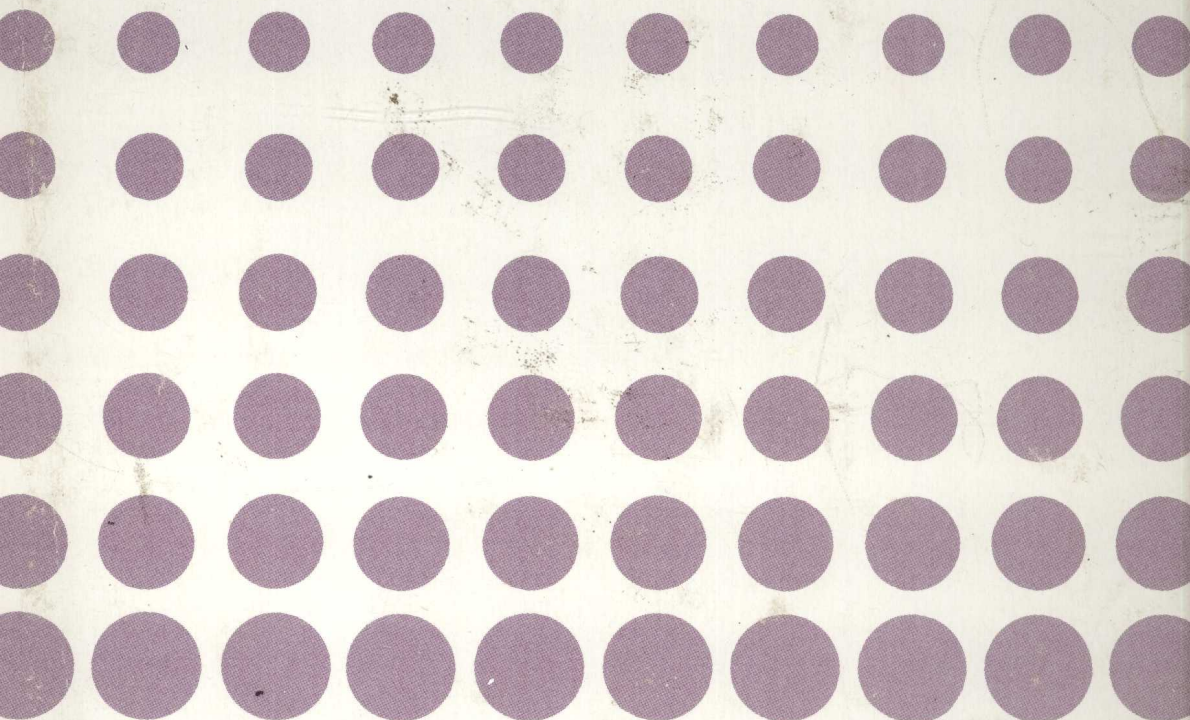


RENEWABLE-RESOURCE MATERIALS

New Polymer Sources



Edited by
Charles E. Carraher, Jr.
and
L. H. Sperling

可回收-资源材料：新聚合物资源

RENEWABLE-RESOURCE MATERIALS

New Polymer Sources

Edited by

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PREFACE

I will plant in the wilderness the cedar
the acacia-tree
and the myrtle
and the oil-tree;
I will set in the desert the cypress,
the plane-tree
and the larch together;
That they may see, and know
and consider
and understand together,
That the hand of the Lord hath done this,...

Isaiah, 41:19 and 20 (first portion)

The need to improve our utilization of the Earth's natural resources is every one's business, from every country. This book presents papers from all parts of the world on the subject of making new or improved polymers from renewable resources, be they plastics, elastomers, fibers, coatings, or adhesives. In important ways, this book constitutes part II of an edited work published by Plenum Press in 1983, "Polymer Applications of Renewable-Resource Materials." To that extent, about half of the authors are the same. However, their papers present an update of their research three years later. The other half of the authors are entirely new. Both of these books grew out of symposia sponsored by the Polymeric Materials: Science and Engineering Division of the American Chemical Society. The papers for the present book are based loosely on a symposium held at the Miami Beach meeting in April, 1985.

Unfortunately, interest in polymers from renewable resources fluctuates with the price and availability of petroleum oil. At the time of writing this preface, the price is low, and appears to be headed lower still. While this is a good thing for the economics of the world, it tends to hide the fact that the long-term shortage of oil is very real, and sooner or later will come back to haunt all of us. However, research on all subjects, including that of natural products, yields best results when developed systematically, with regular support. Let us hope that both low oil prices and high interest in renewable resources may both be true in the future! In any case, all of us must be prepared for state of the art utilization of our natural resources, and the time to begin is now.

The present book is divided into six sections. First, there is a review paper that describes the state of the art in a number of areas of polymers from renewable resources. This chapter tends

to emphasize those aspects of the field not covered by the original papers that follow. The original papers are grouped into sections on saccharides and polysaccharides, graft copolymers from polysaccharides, oils and triglyceride oils, proteins and leather, and rubber, lignin, and tannin. While each of the above general categories is well represented in the world of commerce, many natural products exist for which little or no commercial products exist. One such group of materials are spider webs. For this reason, the editors included a special section in their review paper on this topic in the hope that it may arouse some interest in the mind of some enterprising soul, and to encourage us to revisit some of nature's solutions with the intent of "borrowing" important but yet unused concepts.

The editors wish to take this opportunity to thank all of the authors for their splendid contributions. Since secretaries from the four corners of the globe contributed to the production of this volume, it is difficult to single out one individual to thank. However, they are remembered here.

January, 1986

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

CONTENTS

SECTION ONE: REVIEW

Modern Polymers From Natural Products.....	3
L. H. Sperling and C. E. Carraher, Jr.	

SECTION TWO: SACCHARIDES AND POLYSACCHARIDES

Natural Vegetable Fibers: A Status Report.....	29
M. B. Amin, A. G. Maadhah and A. M. Usmani	
Polysaccharides From Lichens: ¹³ C-NMR Studies on (1-6)-Beta-D-Glucan (Pustulan).....	41
Arthur J. Stipanovic, P. J. Giammatteo and S. B. Robie	
Sugar Containing Polymers Derived From Organostannes and Bis-(Cyclopentadienyl)titanium Dichloride.....	53
Yoshinobu Naoshima, Charles E. Carraher, Jr., Satomi Hirono, Tamara S. Bekele, and Phillip D. Mykytiuk	
Synthesis of Titanium, Zirconium and Hafnium Modified Polysaccharides.....	63
Yoshinobu Naoshima, Charles E. Carraher, Jr. and Koichi Matsumoto	
Newer Applications of Bagasse.....	75
M. B. Amin, A. G. Maadhah, and A. M. Usmani	

SECTION THREE: GRAFT POLYSACCHARIDES

Use of Grafted Wood Fibers in Thermoplastic Composites V. Polystyrene.....	85
Bohuslav V. Kokta, Famakan Dembélé and Claude Daneault	
The Xanthate Method of Grafting: XI. Grafting of Methylmethacrylate on Hardwood Pulp.....	97
Claude Daneault and Bohuslav V. Kokta	
Oil Absorbency of Graft Copolymers From Softwood Pulp.....	107
George F. Fanta, Robert C. Burr, and William M. Doane	

Chemically Modified Carbohydrates as Highly Efficient Regio- and Stereoselective Catalysts for Hydrogenation.....	115
Ernst Bayer, Wilhelm Schumann, and Kurt E. Geckeler	
Dextran Hemopolymers as Model Systems for Biologically Active Proteins.....	127
Ernst Bayer, Martin Keck, and Kurt E. Geckeler	
Graft Copolymerization onto Cellulose Acetate and Wood Using Anionic Polymerization.....	137
Ramani Narayan and Margaret Shay	
Chemical Modification of Wood: Reaction with Thioacetic Acid and Its Effect on Physical and Mechanical Properties and Biological Resistance.....	147
Satish Kumar and Kamini Kohli	

SECTION FOUR: OILS

Behavior of Water in Oriental Lacquers.....	163
J. Kumanotani, K. Inoue, M. Achiwa, and L. W. Chen	
Simultaneous Interpenetrating Networks Based on Vernonia Oil Polyesters and Polystyrene. II. A Comparison of the Reactivities of Vernonia Oil and Castor Oil Toward the Formation of Polyesters.....	177
A. M. Fernandez, J. A. Manson, and L. H. Sperling	
Polymers From Renewable Resources: Crosslinking and Thermal Behavior.....	187
Sukumar Maiti, Sabyasachi Sinha Ray and Achintya K. Kundu	

SECTION FIVE: PROTEINS AND LEATHER

The Optimization of the Mechanical Properties of Reinforced Collagen Films.....	207
Richard O. Mohring and Ferdinand Rodriguez	
Titanium-Containing Poly-Alpha-Amino Acids From Dipeptides.....	225
Charles E. Carraher, Jr., Louis G. Tisinger and William H. Tisinger	
Viscoelasticity of Calf Hide Impregnated with Radiation- Polymerized Polyhydroxyethyl Methacrylate.....	235
Paul L. Kronick, Bohdan Artymyshyn, Peter R. Buechler, and William Wise	

Radiation Polymerized Graft Copolymers for Leather.....	251
Peter R. Buechler, Paul L. Kronick and Frank Scholnick	

SECTION SIX: RUBBER, LIGNIN, AND TANNIN

Chemical Modification of Natural Rubber as a Route to Renewable Resource Elastomers.....	261
Ian R. Gelling	
Short Fibre-Rubber Composites.....	275
Dipak K. Setua	
Kraft Lignins: A New Perspective.....	287
Theodore M. Garver, Jr., and Simo Sarkanen	
Review of the Synthesis, Characterization, and Testing of Graft Copolymers of Lignin.....	305
John J. Meister	
Natural Tannins for Cold-Setting Wood Adhesives.....	323
Antonio Pizzi	
INDEX	329

SECTION I - REVIEW

MODERN POLYMERS FROM NATURAL PRODUCTS

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INTRODUCTION

Modern man was not "born yesterday". At the time man evolved, the only materials about him were inorganics such as rocks, water, and air, and what are called today the "renewable resources" or "natural products". Amazingly, most of these materials are in service still today. These include wool, cotton, animal glue, and natural rubber. This last was used by the American Indians long before Columbus. Other natural products served as important monomers, such as linseed oil; and an early crosslinker for animal skins was tannin, forming leather. More recently, natural product polymers were chemically modified, as in the esterification of cellulose.

A surprising number of 20th century polymers, however, also have their origins in natural products. Sebacic acid is commercially derived from castor oil; it forms the "10" component of nylon 6,10. Alkyd paints are based significantly on triglyceride oils. The point is that even today, natural products are in wide use. While petrochemicals have certainly gotten the lion's share of publicity, renewable resources have continued to be grown, harvested, and used.

Three years ago, the subject of renewable resources was reviewed by the authors (1), to which the reader is referred for many of the basic aspects of renewable resources. The present review will update reference (1) with emphasis on subject matter not extensively covered earlier. Also, since many of the chapters that follow also touch on the topics to be reviewed, some effort was made to avoid repetition.

The emphasis of the first review centered largely on the chemical nature of components derived from natural sources. The present review continues this but also describes the use of raw, chemical mixtures that can give products with unique combinations of properties arising from the product's structural nature.

Before proceeding with specific subject matter, other reviews must be mentioned (2-16). While most of these references are in the chemical literature and are well-known to polymer scientists, reference (6) is in the biological literature. However, it contains a wealth of information about renewable resources, especially their mechanical behavior.

FUNCTIONAL GROUPS

An important theme for natural products chemistry is the general similarity between the kind of reactions possible with synthetic feedstock and natural feedstock. For smaller natural chemicals, this similarity is especially close while for biomacromolecules this similarity may be moderated by intra- and intermolecular effects and steric factors.

Most of the common functional groups employed by the synthetic chemists are present in natural products. Table I contains a listing of a number of these functional groups and an example or two illustrating natural products possessing these functional groups.

Nature also offers a number of ring systems that can be exploited in ring-opening polymerizations (Table II).

TREES

The ultimate source of all life and all natural products is the sun. Major beneficiaries of the sun and the associated conversion of carbon dioxide and water into saccharides (photosynthesis) are trees. Trees are woody, perennial plants that contain a stem that remains from year to year. As a tree grows from a seed, it develops separate, but interrelated parts--roots, stem and crown. The major photosynthesis centers are the leaves. The stem or trunk contains, from outside to center, the bark, wood and pith, wood being the major constituent. The root beneath the earth's surface, which acts as an anchor and draws water and mineral nutrients from surrounding soil for transport to the remainder of the tree.

About one-third of the earth's area, almost 10 billion acres, are occupied by trees. Research in forestry has allowed the development of trees that grow five to ten feet yearly and which can be harvested for lumber and related products within 10 to 20 years. The total wood reserve is about four trillion cubic feet with only about 1% harvested yearly.

Major commercial uses of cut trees are as lumber, pulpwood, veneer logs, posts, pilings, and chemical wood (including particle board).

Wood consists largely of cellulose and lignin, both polymers. The wood cells are arranged longitudinally in the stem, shaped as elongated tubes, actually hollow fibers, giving a tough, flexible but light-weight fiber. Cells vary in exact structure and form depending mainly on the designated function of the particular cell (Figure 1).

Cells are of two major kinds. Food storage cells, parenchyma cells, are short lived, remain alive for about one year. Prosenchyma cells act as support and conduction and usually lose their protoplasm in the year they are formed. The major portion of wood consists of these prosenchyma and parenchyma cells.

Table I. Functional Groups Present In Nature.

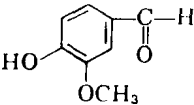
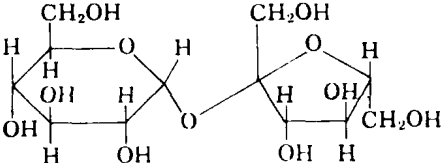
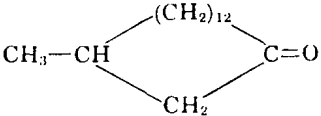
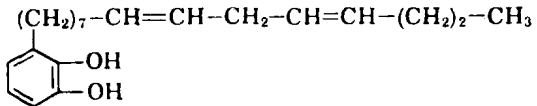
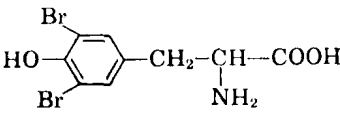
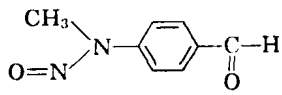
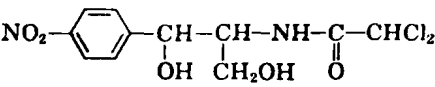
<u>Name</u>	<u>Structure</u>
Vanillin	
Sucrose	
Muscone	
<i>n</i> -Butyl mercaptan	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$
Poison Ivy Urushiol	
Diallyl disulfide	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH}=\text{CH}_2$
3,5-Dibromotyrosine	
<i>p</i> -Methylnitrosoaminobenzaldehyde	
Chloramphenicol (Chloromycetin)	

Table I. Functional Groups Present In Nature (cont.)

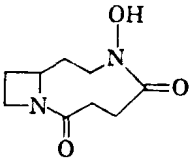
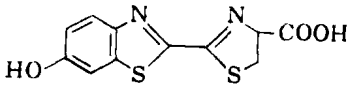
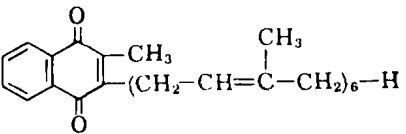
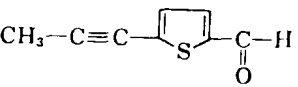
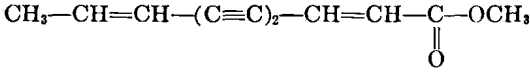
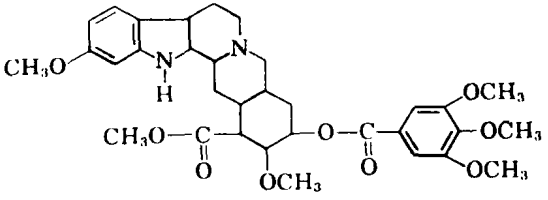
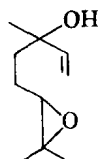
<u>Name</u>	<u>Structure</u>
Norcardamine	
Firefly Luciferin	
Vitamin K ₂	
Junipal	
Matricaria ester	
Reserpine	

Table II. Selected Small and Strained Heteroatomic Natural Occuring Rings.

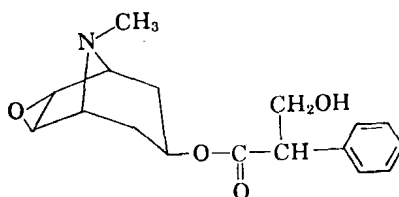
Name

Structure

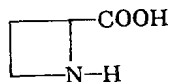
Linalool epoxide



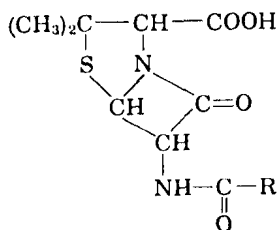
Scopolamine



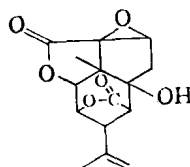
Azetidine-2-carboxylic acid



Penicillin
R=benzyl,
p-hydroxybenzyl,
n-amyl,
1-pent-2-enyl



Picrotoxin n



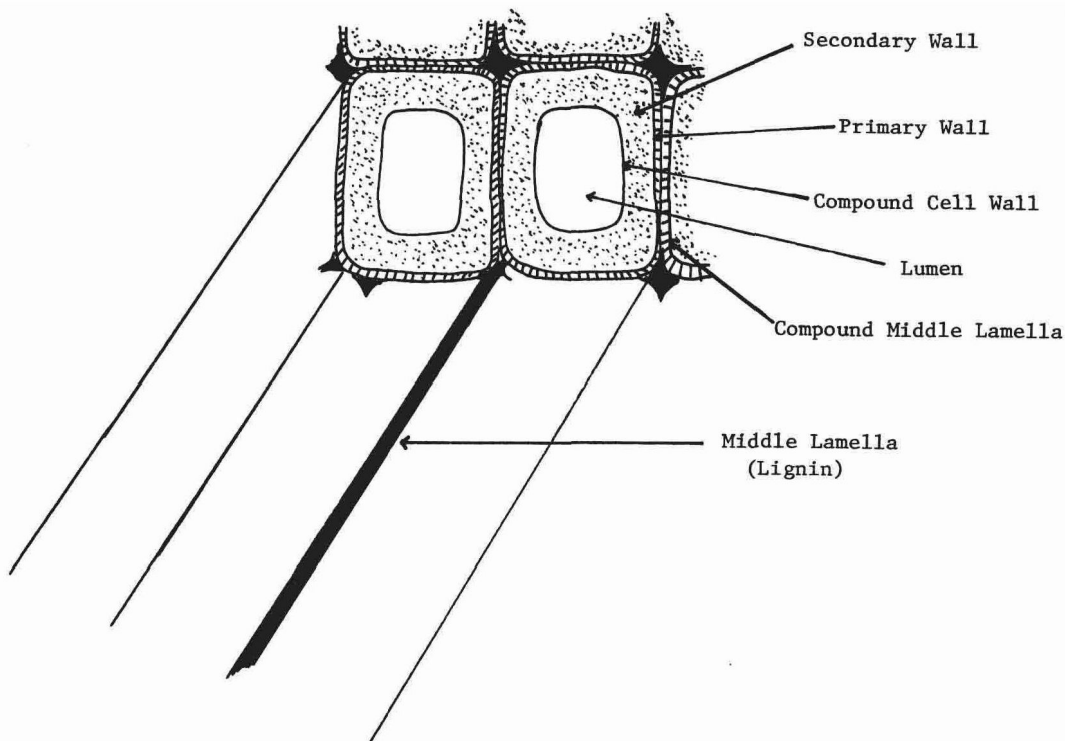


Figure 1. Cross-section of wood, illustrating cellular structure.

Chemically, trees are truly composites containing a variety of chemicals, but are largely macromolecular (excepting water). The general chemical nature of wood is described in Table III. The cell walls are composed of mainly lignin and polysaccharides and in turn the polysaccharides are mainly cellulose (glucose basic unit) and a variety of hemicelluloses derived from pentoses (xylose and arabinose) and hexoses (glucose, mannose and galactose). Acetic acid, uronic acids, and methoxyuronic acids also are derived from the hydrolysis of the hemicelluloses. The extent of each component varies as to the tree age, particular climatical history, and location and type of wood cell. Table IV contains a brief listing of typical values for selected trees. Thus, trees are a ready source of removable natural products, both in itself and in the nature of its components. Much research is continuing in taking advantage of this bountiful, complex natural resource. Wood has been modified utilizing free radical, redox, ionic and radiation methods introducing a wide variety of monomeric and polymeric materials. Composites, grafts, IPN's, etc. have been formed. Still much remains to be done to take advantage of secondary, tertiary and quaternary structures offered by wood.

Just as the chemical composition of wood is quite variable, so also are its physical properties. Even so, general values can be given and found in Table V. Wood is relatively light, varying from about 0.3 g/cc for western red cedar to 0.75 g/cc for osage orange for common USA trees. Because of its highly porous nature, wood possesses a large surface area for chemical modification. Surface areas may reach to 100 to 300 m²/gram.

Table III. Chemical Composition of Wood by Type of Material.

Saccharides	-- cellulose hemicellulose pectins starch arabinoglactans
Acids	-- fatty acids
Alcohols	-- eliphatic alcohols sterols
Proteins	
Phenols	-- lignin phlobaphenes tannins
Terpenes	-- terpene terpenoids resin acids
Inorganic salts and oxides	
Alkaloids	

This large surface area also allows for ready swelling by acid and base solutions allowing the breakage of hydrogen bonding, reshaping, and subsequent neutralization and reformation of hydrogen bonds locking in the new structure. It must be noted that most of these physical properties vary with the direction with which the value is obtained, i.e., along or against the grain, etc.

Shrinkage is a problem for wood products but this can be largely controlled through surface treatment. Dry wood is an excellent electrical and thermal insulator with an extremely low coefficient of linear expansion. Wood also has a high tensile strength comparable to cotton fibers and greater than many metals. Thus, wood itself offers a number of properties that may be usefully incorporated in a modified product.

Plain old wood constitutes the basic material for building homes, making furniture, and even garden stakes, etc. According to Jeronimidis (17), wood has a cellular composite structure with four levels of organization, molecular, fibrillar, cellular, and macroscopic. Wood contains about 40-50% cellulose by dry weight. The primary organization of the cellulose is in the form of microfibrils. These are wound around the cells, or tracheids, that make up the larger part of wood in a complex helical fashion, see Figure 1 (18). The S_2 wall makes up to 80% of the total cell wall area. Because of its low microfibrillar angle, it is the major load bearing component in wood.

Jeronimidis (17) points out that cellulose in wood has a very high theoretical modulus, 250 GPa. Because of amorphous material, lignin, and pores, the actual modulus of wood is nearer 10 GPa, see Figure 2 (17). However, this value remains higher than that of polystyrene at room temperature, 3 GPa, pores and all. However, wood can be improved upon significantly. Wood impregnated with poly(methyl methacrylate) has sufficient environmental resistance to be used for knife handles. Such compositions survive many years of daily washing in hot, soapy water!