

POLYMER SCIENCE AND TECHNOLOGY
Volume 17

POLYMER APPLICATIONS OF RENEWABLE-RESOURCE MATERIALS

Edited by

Charles E. Carraher, Jr.

*Wright State University
Dayton, Ohio*

and

L. H. Sperling

*Lehigh University
Bethlehem, Pennsylvania*

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**POLYMER
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POLYMER SCIENCE AND TECHNOLOGY

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This book is dedicated to our wives
LOYALEA CARRAHER and BONNIE SPERLING

and to our respective natural products
CHARLES, SHAWN, MICHELLE, ERIN, HEATHER,
COLLEEN, and SHANNON CARRAHER
and
REISA and SHERI SPERLING

PREFACE

For there is hope of a tree,
If it be cut down,
That it will sprout again
And that the tender branch
Thereof will not cease.

Job XIV (7)

Mankind has been blessed with a multitude of resources. In the beginning he utilized almost solely replenishable items such as vegetation and animal protein, for both nourishment and shelter. Gradually, such metals as copper and iron were developed and replaced wood as a material of construction. Cement and glass, although more plentiful than other minerals, also replaced the use of growing substances. Coal and oil became the primary sources of heat and power.

Closer to the focus of this book, petroleum products began to replace the vegetable oils, tannin, wool, cotton, leather, silk, rubber, etc. in a host of applications. Surely, it was argued, the new materials did the job better and cheaper. What they didn't say is that soon we would run out of oil. In any case, research on growing natural products, now called renewable resources, slowed, and these industries sought only to maintain their status quo.

The 20th Century saw an unprecedented emphasis and dependence on nonrenewable resources as energy sources (petroleum, coal, uranium) and the fabric of technology (drugs, clothing, shelter, tires, computer parts). The predawn of the 21st Century brings a realization that a cyclic shift back towards the use of renewable resources for technological application is in order.

As with most ancient areas, technology has preceded science in the application of natural products. The area is fertile for the development of a science allowing us not only to understand why past applications worked, but to spark new ventures. The fulfillment of these new opportunities will require both extension from synthetic polymer and small molecule science as well as known science particularly developed for natural products

The purpose of this book is to present a balance between the technology and the science of renewable resources, emphasizing polymer applications. The book illustrates both the breadth of applications available, and the depth of science possible. Naturally, those areas where research activity is the greatest are emphasized.

Many of the chapters included in the book are based on material presented at the August, 1981 American Chemical Society meeting in New York. However, several chapters were contributed by people around the world who could not participate in the ACS meeting. Indeed, every continent except Antarctica is represented between these covers!

A number of authors sent us reviews of their particular sub-fields, rather than original research papers. Thus, the scope of the book was significantly broadened.

The book is divided into five divisions. The first section contains two reviews of the general area of renewable resource materials considering today's setting, historical treatment of renewable resources including specific governmental actions, problems and breadth of natural resource materials along with potential availability and a description of future research required.

The second section contains six chapters emphasizing saccharides and polysaccharides with natural feed stocks derived from sucrose, dextran, cellulose, cotton, xylan, chitin, starch, and bagasse for potential applications as commercial insulation, topical medical applications, fire retardant articles, durable roofing panels, and other building materials.

Section three contains six chapters dealing with the noncellulosic components of plant life including tall oil, wood and gum rosins, lignan, bark extracts, tannin, wood flour, and rice hull flour for use in the preparation of composites, resins, adhesives, and fillers. Filler properties are described in some detail. Substitutes for phenol-formaldehyde resins are described as well as the generation of the industrially important trimellitic anhydride from natural sources. A problem in the rubber elasticity of gutta percha networks is discussed.

Five chapters covering oils and lacquers comprise section four. The structural changes accounting for the extraordinary durability of Japanese lacquer are described along with expanded applications. A series of four chapters emphasize the past, present and future aspects of natural oils. Polymerized vernonia, linseed and tung oils are described as replacements for synthetic polymers. Coatings, adhesive and bulk applications are discussed.

The final section contains six chapters emphasizing the use of proteinaceous materials as leather, wool, polypeptides, and collagen. The chemical modification of leather through the use of radiation, and poly(γ -methyl-L-glutamate) membranes is described as is the modification of collagen, wool, and leather by chemical means.

Throughout the book, attention is given to structure-property relationships particularly with regard to glass transition temperatures, modulus, tensile strength, impact resistance, and toughness. The majority of the data are given with ASTM cited for ready comparison of results with other materials.

The editors wish to take this opportunity to thank each of the authors for their splendid contributions. We also wish to thank Dr. R. Kleiman from the North Central Region USDA for sending to us a sample of tung oil fruits. Lastly, we want to thank the secretaries from around the world and our own laboratories who labored to translate many scientific and engineering ideas into well-typed book chapters.

Charles E. Carraher, Jr.
L.H. Sperling

January, 1982

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RENEWABLE RESOURCE MONOMERS AND POLYMERS

L. H. Sperling* and Charles E. Carraher, Jr.**

*Lehigh University, Materials Research Center #32
Bethlehem, PA 18015

**Wright State University, Department of Chemistry
Dayton, OH 45435

SETTING

Until the beginning of the nineteenth century, it was generally accepted that organic compounds could only be produced in living organisms. A special "vital force" was believed essential for the synthesis of complex organic compounds. Friedrich Wohler, in 1828, heated the inorganic substance ammonium cyanate to form the well known organic compound urea. This discovery is considered by many to mark the beginning of modern synthetic organic chemistry. The development of large quantities of inexpensive "black gold", petroleum technology (including cosmetics, drugs, and plastics), allowed the emergence of a society based on synthetic materials. These two "happenings" coupled to minimize the impact of natural, renewable resources on our current society. With the exceptions of the traditional materials leather, cellulose, and wool, and to a small extent silk and natural rubber, modern society is devoid of large scale uses of renewable resource polymers.

The recognition that the supply of petroleum and coal is limited, and increasing costs, has pointed towards the need to emphasize natural renewable materials as replacements or substitutes for product materials now derived from petroleum and coal. However, going beyond the set idea of replacement or substitute materials, renewable resources have valuable, sometimes different properties of their own. So the natural materials, while "substituting" for the synthetic materials (which themselves substituted for the natural materials in the 1940's and 1950's), will have corresponding, rather than identical behavior profiles. Further, it must be also emphasized that the natural product research developments of the 1920-1940 era bears repeating according to the standards of the

1980's. Already, scientists and engineers are finding that materials impossible even to consider before World War II, may now be synthesized by modern techniques.

In this short review we wish to draw attention to the following: a) availability of renewable resources, b) (potential and real) problems associated with the use of renewable resources, c) variability of actual structure of most natural macromolecules with source and d) complexity of structure for many natural products. Regarding the latter, while the structure of many natural materials is complex it is knowable and in many cases already known.

PROBLEMS

Natural feedstocks must serve many human purposes. Select carbohydrates as raw materials are valuable due to their actual or potential nutritional value. For example, already operating are protein plants utilizing rapidly reproducible bacteria which metabolize cellulose wastes. Thus, bacteria are added to a nutrient broth emphasizing cellulose; the bacteria feed on the mixture, converting it to more protein rich bacteria; the bacteria are harvested and used as a protein feed meal. However, there is potentially available enough renewable carbohydrates to serve both the food and the polymer needs, and research into the modification of carbohydrates must continue at a heightened pitch.

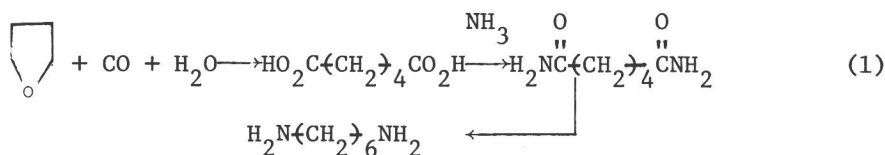
However, we must meet the problem concerning the ability to produce industrial quantities of a number of interesting renewable materials and provide needed foodstocks. These difficulties are valid for some natural materials, but for many others a judicious choice of growing location and conditions will permit industrial quantities of the natural material to be raised without competition. The sea, for example, is a large cauldron of nutrients thus far singularly untouched; hydroponics can be considered based on the availability of necessary additives; multitiered growing areas may eventually be utilized to make fuller use of both growing area and sunlight.

Most of the potential natural feedstocks are actually complex products of varying composition, changing with source, pretreatment, etc. Further, the chemistry of these complex materials is not well known relative to petrochemical materials. While variation in processing will be necessarily dependent on the exact properties of a given material from a specified source, such problems are solvable. Indeed, the petroleum industry has faced and overcome this problem since the raw petroleum material derived from one source is unlike that derived from another source, differing, for example, in aromatic content. While defined structure-property relationships are desirable, they are not necessary in developing a useful product. Thus

the polymer industry grew up, becoming a giant by the 1950's, before some scientists even accepted the concept of the macromolecule. For others, there exists sufficient chemical and physical data on analogous compounds, which may be transferred, allowing the use of such materials as feedstocks.

Finally, many potential renewable feedstocks are currently summarily destroyed or utilized in a noneconomical manner. Thus leaves and other plantstocks are "ritualistically" burned each fall. A number of these seemingly useless natural materials have already been utilized as feedstock sources and more must be included.

Furfural, obtained by the steam-acid digestion of corn cobs, bagasse, rice hulls, and oat hulls, acts as the precursor to hexamethylene diamine and adipic acid, the latter two utilized to form nylon-66.



Sebacic acid is produced from the dry distillation of castor oil (triglyceride of ricinoleic acid) with sodium hydroxide, etc. Several natural oils, mostly triglycerides, have long been in use commercially. Thus, linseed oil and tung oil have formed the basis for paints; drying is actually a polymerization through the double bonds to make a crosslinked network.

A partly synthetic analog of the oil-based paints are the alkyd resins. The alkyds are esters formed from alcohols and acids through transesterification reactions. A direct source of unsaturated fatty acids is frequently used, for example, tall oil from the sulfate pulping process.

A word about the pricing problem must be said. Before the oil crisis of 1973-1974, petroleum products were frankly cheaper than their renewable resource counterparts. While all prices have inflated by a factor of two since then, petroleum oil and oil product prices have increased faster. Thus, while the renewable resource product is still uneconomical in many cases, modern industry must prepare now for a price inversion which may take place during the 1980's.

Potential Renewable Materials

When plant or animal tissues are extracted with a nonpolar solvent a portion of the material typically dissolves. The components of this soluble fraction are called lipids and includes fatty

acids, triacylglycerols, waxes, terpenes, prostaglandins and steroids. The insoluble portion contains the more polar plant and animal components and crosslinked materials including carbohydrates, lignin, proteins and nucleic acids.

There are numerous natural materials and almost as many lists and ways to partition such materials. Table 1 contains one such listing along with suitable general references. Table 2 is a listing for a number of natural products as a function of general availability. Brief descriptions follow of the more abundant natural product groupings. Each has already shown itself viable in today's industrial market place but with a potential for exceeding present use.

LIGNIN

Lignin is a major polymeric component of woody tissue. During synthesis of plant cell-walls, polysaccharides (principally cellulose) are first deposited, with lignin filling the spaces between the polysaccharides fibers, cementing them together. Except for water transport, the lignified fiber appears to be relatively inactive in the metabolic role of the plant, acting largely as a support. Lignin constitutes about 25% of wood and is therefore an abundant renewable resource material currently underused.

Lignin's structure is complex, varying with source and within a given source. Phenol, aliphatic alcohol, ether, ketone and aldehyde functional groups are contained within each lignin and are available for classical synthetic organic chemistry reactions. The structure of lignin as a three dimensional network is shown in Figure 1. Note its general relationship to phenol-formaldehyde-type resins.

The vast majority of lignin, along with associated carbohydrates, is permitted to rot, returning to the biosphere. The majority of lignin removed during wood processing is burned as a fuel which serves to drive the pulping process. Some is converted to lignin sulphonates and used as additives in oil-well drilling-muds, adhesives, industrial cleaners, leather tanning, road binders, cement products and in the production of vanillin. However, better processing knowledge is needed, particularly a know-how of recovering linear high molecular weight lignins before large-scale polymer uses can be instituted.

NATURAL POLYISOPRENES

While the best known polymer in this category is natural rubber, a cis-polyisoprene originating from the tree *Hevea brasiliensis*,

Table 1. Renewable, Natural Material Groupings

Group	General Reference(s)
Illustrative Subgroups	
Alkaloids	1,2
Pyrrolidine, Pyridine, Pyrrolizidine, Tropane	
Quinolizidine, Isoquinoline, Piperidine, Indole	
Quinoline, Quinazoline, Acridone, Steroidal,	
Terpenoid	
Amino Acids	2,3
Carbohydrates	4-9
Simple (glucose, sucrose, fructose, lactose,	
galactose)	
Complex (starch, cellulose, glycogen)	
Drying Oils and Alkyd Resins	5,10-12
Linseed, Cottonseed, Castor, Tung, Soybean,	
Oiticica, Perilla, Menhaden, Sardine, Corn,	
Safflower, Vernonia	
Fossil resins-Amber, Kauri, Congo	
Oleoresins-Damar, Ester Gum	
Fungus, Bacteria and Their Metabolites	2
Heme, Bile and Chlorophylls	2
Lignins	5,9,13,14
Lipids	2,15
Simple (Glycerol Esters, Cholesterol Esters)	
Phosphoglycerides	
Sphingolipids (Mucolipids, Sulfatide,	
Sphingomyelin, cerebroside)	
Complex (Lipoproteins, Proteolipids,	
Phosphatidopeptides)	
Phenolic Plant Products	2
Phenols, Resorcinols, Anthraquinones,	
Naphthoquinones, Hydrangenol, Stilbenes,	
Coumarins	
Polyisoprenes	5,9,16-20

(continued)