Cellulose

Structure, Accessibility and Reactivity

Polymer Monographs
Volume 11

Hans A. Krässig

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STRUCTURE, ACCESSIBILITY AND REACTIVITY

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Volume 11
CELLULOSE—Structure, Accessibility and Reactivity
HANS A. KRÄSSIG

The publisher will accept continuation orders which may be cancelled at any time and which provide for automatic billing and shipping of each title in the series upon publication. Please write for details.

I dedicate this book to my dear wife Gerti – I could never have written it without her understanding and encouragement – and in grateful remembrance to
Professor Dr. Dr. h. c. mult. Hermann Staudinger†
and Professor Dr. Dr. h. c. mult. Hermann F. Mark†

Series Editor's Preface

"If a book is worth reading, it is worth buying." (John Ruskin)

Two trends, which are not especially favourable to a series such as this, have become noticeable in recent years; viz., the reluctance of the polymer industry to invest in the development of entirely new homopolymers, and the increasing costs of scientific book production. Enquiry and feedback revealed, perhaps surprisingly, but nonetheless emphatically, a genuine need for authoritative up-to-date treatments on several existing polymers. Consequently, most volumes are devoted to one specified polymer. The interests of an industry or an institution usually dictate that research and/or development be conducted over an extended period of time on the particular polymer of relevance. It is hoped that individuals will be able to select their specific volume from **Polymer Monographs** and thus be freed from the inconvenient and unfair obligation to pick sections out of the commoner, larger treatises devoted to classes of polymer.

With regard to the topics themselves, proven useful application is considered a *sine quo non*, and hence macromolecules of purely academic interest are excluded from this series. An innovation is the inclusion of biopolymers and their synthetic prototypes. Since polymer science has now become truly interdisciplinary in scope, the monographs are addressed to a broad spectrum of potential readers.

These volumes aim to present the maximum of current information in the minimum of space. Fortunately the authors, who are all pre-eminent in their respective fields, have not only complied with this difficult and stringent condition, but have succeeded in doing so without sacrificing readability. I trust these volumes will prove useful and welcome comments and suggestions for future topics.

MALCOLM B. HUGLIN

Preface

Until relatively recently the degree of order defined by "crystallinity" and the "crystalline orientation" was considered the main structural factor influencing the accessibility and chemical reactivity of cellulose.

The existence of defined morphological elements, namely elementary fibrils, setting up the fiber structure, their aggregation to micro- and macrofibrils, and their arrangement determined by morphological growth in the cell wall of native cellulosic substrates or in the fibrillar network of regenerated cellulose fibers as factors determining accessibility and reactivity have too often been ignored.

In this book, an attempt is made to review, combine and discuss, on the basis of established and widely accepted concepts of the fine structure and morphology of cellulose fiber substrates, today's views on the interrelations between these concepts and the accessibility for and reactivity of cellulose with swelling agents and reactants. A special effort has been made to keep the expositions understandable to students and postgraduates entering the field of cellulose fiber science and technology, while still being an interesting and informative reference work to cellulose experts.

The chapters deal with: (1) fibrous cellulose as a year-for-year renewable raw material source; (2) the molecular characteristics of the cellulose molecules, their intra- and intermolecular interactions, their association to fibrillar assemblies, and the organization of the latter to growth determined lamellae in native cellulose fibers or to fibrillar networks in regenerated cellulosic fibers; (3) methods for determining molecular, fine structure and morphology characteristics of cellulosic fiber substrates; (4) the interrelations between fiber structure and physico-mechanical properties; and (5) the effect of morphology and structure on accessibility and reactivity.

In the discussions, particular attention is drawn to the following morphological and structural parameters influencing the accessibility and reactivity of cellulosic fiber substrates:

(i) the swelling restriction effect of the lamellar growth layers in native cellulosic fibers, especially the outer cell wall layer of cotton or wood fibers.

(ii) the importance of capillaries, voids and interfibrillar interstices as a

basic condition of the accessibility of reactants to reactive fibrillar surfaces of the fiber substrate.

(iii) the availability of the maximum internal fibrillar surface, which determines the number of hydroxyls initially available for chemical interactions.

(iv) the effect of the participation of hydroxyls in intra- and interplanar hydrogen bonds which hold together the crystal lattice layers in chemical reactions, thus determining the proportion in which primary and secondary hydroxyls on accessible fibrillar surfaces are initially available for interactions.

In the citation of literature references supporting the text, findings and conclusions of earlier researchers are also acknowledged in order to highlight corresponding results and to provide a broader understanding of current knowledge. In this context, it is shown that too often novel theories and hypotheses are developed without prior attempts to analyse the results and conclusions for their possible accordance with earlier findings and concepts.

In writing this book I have reported and summarized results of my own lifelong research in the field of cellulose fiber science and technology and presented my own concepts and views on the problems of the interrelations of cellulose fiber morphology and structure with the physical and mechanical properties of the fibers and the accessibility and reactivity of cellulose fibers in interactions with swelling media and reactants. Incorporating results of my own work into this book has also been for me a welcome opportunity to again judge—and in a few cases to correct—the results of my own work, and to critically appraise conclusions drawn earlier, in the much broader context of a comprehensive discussion of the interrelations of cellulose structure with accessibility and reactivity.

HANS A. KRÄSSIG

Acknowledgements

A book on such an extensive subject as the interrelations between the morphology and structure of cellulose fiber substrates and their accessibility for and reactivity with chemical agents could never be the result of the work of one person alone. The roots of this book go back to my association as postgraduate assistant with Professor Dr. Dr. h. c. mult. Herman Staudinger at Freiburg University, who aroused and promoted my interest in cellulose science. When I left Freiburg in 1956 and joined ICR-Industrial Cellulose Research Limited in Hawkesbury, Ontario, the research subsidiary of the International Paper Company, Professor Dr. Dr. h. c. mult. Herman F. Mark, a consultant to ICR, promoted and deepened this interest and accompanied me throughout my industrial career in pulp, textile and fiber processing companies.

The impetus to write this book came some years ago from Professor Dr. Malcolm B. Huglin of the University of Salford. I am very indebted to him for his constant encouragement, his proofreading of the manuscript and his valuable advice and suggestions. Individual parts of the manuscript have been read by several friends and colleagues. The suggestions and critical comments of Erich Treiber (Stockholm), Professor Dr. Josef Schurz (University of Graz), and Professor Dr. Burkhard Philipp (Institut für Polymerenchemie, Teltow-Seehof) have been of great help. Special thanks are also due to Professor Dr. B. Philipp, Professor Dr. J. Schurz, Professor Dr. J. Lenz (Lenzing AG), Professor Dr. R. Bonart (University of Regensburg), Professor Dr. B. Wunderlich (University of Tennessee), Professor Dr. H. Friebolin (University of Heidelberg) and Dr. A. Nissan (Scarsdale, New York) for providing or permitting the use of original material and illustrations for publication in this book. I owe sincere thanks to the management of Lenzing Ab for the assistance granted to me by their library services.

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Contents

1. INTRODUCTION

Before considering the relationship between the structure of cellulose substrates and their physical and chemical properties it seems appropriate to examine the comparative position of cellulose in our basic raw material resources.

Through the studies of the "Club of Rome", whose results were published in 1972 under the title *Limits to Growth*[1], dealing with the finite availability of raw material supplies on earth, controversial as their conclusions may be, and through the shocking experience of the various oil crises during the last decades, the awareness for a more rational and economical use of mineral and fossil reserves has risen. The energy requirements for all private, commercial and industrial activities of mankind depend to a large and often underestimated extent on the disposability of these resources found in the outer and relatively easily accessible crust of the earth. These mineral and fossil reserves, however, were deposited and formed over billions of years and are, therefore, limited in stock.

On the other hand, the earth is blessed with an almost inexhaustible reservoir of plant (phytogenic) and animal life, which is reproduced in abundance year after year with the help of solar energy. Besides proteins, fats and oils, saccharides and polysaccharides – especially cellulose and starch – are quantitatively the most important product group of the photoinitiated biosyntheses.

It, therefore, seems worthwhile to compare the annual yield of plant and animal products with the non – recurring reserves of the mineral and fossil raw materials, as done in Table 1.[2]

The comparison made in Table 1 demonstrates the importance of annually renewable biomass products. Their total annual volume is of the same order of magnitude as the finite reserves of the most important mineral and fossil resources created by nature over billions of years and under tectonic conditions no longer existing.

Under the legitimate assumption that biomass consists of about 40% polysaccharides, the annual production output of the photoinitiated biosyntheses of cellulose and starch amounts to approximately 70 billion tonnes, an enormously high yield when compared with the finite world reserves of the major non-recurrent raw materials, such as petroleum, natural gas, coal, metals and ores.

Table 1 Comparison of yearly created biomass and estimated world reserves in mineral and fossil raw materials (in tonnes).

Biomass, yearly photosynthesis yield:		170×10^9
Utilized by or in form of:		
Felling of trees (only major countries)	0.80×10^9	
- use for paper	0.15×10^9	
- use in chemical applications	0.007×10^9	
Cereals (all kinds)	1.45×10^9	
Natural fibers (all kinds)	0.022×10^9	
Seed products (incl. oil seeds)	0.18×10^9	
- vegetable oils	0.05×10^9	
Potatoes	0.37×10^9	
Sugar cane and sugar beets	0.58×10^9	
Fruits (all kinds)	0.28×10^9	
Foodstuffs (of animal origin)	0.28×10^9	
Animal feed	0.80×10^9	
Total ascertainable utilization	4.969×10^9 (approx. 2.9%)	
Mineral and fossil raw materials, estimated world reserves:		
Petroleum	150×10^9	
Natural gas	75×10^9	
Mineral coal	300×10^9	
Brown coal	250×10^9	
Pig iron and crude steel (from the iron ore reserves)	75×10^9	
Aluminium	2×10^9	
Copper ores	1×10^9	

Furthermore, it is interesting to note that only about 3% of these annually renewed natural raw materials are being used. productively. This clearly illustrates the immense and scarely utilized resource—a resource that nature offers us year after year.

The main source of the cellulose used in industries producing paper, board, fibers, films, or cellulose derivatives is forests and, to a lesser extent, cotton plantations. In wood and in many plants cellulose is actually part of an ingeniously constructed fiber-reinforced composite in which the long, stiff cellulose chain molecules constituting the plant reticulum material are held together and protected by hydrophobic lignin. Every tree produces, on average, approximately 13 to 14 grams of cellulose per day.

In order to isolate cellulose from wood for industrial applications, the wood composite must be broken up by "pulping" processes using acidic or alkaline sulfite liquors for hydrolytic removal of the lignin. The yields in wood pulp dif-

fer widely—between 50 and 80% for pulps suitable for paper and board manufacture and 30 to 40% based on wood for chemically utilized "dissolving" pulps. So far the lignin, resins, pectins and hemicelluloses removed during the pulping procedure are used only to a minor extent. In most cases wood pulp manufacturers concentrate the waste pulping liquors to concentrations of about 5% solids content and use the dissolved organic matter as fuel to produce steam and electric power, simultaneously recovering the inorganic pulping chemicals (sodium, magnesium, ammonia and sulfur dioxide). These recovery processes have practically solved the long-standing environmental problems of the wood pulp industry, made the pulping processes more economical, and made pulping and paper making widely energy self-sufficient. However, in the long run, burning waste liquor may not be the only use for lignin and other wood constituents dissolved in the pulping process.

Making more effective and more versatile use of the natural raw material "wood" and its valuable constituents represents one of the most challenging tasks of the future. With today's methods of wood harvesting, only approximately 70% of the biomass contained in the trees is being used. The stump, the bark, most of the side branches, and the leaves or needles are being disposed of and left in the forests to rot. In the recent past forestry experts have been promoting the concept of so-called "whole tree utilization". In North America novel techniques of wood harvesting have been developed in which the central rootstock and the thicker side branches are also used in the pulp, paper or particle board industry. At the same time efforts are being intensified to isolate more valuable organic constituents from bark, leaves or needles by the use of novel extraction, separation and chemical modification techniques.

The efforts for more rational and effective utilization of the wood resources also include intensive development work for better, more selective and environmentally improved pulping methods. In today's commonly used sulfite and sulfate wood pulping processes between 30 to 70% of the wood substance is being dissolved and widely lost. One of the leading American pulping experts[3] has defined the ultimate development goal for the pulp and paper industry in such a way that it should be our endeavor in the near future to develop pulping processes giving 90% yield on wood pulps with 90% whiteness having the same good paper forming ability and the same long-term brightness stability as our present sulfate paper pulps. Worldwide efforts to further develop high-yield pulping procedures, such as mechanical, thermo-mechanical, chemo-mechanical and alkali-oxygen pulping have this as their ultimate target.

Similar ambitious endeavors to develop higher yield dissolving pulps for the manufacture of cellulose fibers or films and cellulose derivatives require, in addition to a modified pulping procedures, the solution of the problems arising from the often inferior influence of the by-products, namely residual lignin,