to modify the polypropylene to get good compatibility with wood pulp fiber. Therefore, composites of three kinds of chemically modified polypropylene were prepared by reaction with maleic anhydride (MAH), glycidylmethacrylate (GMA), and hydroxyethylmethacrylate (HEMA). The tensile strength of the composites was found to increase in order as follows: unmodified PP < HEMA-PP < GMA-PP < MAH-PP (MPP). It was concluded that the more reactive the modified PP with hydroxyl groups in the wood pulp, the better the tensile strength. It is believed that grafting takes place between MPP and wood pulp by esterification during the kneading process. A small amount of MPP (5%) was found to give good adhesion for a composite of refiner pulp (50%) and polypropylene (45%). Japanese investigators also produced a low density board, which consisted of wood pulp fibers, glass fibers and pulverized polyethylene manufactured by a wet forming process (Kawauchi, Murase, and Iida 1988). The board was molded by hot pressing or preheating and successive cold pressing. The pulp fiber provided good paper machine runability, while the glass fiber provided dimensional stability to the product. The fiber component was 10%-30% and the glass/wood fiber ratio was important to the final properties of the product. A minimum of 10% glass fiber was necessary for reasonable dimensional stability. As the polyethylene content was increased from 40%-90% of the product, the bending strength and the dimensional stability decreased. The final molded product exhibited good dimensional stability, water resistance, and impact strength. Applications for automobile interiors and furniture panels were proposed by the investigators.

Shiraishi and coworkers have had a 10 yr program on wood molding at Kyoto University in Japan (Shiraishi, Matsunaga, and Yokota 1979a,b; Shiraishi 1980a,b; Shiraishi et al 1982, 1983). Their approach to rendering wood to a thermoplastic material has been through chemical modification of wood meal. Generally, their work has emphasized esterification of wood. Thermoplasticity of esterified wood was found to depend on the acyl group, the method of preparation, and the degree of substitution. As shown in Table 7, as the size of the aliphatic group is increased, the melting temperature of the modified wood at 3 kg/cm² is decreased. Preparation of the esters by the trifluoroacetic acid (TFAA) method give lower melting points than by the chloride method. Acetylated wood samples prepared by the trifluoroacetic acid method clearly melted at 320°C under a pressure of 3 kg/cm² (Shiraishi et al. 1983). Wood samples acetylated by the chloride method or by a method using the acetic anhydride-pyridine or triethylamine-DMF system (25°C) did not undergo complete flow, but showed considerable thermoplasticity.

Although wood samples fully acetylated with acetic anhydride-acetic acid-sulfuric acid did not show clear melting, their partially saponified samples gave thermo-mechanical diagrams with a sharp drop corresponding to flow. Acetylated wood samples prepared with the acetic anhydride-acetic acid-perchloric acid system did not show clear melting either. Thermal properties of the acetylated wood were enhanced by mixed esterification with other acyl groups. That is, wood esters containing either propionyl or butyryl groups in addition to acetyl exhibited melttable properties, if the mixing ratio was appropriate (Shiraishi et al. 1983).

Shiraishi and coworkers (1982) also found that grafting can convert the unmelt-able, acetylated-propionylated wood sample into more readily melttable materials, and that the apparent melting temperature decreased with an increase in the amount of attached polymer. A further striking finding was that a very small degree of grafting of polystyrene was enough to cause a drastic change in the thermoplastic property of the esterified wood. Even graft products with total weight increases of less than 10%, which were prepared by irradiation to a total dose of less than 0.2 Mrad, behaved as thermally melttable materials. The effect

TABLE 7. Apparent Melting Temperature of Various Higher Aliphatic Acid Esters of Wood Prepared by the TFAA or the Chloride Method^a

Sample (acyl)	Melting temperature (°C)	
	TFAA	Chloride
Butyryl	300	310
Valeryl	235	305
Caproyl	250	260
Caprylyl	210	245
Capryl	205	290
Lauroyl	195	240
Myristyl	200	--
Palmityl	195	295
Stearoyl	--	220

^a Measured under a pressure of 3 kg/cm².

of grafted polystyrene was interpreted as effecting external plasticization to compensate for the limited internal plasticization obtained by acylation.

Matsuda and coworkers (Matsuda 1987; Matsuda, Veda, and Haja 1984; Matsuda and Veda 1985) also extensively investigated esterified woods and were able to circumvent the complicated solvent systems employed by Shiraishi's group at Kyoto University. Matsuda easily produced esterified wood with a solvent by simply heating wood meal with succinic anhydride for 3 h to temperatures greater than 60°C. The wood meal was readily molded at high temperatures (180°C) under pressure (570 kg/cm²) for 10 min. The moldability of various esterified woods decreased in the following order: succinic anhydride > maleic anhydride > phthalic anhydride.

Hon and Ou (1988) produced a moldable product by benzylation of wood powder. The degree of substitution was varied by alterations in the reaction alkalinity, temperature, and time. Sodium hydroxide concentrations greater than 25% were necessary to obtain high weight gain, presumably related to swelling of the lignocellulosic substrate. Different species showed variation in reaction rates. The thermoplasticized woods exhibited good melting properties and were readily moldable in bulk materials or extruded into films and sheets. A wide range of glass transition temperature, from 66°C-280°C, were observed for the benzylated wood, largely dependent on weight gain. The molded and extruded products exhibited acceptable mechanical strength for structural engineering applications.

FUTURE OPPORTUNITIES

Properties such as dimensional instability and susceptibility to degradation by biological organisms and ultraviolet radiation can be greatly improved by modification of lignocellulosic cell wall polymers. These modifications result in a furnish that can be converted into composites of any desired shape, density, and size, and provide an opportunity for a manufacturer to distinguish a product line based on quality, uniformity, and performance.

For some applications, the optimum composite may be a combination of materials to achieve the desired properties and performance. Property improved lignocellulosic fibers can be combined with materials such as metal, glass, plastic, natural polymers, and synthetic fiber to yield a new generation of composite materials. New composites will be developed that utilize the unique properties obtainable by combining many different materials. It is predicted that this trend will increase significantly in the future.

The key to a successful composite made with a lignocellulosic material and another material is to improve compatibility between the two. Composites have been made using lignocellulosic materials in combination with plastics, synthetic fibers, or glass, but in most cases the properties of the resulting composite were not as good as they could have been.

Research is under way in several laboratories in the world to make hygroscopic (polar) lignocellulosics more compatible with hydrophobic (nonpolar) materials. This is being done either by grafting onto the lignocellulosic material or adding a coupling agent to the mixture to make them more compatible.

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3. Cellulose Grafting: Past, Present and Future

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INTRODUCTION

Cellulosic graft copolymerization is of great interest with regard to the increased use of biobased materials. Indeed the graft copolymers are perhaps the clearest example of useful materials bringing together synthetic and natural polymers. These use biomass in all its many lignocellulosic varieties ranging from wood, grasses, and other plants to essentially pure celluloses such as cottons. Coupled with this aspect is the intrinsic biodegradability of the cellulosic component. The challenge of the Energy Conversion Utilization Program (ECUT) and similar programs is to expand and develop useful large scale and hi-tech smaller scale applications of such materials in an economic cost-effective manner. These objectives have not yet been achieved, and increased, well-programmed research is clearly and unequivocally needed. The desperate need to produce plastics, fibers, films, and other materials with biodegradability has given a continuation to such programs, which began with the need (now longer range) of replacing all or part of petroleum and natural gas feedstocks with renewable biomass. The need for a useful degree of photo and other types of degradability should also not be overlooked. This chapter will review the present status of such research, where the future emphasis should be stressed and the relative efforts currently under way in the United States compared with the overall international effort.

The author was privileged to be deeply involved in such research since July 1952, one year before the first conscious, deliberate, and successful synthesis of a cellulose graft copolymer was presented (Waltcher, Burroughs, and Jahn 1953). The preparation of this report was also based on presentations at major international meetings in 1988 (Tenth Cellulose Conference, Syracuse, N.Y., June; Cellucon '88, Kyoto, Japan, November; Nisshinbo Conference on Cellulose Utilization, Tokyo, Japan, December), and literature searches from January 1985 to December 1988 (including U.S. and foreign patents) to ensure adequate coverage of recent and present developments.

EARLIER RESEARCH - 1953-1984

Graft polymerization per se was first reported in 1946 (Carlin and Shakespeare). In 1943, however, vinyl and allyl esters of cellulose were prepared and copolymerized in experiments conducted with them. Although only crosslinked products resulted, certainly grafting must also have taken place (Ushakov 1943). Cellulose and its derivatives have been among the most popular as grafting substrates since 1952. Perceived perhaps as the first new type of cellulose derivatives, grafting was eagerly seized upon for research. By 1984, more than 1000 papers were published and patents granted on the subject. Grafting, which is often carried out heterogeneously, is an excellent method of modifying not only natural polymers but also polymers in fiber form. It was therefore even more attractive to carry out extensive work on the subject. This effort is still continuing. One excellent monograph (Hebeish and Guthrie 1981) and a number of rather thorough reviews (Krassig and Stannett 1965; Arthur 1970, 1985; Stannett and Hopfenberg 1971; Bhattacharya and Maldas 1984; Hon 1982; Samal, Sahoo, and Samataray 1986) on the subject have been published. These may be regarded as

key references. As with polymer science in general, research in cellulose grafts may be broken down into synthesis, characterization, properties, and applications.

Synthesis

Although ionic and condensation methods of grafting to cellulose have been briefly reported, the overwhelming majority of methods employed have been by free radical mechanisms. The general procedure is to generate free radicals on the cellulose molecule and then to introduce a vinyl or diene monomer. The macroradicals then initiate polymerization, forming graft copolymers. The various methods for carrying out this process via free radicals have been classified by Stannett and Hopfenberg (1971). Some notes and key references will be presented under similar headings.

Chain Transfer and Redox Methods

In these methods, a vinyl or diene monomer is polymerized in the presence of a cellulosic material. In the chain transfer method, the growing chain can then abstract hydrogen or another atom leaving behind the desired macroradical to initiate grafting. It is clear that the process is not too efficient and also leads to an equal amount of homopolymer. Nevertheless, it has a certain practicability and, in fact, similar methods are widely used industrially to produce heterogeneous grafts such as high-impact plastics. A useful development with this method is to introduce onto the cellulose groups that contain atoms that are readily extractable by free radicals. This was the first grafting method used, with halogens (Waltcher, Burroughs, and Jahn 1953). More recently, ethylene sulfide was reacted with cellulose to form mercaptan groups. These are very efficient chain-transfer agents. So far the growing chains from free radical polymerizations have been discussed as methods to generate the macroradicals. Radical transfer from the free radical catalysts themselves, although this is not strictly speaking chain transfer, can also be used with considerable success. To achieve this, the catalyst needs to be sorbed into the cellulose matrix itself. Potassium persulfate is a good example. A high concentration of the sulfate ion radicals are then formed, for instance, by heating persulfate, in the cellulose matrix itself. Abstraction can then compete successfully with initiation of homopolymer.

An even more efficient extension of the radical transfer approach is to sorb part of a two component redox system such as ferrous ions into cellulose. The monomer is then introduced with the second component such as hydrogen peroxide. Bridgeford has discussed such methods in detail (1962).

The xanthate method involves a redox system and has considerable promise for industrial exploitation. It was first reported by the Scott Paper Company in 1964 but still has not been commercialized. A number of pilot plants were built, however, and operated successfully. It is possible that the method will still be used on a large scale, but because it is tied to the xanthate rayon process, it has lost favor. However, xanthation can be carried out deliberately to low degrees of substitution. The xanthate group reacts with hydrogen peroxide to yield free radicals. The presence of ferric or ferrous ions may be necessary.

Direct Oxidation

A number of metallic ions have been used for the direct oxidation of cellulose to its macroradicals. The best known examples are ceric salts such as the sulfate and nitrate. The reaction is complex and not completely understood. It is known that the ceric ion forms a complex with cellulose hydroxyl groups in aqueous solution. The complex then dissociates in the presence of acids, into

a cellulose radical, a hydronium ion, and a cerous ion. The monomer is added either simultaneously or following pretreatment of the cellulose with a solution of the ceric salt. Initiation is rapid and efficient and in principle, leads to little homopolymer. In fact, some monomers themselves, notably acrylamide and acrylic acid, react with ceric ion to form radicals and homopolymers.

In addition to cerium (IV) salts, vanadium (V), manganese (III), cobalt (III), and chromium (VI) salts have been used. Other oxidizing agents such as permangates, bromates, and periodates also form radicals and initiate grafting. A considerable number of papers and patents have been published on the direct oxidation method and have been discussed and referenced in the various reviews (Hebeish and Guthrie 1981; Krassig and Stannett 1965; Arthur 1970, 1985; Stannett and Hopfenberg 1971; Bhattacharya and Maldas 1984; Hon 1982; Samal, Sahoo, and Samataray 1986).

Cellulose Initiators

Another general method of grafting to cellulose is to form chemically an initiator, such as a peroxide or hydroperoxide, on the macromolecule. This can then decompose into radicals and initiate graft copolymerization. If a reducing agent is used, the homopolymer formation can be largely eliminated. For example,



Peroxides can be formed by ozonization, a method that has been studied chiefly in the Soviet Union, or by radiation of the substrate in air or in hydrogen peroxide solution. Similar reactions have been carried out with cellulose nitrate, ethylcellulose, and benzylcellulose. There is a danger with these methods that extensive degradation may occur, which has not been assessed adequately in the literature.

In addition to peroxides, other initiating groups can be introduced into the cellulose molecule, such as peroxy esters. Diazonium salts have also been synthesized and used as grafting initiators. As with the hydroperoxides, the addition of a reducing agent such as ferrous ammonium sulfate essentially eliminates the formation of homopolymers. The use of diazonium salts has also been extensively studied in the Soviet Union.

Cellulosic Comonomers

Perhaps one of the most obvious ways to synthesize graft copolymers is to form allyl or vinyl cellulose derivatives and then copolymerize with a suitable vinyl or similar type of monomer. This was indeed probably the first, although not a conscious attempt at grafting (Ushakov 1943). Unfortunately, at that time there was no knowledge of grafting and the degrees of substitution were presumably too high and only crosslinked products were produced. With low degrees of substitution, however, and a proper choice of monomer reactivity ratios, graft polymers without much homopolymer could be prepared by this technique. To our best knowledge, there has been little progress or research on this approach. This was the earliest and perhaps one of the most obvious ways to form cellulose graft copolymers, i.e., to form vinyl or allyl cellulose derivatives. Among the derivatives prepared have been cellulose allyl esters, cellulose methacrylates, and cellulose allyl ethers, as well as cellulose crotonates and maleates. More recently vinyl groups were introduced with cellulose nitrate by reacting with allyl monocarbonate and hexamethylene diisocyanate. Grafting to these derivatives can be accomplished by direct free-radical vinyl copolymerization. It can readily be seen that if there are several unsaturated groups on each cellulose molecule, heavy crosslinking will rapidly result. The situation is in many ways comparable to the polymerization of unsaturated polyesters. With low degrees

of substitution, however, or properly balanced monomer reactivity ratios, graft copolymers that are essentially free from crosslinks can be prepared by this technique.

Radiation Methods

Both ultraviolet light and high-energy radiation have been used to initiate grafting to cellulose and its derivatives. The latter method has, however, been by far the most thoroughly studied. In fact, high-energy radiation grafting has probably been investigated in more detail than any other method. Because the chemistry of the process is relatively obscure, radiation initiation has been used in experiments designed to reveal details of the grafting process itself. No chemical reagents are used normally for the radiation-grafting techniques, so it is essential to make the substrate accessible to the monomer. In fact, with a suitable swelling agent only negligible degrees of grafting are possible. Three methods developed for radiation grafting have been successfully used for cellulose.

Peroxide Method. The cellulose substrate is irradiated in air to form peroxide derivatives, which can later be used for grafting as previously described. This method has been studied less with cellulose than with many other polymers; however, preirradiation grafting in air has been frequently used. Here it seems clear that a combination of peroxide and trapped-radical initiation is operating. The grafting yields have been increased by first soaking the cellulose. In the case of viscose rayon fibers, for example, the fibers are soaked in hydrogen peroxide solution.

Preirradiation Method. This method involves irradiating the cellulosic substrate, preferably in the absence of air, and subsequently contacting the irradiated material with the monomer and swelling agent. Both liquid and vapor-phase grafting has been used, and nearly every kind of cellulosic substrate has been studied. Again, a suitable swelling agent is essential for successful grafting. In general, it is better to irradiate dry to produce the maximum number of free radicals and then to admit the monomer and swelling agent together. In the case of vapor phase grafting, the swelling agent can also be in the form of vapor, such as water vapor. In addition to water vapor, methanol and acetic acid vapors were found to be effective promoters of the grafting process. In liquid-phase preirradiation grafting, these additives were also found to be effective. Generally, the same monomer-swelling agent systems were effective for both the mutual and the preirradiation techniques. These will be discussed further in the section on mutual grafting methods. With the trapped-radical method as opposed to the peroxide method of preirradiation grafting, very little homopolymer is produced. A disadvantage, however, is that the degradation of the cellulosic backbone is usually greater with the preirradiation method. This is particularly true when the grafting is carried out in the presence of air or oxygen. Less degradation is encountered with the mutual method of irradiation because of the protective action of the vinyl monomers present during the actual irradiation. Preirradiation is often carried out in air, and the combination of peroxides and grafted radicals that results is used to initiate the grafting reaction. In spite of the possibly deleterious effects of the concurrent degradation, the preirradiation method is very attractive economically. It has been used for pilot-plant studies of the grafting of styrene and other monomers to rayon.

Mutual Method. In this method, the cellulosic substrate is irradiated directly in contact with the monomer. The cellulosic material can be actually dissolved in the monomer or monomer-solvent mixture, or simply swollen. Either a vapor-phase or liquid-phase monomer can be used. The most usual technique, however, is the irradiation of the swollen cellulosic material in the liquid monomer or

monomer solution. It is clear that much homopolymer will also be generated by direct radiolysis of the monomer, the monomer-solvent, or the monomer-swelling agent mixture, but this can be successfully controlled. The cellulose acetate-styrene system has been studied in considerable detail, and methods have been developed for separating the homopolymers from true graft copolymers. It was apparent from the results of these studies that the degree of swelling of the cellulose substrate has a profound effect on both the yield of graft and the molecular weight of the grafted side chains.

Ultraviolet-Light Grafting

This method of direct radical formation and grafting has received comparatively little study, although the first experiments started as early as 1959. Cellulose derivatives have been investigated more than cellulose itself. The latter normally involves the addition of photosensitizers. In principle, the preirradiation and the mutual methods can be used. It is also clear that photochemical grafting can be useful for the surface modification of grafting. Hon has described some more recent experiments on ultraviolet grafting.

Other Methods of Free Radical Grafting

A number of methods have been developed to form graft (and block) cellulose copolymers. In general, they involve some mechanical breaking of the cellulosic chain such as mastication, vibratory milling, extrusion, or even ultrasonics and swelling techniques, in the presence of a vinyl monomer. Electrical discharge and plasma procedures have also been studied mainly for surface grafting.

The mechanical treatments together with grafting carried out simultaneously with certain pulping processes represent less well defined but in principle practical methods capable of being scaled up for industrial exploitation. Some key workers in this approach have been Young, Hon, and their coworkers (Young, Achmodi, and Barkalow 1985; Hon 1985).

Ionic Polymerization Methods

These were studied very little in the early period under review. Normally such methods involve the use of nonaqueous solvents, which are less attractive to the cellulose and allied industries than aqueous methods. Nevertheless, there were a number of approaches using anionic routes, which have been discussed rather fully in the key reviews. In general, shorter grafted side chains but rather higher degrees of substitution were obtained compared with free radical methods.

One very interesting cationic method has been described using boron trifluoride in nitrogen to form the cations, which were then reacted with isobutylene. Like the National Lead Process involving the Ziegler-Natta type of polymerization, it seems clear that little or no true grafting was obtained. However, in both cases the coated or encapsulated celluloses produced had excellent water resistance and other useful properties.

Ring Opening Methods

A number of reactive rings such as ethylene oxide, ethyleneimine, propiolactone, and ethylene and propylene sulfides have been reacted directly with cellulose following a suitable pretreatment. Generally, low-molecular-weight grafted side chains but relatively high degrees of substitution were obtained. Polyamides were successfully grafted to celluloses by reacting caprolactam with suitable cellulosic acid chlorides. Again, low DP grafts were obtained.

Condensation Methods

Methods of this type have received little study compared with the grafting of vinyl polymers. The most extensive studies have been made in the Soviet Union. A distinction can be made between adding an already formed polymer to a reactive functional group of the cellulosic material and using reactive groups on the cellulosic molecule to initiate condensation or ring-opening polymerization.

An example of preliminary work on the former method is the reaction of a low-molecular-weight poly(ethylene adipate) acid chloride with cellulose, using either a solvent-exchange or interfacial polymerization technique. A somewhat analogous study involved the reaction of telomers of poly(acrylic acid) having chlorine end groups with β -aminoethylcellulose. Only a small proportion of telomer became attached. Alkali cellulose also did not react extensively with the poly(acrylic acid) telomer.

Direct polycondensation grafting of aminoanthric acid chloride to cellulose and its derivatives has also been achieved. A low degree of substitution and molecular weight was found. An interfacial approach with cellulose xanthate gave similar results. In principle, the direct addition of a polymer with suitable functional groups could be attractive. However, the accessibility of one polymer to another except in solution and reactivity considerations has negated this method of synthesis.

In conclusion, it can be said that studies of methods of synthesis of cellulosic graft copolymers (mainly free radical in nature) dominated work through 1983. Comparatively little attention has been given to characterization, properties, and applications of such products.

Characterization of the Graft Copolymers

In addition to developing methods of grafting and examining their properties, it is necessary to characterize as closely as possible the pure grafts and to estimate the extent and molecular nature of the resulting graft. In some respects, cellulosic graft copolymers are rather easy to investigate because the solubilities of the two homopolymers and the grafts themselves are often quite different from one another. Furthermore, the cellulosic backbone can be destroyed by acid hydrolysis, and the molecular weight and other properties of the isolated side chains can be determined. This has made research on the structure of cellulosic grafts attractive not only for the grafts themselves but as models for grafting in general.

Whether the grafting reaction takes place in solution or within a swollen, insoluble cellulosic substrate, such as film or fiber, it seems inevitable that some homopolymers are present together with the graft and unreacted cellulose. In rather early work, the grafting of acrylamide to cellulose film was carried out by an ultraviolet-light technique. It was found that the graft copolymer, polyacrylamide, and the cellulose itself were all soluble in cuprammonium hydroxide. On acidifying, however, only the ungrafted cellulose and the graft copolymer precipitated. By weighing the precipitate, the amount of the grafting could be measured, but the amount of ungrafted cellulose could not be determined. This simple procedure was later applied to a number of other grafting methods. It was seen that each method of grafting gave different efficiencies of grafting and that the preirradiation technique was the most efficient.

With heterogeneous grafting to semicrystalline polymers, especially fibers such as cotton, the morphology and orientation can be changed. This, in turn, can greatly change the properties and will depend on the grafting method used and the choice of monomers and swelling agents and other additives. This aspect of

the structure-property relationships of cellulose graft copolymers has been studied in depth, particularly by Arthur and his coworkers (1985).

Properties

The properties of cellulosic materials--pulp and paper, textiles, and regenerated cellulose--and cellulose derivatives can be dramatically changed by graft copolymerization. Although data concerning properties and applications are scant in comparison with data concerning synthesis and physicochemical characterization, a sufficient technology has emerged to permit the beginning of a rational tailoring of properties in cellulose via graft copolymerization.

Graft copolymerization has resulted in improvements in a wide variety of properties, including tensile strength; resistance to microbial degradation, abrasion, and acids; dye receptivity; wet strength of paper; and, adhesion. In addition, an entirely new spectrum of properties can be imparted, such as changing pulp, paper, cellophane, and fibers into ion-exchange materials including membranes by the controlled grafting of anion- and/or cation-exchange groups onto the cellulose. It has been demonstrated that moisture regain in cellulose and cellulose acetate can be reduced by controlled radiation-induced grafting of styrene. The water uptake can also be increased by grafting hydrophilic monomers including the synthesis of the so-called super water absorbing celluloses. It has also been demonstrated that the compatibility of dissimilar polymers can be markedly improved by adding small quantities of cellulosic graft copolymers "constructed" from the two incompatible backbones. The latter observation has considerable implications regarding the formation of stable and useful "polymer alloys," or "polyblends."

Cellulose itself is relatively inexpensive but cellulose derivatives are often expensive. Property improvements and alterations in properties achieved by grafting will usually be accompanied by an increase in cost. This immediately suggests that applications of some such end products will tend to be more specialized than those of the starting material.

It is recognized that the grafting process results in the formation not only of true covalently bonded graft copolymers but also of residual homopolymers of the substrate polymer and newly formed homopolymers corresponding in the chemical repeat unit to the grafted side chains. Many workers have scrupulously attempted to synthesize, isolate, and subsequently characterize the pure graft, whereas others, though acknowledging the presence of residual homopolymers, have proceeded to evaluate the end properties of the graft contaminated by the homopolymer impurities. Although a definitive study on the effect of homopolymer content in the properties of graft mixtures has not been made, it is cautioned that graft copolymers containing unextracted homopolymer will have properties that differ from those of a pure graft.

Many studies have been reported on the properties of grafted cellulose fibers--mainly on cotton and rayon, but also on jute and other natural fibers (Mohanty 1987, 1988). Such studies have included water moisture regain, resistance to soil burial, dyeability, mechanical, and thermal properties. Properties of grafted pulp and paper have also been extensively studied. All the property studies are well reported in the references and need not be repeated here. The subject of biodegradability will be discussed separately.

Applications

A considerable number of applications have been explored. In general, researchers have concentrated on synthesis, and to a lesser extent, characterization and properties rather than on developing suitable applications. For example, in the

excellent monograph on cellulosic graft copolymers by Hebeish and Guthrie (1981), only 16 pages out of 345 are devoted to applications. Nevertheless, there were 141 references through 1979, and there have been many more since then. In more recent years, increased attention has been given to this area. The subject of applications will be discussed in the present and future sections of this review. In general, there are applications to wood itself (Czikovsky 1968), to textile fibers (Arthur 1985), to pulp and paper (Phillips et al. 1972), and to membranes. There are also a number of miscellaneous applications. Some key references are given plus the reviews.

PRESENT SITUATION - 1985-1988

About 450 papers and patents were published in this 4-year period. Of these, about 350 were concerned with grafting to cellulose itself. As with the earlier years, synthesis and research on mechanisms and variations on established methods have been the major thrust. Recently, the effect of reaction variables on the composition of the grafts and the amounts of both homopolymers has been emphasized more than in earlier years. This research has inevitably included characterization and property studies. Together, however, the three areas of synthesis, characterization, and properties make up only about 62% of the published work. The remaining 38% was concerned with papers and patents discussing possible applications. This is in marked contrast to the earlier years when synthesis probably made up at least 75% of the total effort. The contrast was even greater in 1988.

In the area of synthesis, research into various features of the conventional free radical methods has continued. The effects of changes in the reaction variables on the yields, homopolymers and molecular weights of the side chains have been emphasized. The ceric ion and xanthate initiation techniques have dominated chemical methods. High energy radiation and photochemical grafting continued to be active areas of research. Studies on the latter method have increased markedly and it was by far the subject of the greatest number of publications on synthesis. This may be linked to a number of hi-tech types of imaging processes apparently under development.

There has also been a sharp increase in ionic grafting. Anionic grafting which links preformed living polymers to substituted celluloses has been explored in depth by Narayan and his coworkers (Biermann, Chung, and Narayan 1987; Narayan and Shay 1986). Their methods have the advantage of being able to achieve controlled degrees of substitution, molecular weights, and molecular weight distributions of the side chains. This is in marked contrast to the free radical techniques developed to date. At the moment, the need for rather dry solvent systems and cellulose derivative substrates make anionic grafting economically unattractive on a large scale except for specialized products. These anionic polymerization products could, however, be high value added materials. More importantly, at the moment, they have great value for exploring property-structure relationships of the grafts of well-defined structure. There have also been a few papers using cationic methods. Although it is difficult to envisage it being practical on a large scale, the cationic approach widens the range of side chain monomers available. One method, however, uses tosylated bleached kraft pulp to initiate the cationic grafting of 2-methyl oxazoline and is potentially more attractive for industrial exploitation (Cheradame, Ambo, and Gandini 1986).

Characterization methods have continued along similar lines to those developed in the earlier years. Somewhat more attention has been given, however, to improving the acid hydrolysis of the grafts to isolate the synthetic side chains for their characterization.

The property studies reported during the past few years have also continued along the lines developed during the previous years. But more emphasis has been given to water sorption, retention, and diffusion. There were also a few isolated studies on polymer blends used with compatibilizing grafts, on acid resistance, and on thermal and photo degradation. Various biological, bioactive, enzyme immobilization, antimicrobial, cell attachment, and related studies have been emphasized much more than in earlier years. Curiously, no studies of the biodegradability per se of the grafts were reported, in spite of its obvious importance.

Research into possible applications of cellulosic graft copolymers has been very active in the past 4 years' particularly in Japan. Most activity has centered on grafted cellulosic membranes for gas and other separation processes, including alcohol from water. Nearly 27% of the reports were on membranes and ion exchange materials. Applications based on water sorption were emphasized, particularly for super sorbing materials for uses such as sanitary napkins, tampons, and diapers, and for soil stabilization and other agricultural uses. Miscellaneous applications such as for bandages and other medical uses were also important. Equally emphasized were applications for the immobilization of enzymes, antimicrobials, and for hemostatic and biomaterial related uses including controlled drug release and biocompatibility.

Applications of the graft copolymers in the coatings industry have been investigated to a considerable degree to increase adhesion and to impart other useful properties. Applications in plastics were studied, including the use of grafts for compatibilizing blends, such as molding compositions and composites. Newer areas have been developed particularly in uses for diazoprinting, copying, and recording applications--some based on photosensitive materials; these were chiefly Japanese developments. Water soluble grafts and uses for the cosmetic industry have been reported. Applications to the textile and pulp and paper industries continued to be explored, but along similar lines to those developed in previous years including waste water treatment.

Minor activities included the use of cellulosic grafts for adhesives, catalyst support systems, latex coagulating agents, oil absorbers, and foaming agents.

FUTURE RESEARCH NEEDS

There is a strong need for research in a number of areas, which include the following:

1. Much more work on the biodegradability of cellulosic graft copolymers is needed. The extraordinary fact is that in the past four years (through 1988) not a single paper concerning this problem appears to have been published¹. Even across all the years of research into cellulosic graft copolymers, the enzymatic and microbial degradability of such copolymers have been studied to only a small extent. With available landfill capacity rapidly diminishing, the disposal of over 160 million tons of waste annually in the United States is emerging as a key environmental problem of the future. More than half the municipal solid waste stream is made

¹ Editor's note: The past year (1988-1989) has seen a number of attempts to measure the biodegradability of graft copolymers and composite materials. However, standard methods of analyses are not yet available, making the definition and assessment of the biodegradability of materials an area of intensive and extensive research (see chapter 8).

of paper-based and synthetic plastic materials, which biodegrade quite slowly in the environment. The use of grafting and other chemical means to enhance the degradability of this fraction of waste will allow faster "recycling" of the landfill volume and also serve to reduce urban litter.

The grafting of short chain moieties to cellulose to alter the rate of both the light-induced degradability and the biodegradability of the material is one such possibility. Sensitized photooxidation of cellulose has been extensively discussed in the literature. With judicious choice of functional groups, light-sensitive centers and even photooxidation catalysts might be incorporated into the cellulose structure. An allied field of interest is the chemical modification of the structure of cellulose itself to increase its degradability in the environment.

Plastics are practically non-biodegradable in the soil. Grafting a significant fraction of the relatively more biodegradable cellulose derivatives to the synthetic polymer is likely to enhance its biodegradability. Rapid microbial degradation of the grafted cellulose component will in turn generate a network of voids in the plastic matrix, weakening the structure and at least causing brittleness, which will decrease the harm the plastic material may cause to the environment.

Cellulose-synthetic polymer grafting reactions have been studied by Narayan and others (see Chapter 7). Further research based on these pioneering studies may extend these techniques to achieve high levels of grafting in slurry (or solid reactant) systems in a continuous, fast process.

2. With all the work on methods of grafting, the effect of the lignin content on grafting yields and the characteristics and properties of the resulting grafts have been little studied. Most of the research has concentrated on pure forms of cellulose and its derivatives. More work is needed on this subject. The direct use of whole wood, steam-exploded woods, and high-yield pulps as grafting substrates is clearly of considerable industrial importance. Some such studies are under way by Glasser and others.

Some work has been reported, particularly by Kokta and coworkers (see Chapter 2), on the effects of lignin on grafting. Coupled with this aspect, the possibility of grafting during the pulping process or on whole wood should be further explored. An important example is the work of Young, Rowell and colleagues.

3. Work on the super water-absorbing cellulose grafts needs to be expanded. Methods of reducing the effects of salts on the water sorbency and retention need to be explored, but an initial finding of Salamone et al. (1985) is a good start on the problem. The biodegradability of the "supersorbents" is also important and should lead to a new emphasis on cellulose and starch based sorbents compared with the overwhelming use of the purely synthetic polymers currently on the market.
4. Finally, cost-effectiveness of the resulting products are all-important. A reasonable economic analysis of the various methods of grafting with various substrates is needed. Even if somewhat tentative and speculative, such a study would be most helpful for the further development of grafting technology. The three subjects summarized above represent examples that could benefit from an economic analysis.

INTERNATIONAL ASPECTS

An analysis of the research reported during the past four years, up to December 1988, showed that 28 countries had published work on cellulose grafting. Japan led the way with 50 papers and patents followed by the Soviet Union with 40 entries and the United States with 33 published works. Other active countries are Egypt, Czechoslovakia, and Canada, but these all have less than 15 entries each.

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