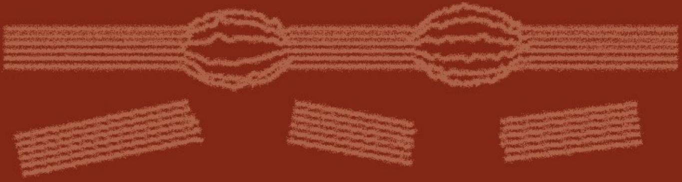
S. Kalia
B. S. Kaith
I. Kaur (Eds.)



Cellulose Fibers: Bio- and Nano-Polymer Composites

Green Chemistry and Technology

Springer

Cellulose Fibers:
Bio- and Nano-Polymer Composites

Susheel Kalia • B. S. Kaith • Inderjeet Kaur
Editors

Cellulose Fibers: Bio- and Nano-Polymer Composites

Green Chemistry and Technology

Springer

Editors
Dr. Susheel Kalia
Department of Chemistry
Bahra University
Waknaghat (Shimla Hills)-173 234
Dist. Solan
Himachal Pradesh, India
susheel_kalia@yahoo.com
susheel.kalia@gmail.com

Dr. B. S. Kaith
Department of Chemistry
Dr. B.R. Ambedkar National Institute
of Technology
Jalandhar -144 011
Punjab, India
bskaith@yahoo.co.in

Dr. Inderjeet Kaur
Department of Chemistry
Himachal Pradesh University
Shimla – 171 005
Himachal Pradesh, India
ij_kaur@hotmail.com

ISBN 978-3-642-17369-1 e-ISBN 978-3-642-17370-7
DOI 10.1007/978-3-642-17370-7
Springer Heidelberg Dordrecht London New York

Library of Congress Control Number: 2011924897

Cover design: eStudio Calamar S.L.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

Present is an era of advance materials including polymer composites, nanocomposites, and biocompatible materials. With advancements in science and technology and increase in Industrial growth, there is a continuous deterioration in our environmental conditions. Emission of toxic gases such as dioxin on open burning of plastics in the air and the poisoning of soil-fertility due to nonbiodegradability of plastics disposed in the soil are continuously adding pollution load to our surrounding environment. Therefore, keeping in view the deteriorating conditions of the living planet earth, researchers all over the world have focused their research on eco-friendly materials, and the steps taken in this direction will lead toward Green-Science and Green-Technology.

Cellulosics account for about half of the dry weight of plant biomass and approximately half of the dry weight of secondary sources of waste biomass. At this crucial moment, cellulose fibers are pushed due to their "green" image, mainly because they are renewable and can be incinerated at the end of the material's lifetime without adding any pollution load in the atmosphere. Moreover, the amount of CO_2 released during incineration process is negligible as compared to the amount of CO_2 taken up by the plant throughout its lifetime. Polysaccharides can be utilized in many applications such as biomedical, textiles, automobiles, etc. One of the promising applications is using them as a reinforcing material for the preparation of biocomposites. The most important factor in obtaining mechanically viable composite material is the reinforcement–matrix interfacial interaction. The extent of adhesion depends upon the chemical structure and polarity of these materials. Owing to the presence of hydroxyl groups in cellulose fibers, the moisture regain is high, leading to poor organic wettability with the matrix material and hence a weak interfacial bonding between the reinforcing agent and hydrophobic matrices. In order to develop composites with better mechanical properties and environmental performance, it becomes necessary to increase the hydrophobicity of the reinforcing agent and to improve the compatibility between the matrix and cellulose fibers. There exist several pretreatments that are conducted on cellulose fibers for modifying not only the interphase but also the morphological changes in fibers. Nowadays, to improve the compatibility between natural fibers and hydrophobic polymer matrices, various greener methods such as plasma treatment and treatments using fungi, enzymes, and bacteria have been explored.

Reinforcement of thermoplastic and thermosetting composites with cellulose fibers is increasingly regarded as an alternative to glass fiber reinforcement. The environmental issues in combination with their low cost have recently generated considerable interest in cellulose fibers such as isora, jute, flax, hemp, kenaf, pineapple leaf, and man-made cellulose fibers as fillers for polymer matrices-based composites.

Criteria for cleaner and safer environment have directed enormous parts of the scientific research toward bioplastic materials that can easily be degraded or bio-assimilated toward the end of their life cycle. Degradation of the biocomposites could be either a photodegradation or microbial degradation. Photodegradation of biofilms plays an important role as mulching sheets for plants in agricultural practices that ultimately gets degraded in the soil as an organic fertilizer. Microbial degradation plays a significant role in the depolymerization of the biopolymers, and final degradation products are carbon dioxide and water, thereby adding no pollution load to the environment.

Development of polymer nanocomposite is a fast-growing area of research. Significant efforts are focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual constituents but also on their morphology and interfacial characteristics. This rapidly expanding field is generating many exciting new materials with novel properties. All types and classes of nanocomposite materials lead to new and improved properties when compared to their macrocomposite counterparts. Therefore, nanocomposites promise new applications in diversified fields such as high-strength and light-weight components for aerospace industry, corrosion-resistant materials for naval purpose, etc.

Researchers all over the world are working in this field, and only a few books are available on cellulose fiber polymer composites and nanocomposites. Therefore, this book is in the benefit of society, covering all the essential components of green chemistry. The book is divided into four parts. It starts off with Part-I: structure and properties of cellulose fibers and nanofibers and their importance in composites, medical applications, and paper making. Part-II of the book covers the polymer composites and nanocomposites reinforced with cellulose fibers, nanofibers, cellulose whiskers, rice husk, etc. Greener surface modifications of cellulose fibers, morphology, and mechanical properties of composites are also covered in this part. Part-III of the book covers the biodegradable plastics and their importance in composite manufacturing, reinforced with natural and man-made cellulose fibers. Present section also discusses the biodegradation of polymer composites. Part-IV of the book includes the use of cellulose fiber-reinforced polymer composites in automotives, building materials, and medical applications.

Book covering such vital issues and topics definitely should be attractive to the scientific community. This book is a very useful tool for scientists, academicians, research scholars, polymer engineers, and industries. This book is also supportive for undergraduate and postgraduate students in Institutes of Plastic Engineering and Technology and other Technical Institutes. The book is unique with valuable contributions from renowned experts from all over the world.

The Editors would like to express their gratitude to all contributors of this book, who made excellent contributions. We would also like to thank our students, who helped us in the editorial work.

Solan (Shimla Hills), India — Susheel Kalia
Jalandhar, India — Balbir Singh Kaith
Shimla, India — Inderjeet Kaur
February 2011

Contents

Part I Cellulose Fibers and Nanofibers

Part II Cellulosic Fiber-Reinforced Polymer Composites and Nanocomposites

Part III Biodegradable Plastics and Composites from Renewable Resources

Part IV Applications of Cellulose Fiber-Reinforced Polymer Composites

Contributors

S.H. Ahn School of Mechanical and Aerospace Engineering Seoul National University, Kwanak-Ro 599, Seoul 151-742, South Korea

Danny Akin Light Light Solutions LLC, PO Box 81486, Athens, GA 30608, USA

Pratheep Kumar Annamalai Division of Polymer Science and Engineering, National Chemical Laboratory, Dr. Homi Bhaba Road, Pune 411 008, India; Laboratoire Génie des Procèdes d'élaboration des Bioproduits (GPEB), Université Montpellier II, Place Eugène Bataillon, F-34095, Montpellier, France

Luc Avérous LIPHT-ECPM, EAC (CNRS) 4375, University of Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

Paulina Batkowska Poznan University of Technology, Institute of Chemical Technology and Engineering, 60-965 Poznan, Poland

M.N. Belgacem Laboratoire de Génie des Procédés Papetiers UMR CNRS 5518, Grenoble INP-Pagora, B.P. 65, 38402 Saint Martin d'Hères Cedex, France

Alexander Bismarck Department of Chemical Engineering, Imperial College London, Polymer and Composite Engineering (PaCE) Group, South Kensington Campus, London SW7 2AZ, UK

J.P. Borges Departamento de Ciência dos Materiais and CENIMAT/I3N, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

Slawomir Borysiak Poznan University of Technology, Institute of Chemical Technology and Engineering, Sklodowskiej-Curie 60-965 Poznan, Poland

Lucas L. da Costa Laboratory for Advanced Materials, LAMAV; State University of the Northern Rio de Janeiro, UENF; Av. Alberto Lamego, 2000, 28013-602, Campos dos Goytacazes, RJ, Brazil

B. Deepa Department of Chemistry, Bishop Moore College, Mavelikkara, Kerala, India

Anne Delille Polymer and Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

Roy Dodd Department of Agriculture and Biological Engineering, Clemson University, McAdams Hall, Clemson, SC 29634, USA

Alain Dufresne Grenoble Institute of Technology, The International School of Paper, Print Media and Biomaterials (Pagora), BP 65, 38402 Saint Martin d'Hères cedex, France; Universidade Federal do Rio de Janeiro (UFRJ), Departamento de Engenharia Metalurgica e de Materiais, Coppe, Rio de Janeiro, Brazil

J.L. Figueirinhas Departamento de Física, IST-TU, Av. Rovisco Pais, 1049-001, Lisbon, Portugal

Hans-Peter Fink Fraunhofer Institute for Applied Polymer Research IAP, Geiselbergstr. 69, 14476 Potsdam, Germany

Jonn Foulk Cotton Quality Research Station, USDA-ARS, Ravenel Center room 10, Clemson, SC 29634, USA

Patrick A.C. Gane Omya Development AG, Baslerstrasse 42, 4665 Oftringen, Switzerland; Department of Forest Products Technology, School of Science and Technology, Aalto University, 02150 Espoo, Finland

Johannes Ganster Fraunhofer Institute for Applied Polymer Research IAP, Geiselbergstr. 69, 14476 Potsdam, Germany

S.D. Genieva Department of Inorganic Chemistry, Assen Zlatarov University, 8010, Burgas, Bulgaria

M.H. Godinho Departamento de Ciência dos Materiais and CENIMAT/I3N, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal

M. Gupta CSIR-Central Building Research Institute, Roorkee 247 667, India

Youssef Habibi Department of Forest Biomaterials, North Carolina State University Campus, PO Box 8005, Raleigh, NC 27695-8005, USA

Ruhi Haque Advanced Materials and Processes Research Institute (AMPRI), CSIR, HabibGanj Naka, Bhopal 462064, India

Eero Hiltunen Department of Forest Products Technology, School of Science and Technology, Aalto University, 02150 Espoo, Finland

Rajeev Jindal Department of Chemistry, Dr. B.R. Ambedkar National Institute of Technology, Jalandhar 144 011, Punjab, India

Jyoti P. Jog Polymer Science and Engineering Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008, India

Rani Joseph Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, Kerala, India

M.K. Joshy Department of Chemistry, S.N.M. College, Malienkara, Kerala, India

B.S. Kaith Department of Chemistry, Dr. B.R. Ambedkar National Institute of Technology, Jalandhar 144 011, Punjab, India

Susheel Kalia Department of Chemistry, Bahra University, Waknaghat (Shimla Hills), 173 234, Solan, Himachal Pradesh, India

Kambiz Kayvantash Société CADLM, 9 rue Raoul Dautry, 91190 GIF-SUR-YVETTE, Paris, France

M. Kottaisamy Centre for Nanotechnology, Kalasalingam University, Anand Nagar, Krishnankoil, 626 190 Virudhunagar, Tamil Nadu, India

Koon-Yang Lee Polymer and Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

Felipe Perisse Duarte Lopes Laboratory for Advanced Materials, LAMAV; State University of the Northern Rio de Janeiro, UENF; Av. Alberto Lamego, 2000, 28013-602, Campos dos Goytacazes, RJ, Brazil

Alcides Lopes Leao Department of Natural Science, College of Agricultural Sciences, UNESP – São Paulo State University, Botucatu 18610-307, Brazil

Mithu Maiti Department of Chemistry, Dr. B.R. Ambedkar National Institute of Technology, Jalandhar 144 011, Punjab, India

Jerzy Mankowski Institute of Natural Fibres and Medicinal Plants, Wojska Polskiego 71b, 60-630, Poznan, Poland

Frederico Muylaert Margem Laboratory for Advanced Materials, LAMAV; State University of the Northern Rio de Janeiro, UENF; Av. Alberto Lamego, 2000, 28013-602, Campos dos Goytacazes, RJ, Brazil

Lovely Mathew Department of Chemistry, Newman College, Thodupuzha, Kerala, India

Bibin Mathew Cherian Department of Natural Science, College of Agricultural Sciences, São Paulo State University (UNESP), Botucatu 18610-307, São Paulo, Brazil

Hemant Mittal Department of Chemistry, Dr. B.R. Ambedkar National Institute of Technology, Jalandhar 144 011, Punjab, India

A.R. Mohamed Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, University of Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Sergio Neves Monteiro Laboratory for Advanced Materials, LAMAV; State University of the Northern Rio de Janeiro, UENF; Av. Alberto Lamego, 2000, 28013-602 Campos dos Goytacazes, RJ, Brazil

Sanjay Naithani Chemistry Division, Forest Research Institute, Dehra Dun 248 006, India

Denise Cristina Oliveira Nascimento Laboratory for Advanced Materials, LAMAV; State University of the Northern Rio de Janeiro, UENF; Av. Alberto Lamego, 2000, 28013-602, Campos dos Goytacazes, RJ, Brazil

James Njuguna Department of Sustainable Systems, Cranfield University, Bedfordshire MK43 0AL, UK

J.K. Pandey School of Mechanical and Aerospace Engineering Seoul National University, Kwanak-Ro 599, Seoul 151-742, South Korea

Asokan Pappu Advanced Materials and Processes Research Institute (AMPRI), CSIR, HabibGanj Naka, Bhopal 462064, India

Januar Parlaungan Siregar Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, University of Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Dominik Paukszta Poznan University of Technology, Institute of Chemical Technology and Engineering, 60-965 Poznan, Poland

S.A. Paul Department of Chemistry, Bishop Moore College, Mavelikkara, Kerala, India

Krzysztof Pielichowski Department of Chemistry and Technology of Polymers, Cracow University of Technology, ul. Warszawska 24, 31-155 Kraków, Poland

M.N. de Pinho Departamento de Química and ICEMS, IST-TU, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

L.A. Pothan Department of Chemistry, Bishop Moore College, Mavelikkara, Kerala, India

Maria Wladyka Przybylak Institute of Natural Fibres and Medicinal Plants, Wojska Polskiego 71b, 60-630 Poznan, Poland

Anamika Randhawa CSIR-Central Building Research Institute, Roorkee 247 667, India

Mohamad Ridzwan Ishak Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, University of Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

D.R. Saini Department of Polymer Science and Engineering, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

Helvio Pessanha Guimaraes Santafe Jr. Laboratory for Advanced Materials, LAMAV; State University of the Northern Rio de Janeiro, UENF; Av. Alberto Lamego, 2000, 28013-602, Campos dos Goytacazes, RJ, Brazil

Salit Mohd Sapuan Department of Mechanical and Manufacturing Engineering, University of Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Kestur Gundappa Satyanarayana Laboratory for Advanced Materials, LAMAV, State University of the Northern Rio de Janeiro, UENF, Av. Alberto Lamego 2000, Horto, Campos dos Goytacazes, Rio de Janeiro, Brazil; UFPR, Curitiba, Paraná, Brazil; Acharya Institutes, BMS College of Engineering and Poornaprajna Institute of Scientific Research, Bangalore, India

Mohini Saxena Building Materials Development Group, Advanced Materials and Processes Research Institute (AMPRI), CSIR, HabibGanj Naka, Bhopal 462064, India

Anusha Sharma Advanced Materials and Processes Research Institute (AMPRI), CSIR, HabibGanj Naka, Bhopal 462064, India

Ailton da Silva Ferreira Laboratory for Advanced Materials, LAMAV; State University of the Northern Rio de Janeiro, UENF; Av. Alberto Lamego, 2000, 28013-602, Campos dos Goytacazes, RJ, Brazil

B. Singh CSIR-Central Building Research Institute, Roorkee 247 667, India

Raj Pal Singh Division of Polymer Science and Engineering, National Chemical Laboratory, Dr. Homi Bhaba Road, 411 008, Pune, India

Sivoney Ferreira de Souza Department of Natural Science, College of Agricultural Sciences, UNESP – São Paulo State University, Botucatu 18610-307, Brazil

Kelley Spence Department of Forest Biomaterials, North Carolina State University Campus, PO Box 8005, Raleigh, NC 27695-8005, USA

Ramjee Subramanian Omya Development AG, Baslerstrasse 42, 4665, Oftringen, Switzerland

Hina Tarannum CSIR-Central Building Research Institute, Roorkee 247 667, India

Sabu Thomas School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India

S. Ch. Turmanova Department of Material Science, Assen Zlatarov University, 8010, Burgas, Bulgaria

Chad Ulven Department of Mechanical Engineering and Applied Mechanics, North Dakota State University, 103 Dolve Hall, Fargo, ND 58105, USA

V.K. Varshney Chemistry Division, Forest Research Institute, Dehra Dun 248 006, India

L.T. Vlaev Department of Physical Chemistry, Assen Zlatarov University, 8010 Burgas, Bulgaria

Paul Wambua Department of Manufacturing, Industrial and Textile Engineering, Moi University, PO Box 3900, Eldoret 30100, Kenya

Santosh D. Wanjale Polymer Science and Engineering Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008, India

Malgorzata Zimniewska Institute of Natural Fibres and Medicinal Plants, Wojska Polskiego 71b, 60-630, Poznan, Poland

Part I
Cellulose Fibers and Nanofibers

Chapter 1
Natural Fibres: Structure, Properties and Applications

S. Thomas, S.A. Paul, L.A. Pothan, and B. Deepa

Abstract This chapter deals with the structure, properties and applications of natural fibres. Extraction methods of Natural Fibres from different sources have been discussed in detail. Natural fibres have the special advantage of high specific strength and sustainability, which make them ideal candidates for reinforcement in various polymeric matrices. Natural fibres find application in various fields like construction, automobile industry and also in soil conservation. It is the main source of cellulose, an eminent representative of nanomaterial. Extractions of cellulose from plant-based fibres are discussed in detail. Various methods used for characterization of cellulose nanofibres and advantages of these nanofibres have also been dealt with.

Keywords Animal fibre · Cellulose · Nanofibre · Plant fibre

Contents

S. Thomas (✉)
School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India
e-mail: sabupolymer@yahoo.com; sabuchathukulam@yahoo.co.uk

S. Kalia et al. (eds.), *Cellulose Fibers: Bio- and Nano-Polymer Composites*,
DOI 10.1007/978-3-642-17370-7_1, © Springer-Verlag Berlin Heidelberg 2011

1.1 Introduction

The growing ecological, social and economic awareness, high rate of depletion of petroleum resources, concepts of sustainability and new environmental regulations have stimulated the search for green materials compatible with the environment. The waste disposal problems, as well as strong European regulations and criteria for cleaner and safer environment, have directed a great part of the scientific research to eco-composite materials that can be easily degraded or bio-assimilated. The worldwide availability of natural fibres and other abundantly accessible agrowaste is responsible for the new interest in research in sustainable technology [1, 2]. Bioresources obtained from agricultural-related industries have received much attention, because they can potentially serve as key components of biocomposites. The possibilities of using all the components of the fibre crop provide wide ranging opportunities both in up and down stream processing for developing new applications in packaging, building, automotive, aerospace, marine, electronics, leisure and household [3]. Agricultural crop residues such as cereal straw, corn stalk, cotton, bagasse and grass, which are produced in billions of tonnes around the world, represent an abundant, inexpensive and readily available source of lignocellulosic biomass. Among these enormous amounts of agricultural residues, only a minor quantity of residues is reserved as animal feed or household fuel and a major portion of the straw is burned in the field, creating environmental pollution. The exploration of these inexpensive agricultural residues as bio resource for making industrial products will open new avenues for the utilisation of agricultural residues by reducing the need for disposal and environmental deterioration through pollution, fire and pests and at the same time add value to the creation of rural agricultural-based economy [4].

Most of the natural fibres are lighter due to their favourable density in comparison with other synthetic fibres and metallic materials. This attribute in combination with their excellent mechanical properties are beneficial, where stronger and lighter materials are required especially in transportation application where energy efficiency is influenced by the weight of the fast moving mass. The physical and chemical morphology of natural fibres, their cell wall growth, patterns and thickness, dimensions and shape of the cells, cross-sectional shapes, distinctiveness of lumens, etc., besides their chemical compositions, influence the properties of the fibres [5]. These fibres will also provide important opportunities to improve people’s standard of living by helping generate additional employment, particularly in the rural sector. Accordingly, many countries that have these natural sources has started to conduct R&D efforts with lignocellulosic fibres, seeking to take advantage of their potential social advantages.

1.2 Natural Fibres

1.2.1 Animal Fibres and Their General Structure

1.2.1.1 Silk Fibre

Silks are protein materials produced by a wide range of insect and spider species. They are used for applications requiring high-performance fibres. Silk is produced by insects and arachnids to make structures such as webs, cocoons and nests. Silk from silkworm cocoons (of the moth *Bombyx mori*) has been used by mankind to make fabrics, because it has excellent mechanical properties, particularly its high tensile modulus [6]. The silk of the domesticated silkworm, *B. mori*, has been used as a suture biomaterial for centuries, and in recent years farmed silkworm silk has also been reprocessed into forms such as films, gels and sponges for medical applications. Spider silks also have outstanding strength, stiffness and toughness that, weight for weight, are unrivalled by synthetic fibres.

Structural proteins are commonly fibrous proteins such as keratin, collagen and elastin. Skin, bone, hair and silk all depend on such proteins for their structural properties. The structures (several types have been recorded) all consist of silk based on anti-parallel sheets of the fibrous protein fibroin. Long stretches of the polypeptide chain consist of sequences (Glycine- Sericin- Glycine-Alanine-Glycine-Alanine), where the symbols indicate different amino acids. The Gly chains extend from one surface of the-sheets and the Ser and Ala from the other, forming an alternating layered structure. The orientation of the chains along the sheet underpins the tensile strength of silk, while the weak forces between sheets ensure that silk fibres are flexible. Silk fibres have a complex hierarchical structure, in which a fibroin core is surrounded by a skin of the protein sericin. Within the core, termed bave, there are crystalline regions containing layered sheets and amorphous regions that may contain isolated sheets [7–9]. Vintage X-ray fibre diffraction work demonstrated that honeybee silk contains α-helical proteins assembled into a higher order coiled coil conformation [10]. A more detailed study indicated a tetrameric coiled coil. As the four silk proteins of honeybees are expressed at approximately equal levels, they likely correspond to the four strands of the coiled coil structure [11].

1.2.1.2 Agriculturally Derived Proteins

Other than animals, agricultural materials can also be considered as an ideal source of protein and are prospective materials for the preparation of fibres. Fibres of regenerated protein were produced commercially in between 1930 and 1950, and by today’s standards, they would be considered natural, sustainable, renewable, and biodegradable. Casein from milk was used by M/s Courtaulds Ltd. to make Fibrolane and by M/s Snia to make Lanital; groundnut (peanut) protein was used by

M/s ICI to make Ardil; Vicara was made by the M/s Virginia–Carolina Chemical Corporation from zein (corn protein); and soybean protein fibre was developed by the Ford Motor Company [12]. The regenerated fibres had several qualities typical of the main protein fibres, wool and silk; they were soft, with excellent drape and high moisture absorbency. They could be processed on conventional textile machinery and coloured with conventional dyes. Superior to wool in some regards, they did not prickle, pill or shrink. They could be produced as staple or filament, crimped or straight, with control over diameter, and dope-dyed if required. Regenerated protein fibres are potentially environmentally sustainable, renewable and biodegradable. Two protein sources, feather keratin and wheat gluten, have been considered for their suitability to make an eco-friendly regenerated fibre. Both appear to be viable, although low wet strength may make it problematic. The inclusion of nanoparticles and use of cross-linking technologies offer the potential to improve mechanical strength to make them fit for use in apparel or technical textile applications. Wool is similar to feather in some regards, both keratins being highly cross-linked, although wool proteins are heterogeneous with a generally higher molecular weight (10–55 kDa) and higher cysteine content.

1.2.2 Plant Fibres and Their General Structure

1.2.2.1 Different Types of Plant Fibres

Fibres obtained from the various parts of the plants are known as plant fibres. Plant fibres include bast, leaf and seed/fruit fibres. Bast consists of a wood core surrounded by a stem. Within the stem, there are a number of fibre bundles, each containing individual fibre cells or filaments. Examples include flax, hemp, jute, kenaf and ramie. Leaf fibres such as sisal, abaca, banana and henequen are coarser than bast fibres. Cotton is the most common seed fibre. Other examples include coir and oil palm. Other source of lignocellulosics can be from agricultural residues such as rice hulls from a rice processing plant, sun flower seed hulls from an oil processing unit and bagasse from a sugar mill. The properties of natural fibres vary considerably depending on the fibre diameter, structure, degree of polymerization, crystal structure and source, whether the fibres are taken from the plant stem, leaf or seed, and on the growing conditions [13–15]. List of important plant fibres are given in Table 1.1.

1.2.2.2 General Structure of Plant Fibres

A single or elementary plant fibre is a single cell typically of a length from 1 to 50 mm and a diameter of around 10–50 μm. Plant fibres are like microscopic tubes, i.e., cell walls surrounding the central lumen. The lumen contributes to the water

Table 1.1 List of important plant fibres

Fibre source	Origin
Abaca	Leaf
Bagasse	Grass
Bamboo	Grass
Banana	Stem
Coir	Fruit
Cotton	Seed
Curaua	Leaf
Date palm	Leaf
Flax	Stem
Hemp	Stem
Henequen	Leaf
Isora	Stem
Jute	Stem
Kapok	Fruit
Kenaf	Stem
Oil palm	Fruit
Piassava	Leaf
Pineapple	Leaf
Ramie	Stem
Sisal	Leaf
Sponge gourd	Fruit
Straw (Cereal)	Stalk
Sun hemp	Stem
Wood	Stem

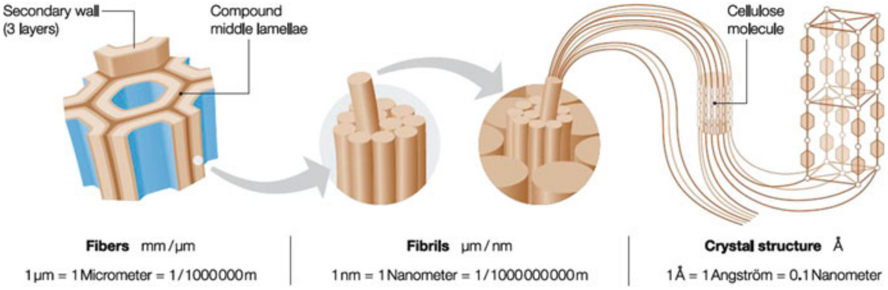


Fig. 1.1 Arrangement of microfibrils and cellulose in the plant cell wall [Zimmermann et al. [17]]

uptake behaviour of plant fibres [16]. The fibre consists of several cell walls. These cell walls are formed from oriented reinforcing semi-crystalline cellulose microfibrils embedded in a hemicellulose–lignin matrix of varying composition. Such microfibrils have typically a diameter of about 10–30 nm and are made up of 30–100 cellulose molecules in extended chain conformation and provide mechanical strength to the fibre. Figure 1.1 shows the arrangement of fibrils, microfibrils and cellulose in the cell walls of a plant fibre.

The hemicellulose molecules of the matrix phase in a cell wall are hydrogen bonded to cellulose and act as a cementing matrix between the cellulose microfibrils, forming the cellulose/hemicellulose network, which is thought to be the main structural component of the fibre cell. The hydrophobic lignins on the other hand act as a cementing agent and increase the stiffness of the cellulose/hemicellulose composite.

The cell walls are divided into two sections, the primary cell wall containing a loose irregular net work of cellulose microfibrils, which are closely packed, and the secondary wall. The secondary wall is composed of three separate and distant layers – S_1 (outer layer), S_2 (middle layer) and S_3 (inner layer). S_2 layer is the thickest and the most important in determining mechanical properties [16]. Schematic representation of the fine structure of a lignocellulosic fibre is presented in Fig. 1.2. These fibre cell walls differ in their composition, i.e., the ratio between cellulose and lignin/hemicellulose and in the orientation or spiral angle of the cellulose microfibrils [18]. The spiral angle is the angle that the helical spirals of cellulose microfibrils form with the fibre axis. The spiral angle or the microfibrillar angle varies from one plant fibre to another. The mechanical properties of the fibre are dependent on the cellulose content, microfibrillar angle and the degree of polymerization. Degree of polymerization also depends on the part of the plant from which fibres are obtained. Fibres with higher cellulose content, higher degree of polymerization and a lower microfibrillar angle exhibit higher tensile strength and modulus.

Cellulosic fibres have amorphous and crystalline domains with a high degree of organisation. The crystallinity rate depends on the origin of the material. Cotton, flax, ramie, sisal and banana have high degrees of crystallinity (65–70%), but the crystallinity of regenerated cellulose is only 35–40%. Progressive elimination of the less organised parts leads to fibrils with ever-increasing crystallinity, until almost 100%, leading to whiskers. Crystallinity of cellulose results partially from hydrogen bonding between the cellulosic chains, but some hydrogen bonding also

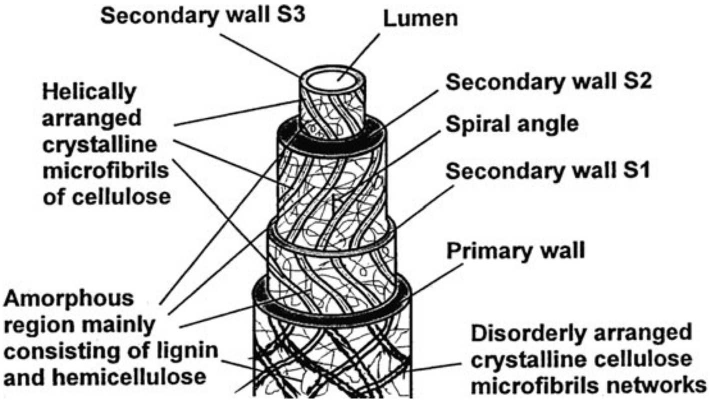


Fig. 1.2 Structural constitution of natural vegetable fibre cell [18]

occurs in the amorphous phase, although its organisation is low [18]. In cellulose, there are many hydroxyl groups available for interaction with water by hydrogen bonding. They interact with water not only at the surface but also in the bulk. The quantity of water absorbed depends on the relative humidity of the confined atmosphere with which the fibre is in equilibrium. The sorption isotherm of cellulosic material depends on the purity of cellulose and the degree of crystallinity. All –OH groups in the amorphous phase are accessible to water, whereas only a small amount of water interacts with the surface –OH groups of the crystalline phase. The main components of natural fibres are cellulose (α-cellulose), hemicellulose, lignin, pectins and waxes.

1.2.3 Processing Techniques for Obtaining Natural Fibres

Extraction of fibres from the plant stems is achieved by various methods. Retting is a process of controlled degradation of the plant stem to allow the fibre to be separated from the woody core and thereby improving the ease of extraction of the fibres from the plant stems [19]. The retting of the straw is caused with time by exposure to moisture and, sometimes, by the help of a mechanical decorticator. Most available methods of retting rely on the biological activity of microorganism, bacteria and fungi from the environment to degrade the pectic polysaccharides from the non-fibre tissue and, thereby, separate the fibre bundles. Microbial/enzymatic retting is one of the widely used techniques to extract good quality cellulosic fibres from the agricultural plants such as hemp, flax and jute [5, 20, 21]. Sain and Panthapulakkal [4] used fungal retting of wheat straw before extracting the fibres. They explored the use of a fungus, which was isolated from the bark of an elm tree, for retting of wheat straw. They mechanically defibrillated wheat straw using a laboratory-scale mechanical refiner before and after fungal retting. The enzymes produced by the fungus or bacteria weaken or remove the pectinic glue that bonds the fibre bundles together and release the cellulosic fibres from the fibre bundle. The fibre separation and extraction process has a major impact on fibre yield and final fibre quality. It influences the structure, chemical composition and properties of the fibres. Retting procedures can be divided into biological, mechanical, chemical and physical fibre separation process.

1.2.3.1 Biological Retting

Biological retting includes natural and artificial retting. Natural retting comprises dew or field retting and cold water retting. Dew or field retting [22] is the most commonly applied retting process in regions that have appropriate moisture and temperature ranges. After being mown, the crops should remain on the fields until the microorganisms have separated the fibres from the cortex and xylem.

After retting, the stalk is dried and baled. The retting process has to be stopped at the right time to prevent over-retting. Under-retting results in fibres that are difficult to separate and to further process. Therefore, it is necessary to monitor the retting process to ensure the quality of the fibres. A modified field-retting process is the thermally induced stand-retting process [23].

Cold water retting [24] utilises anaerobic bacteria that breakdown the pectin of plant straw bundles submerged in huge water tanks, ponds, hamlets or rivers and vats. The process takes between 7 and 14 days and depends on the water type, temperature of the retting water and any bacterial inoculum. Even though the process produces high quality fibres, environmental pollution is high due to unacceptable organic fermentation waste waters.

Artificial retting [25] involves warm-water or canal retting and produces homogeneous and clean fibres of high quality in 3–5 days. Plant bundles are soaked in warm water tanks. After sufficient retting, the bast fibres are separated from the woody parts. The sheaves or hurds are loosened and extracted from the raw fibres in a breaking or scotching process.

1.2.3.2 Mechanical or Green Retting

It is a much simpler and more cost-effective alternative to separate the bast fibre from the plant straw [26]. The raw material for this procedure is either field dried or slightly retted plant straw. The bast fibres are separated from the woody part by mechanical means. Weather-dependent variations of fibre quality are eliminated. However, the produced green fibres are much coarser and less fine as compared to dew or water retted fibres.

1.2.3.3 Physical Retting

Physical retting [27, 28] includes ultrasound and steam explosion method. In ultrasound retting, the stems obtained after the harvest are broken and washed. Slightly crushed stems are immersed in hot water bath that contains small amounts of alkali and surfactants and then exposed to high-intense ultrasound. This continuous process separates the hurds from the fibre. The steam explosion method represents another suitable alternative to the traditional field-retting procedure. Under pressure and increased temperature, steam and additives penetrates the fibre interspaces of the bast fibre bundles. The subsequent sudden relaxation of the steam leads to an effective breaking up of the bast fibre composite, which results in an extensive decomposition into fine fibres. Another alternative for producing high and consistent quality fibres is enzyme retting. This retting procedure uses pectin-degrading enzymes to separate the fibres from the woody tissue. The use of enzymes promotes the controlled retting of the fibre crops through the selective biodegradation of the pectinaceous substances. The enzyme activity increases with increasing temperature up to an optimum temperature above which the enzyme starts to denature.

1.2.3.4 Chemical and Surfactant Retting

Chemical and surfactant retting [29] refers to all retting process in which the fibre crop's straw is submerged in heated tanks containing water solutions of sulphuric acid, chlorinated lime, sodium or potassium hydroxide and soda ash to dissolve the pectin component. The use of surface active agents in retting allows the simple removal of unwanted non-cellulosic components adhering to the fibres by dispersion and emulsion-forming process. Chemical retting produces high quality fibres but adds costs to the final product. An investigation of the extraction procedures of vakka (Roystonea regia), date and bamboo fibres was reported by Murali and Mohana [19]. In their studies, the manually decorticated bamboo fibrous strips were extracted by means of a chemical process of decomposition called degumming, in which the gummy materials and the pectin are removed. The chemical extraction process yields about 33% of fibre on weight basis.

1.2.4 Chemical Composition of Plant Fibres

The chemical composition as well as the morphological microstructure of vegetable fibres is extremely complex due to the hierarchical organisation of the different compounds present at various compositions. Depending on the type of fibre, the chemical composition of natural fibres varies. Primarily, fibres contain cellulose, hemicellulose and lignin. The property of each constituent contributes to the overall properties of the fibre.

1.2.4.1 Cellulose

Cellulose forms the basic material of all plant fibres. It is generally accepted that cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units joined together by β-1,4-glycosidic linkages. Cellulose is thus a 1,4-β-D-glucan [15]. The molecular structure of cellulose, which is responsible for its supramolecular structure determines many of its chemical and physical properties. In the fully extended molecule, the adjacent chain units are oriented by their mean planes at the angle of 180° to each other. Thus, the repeating unit in cellulose is the anhydrocellobiose unit, and the number of repeating units per molecule is half the DP. This may be as high as 14,000 in native cellulose.

The mechanical properties of natural fibres depend on the cellulose type. Each type of cellulose has its own cell geometry, and the geometrical conditions determine the mechanical properties. Solid cellulose forms a microcrystalline structure with regions of high order, i.e., crystalline regions, and regions of low order, i.e., amorphous regions. Cellulose is also formed of slender rod like crystalline microfibrils. The crystal nature (monoclinic sphenodic) of naturally occurring cellulose is known as cellulose I. Cellulose is resistant to strong alkali (17.5 wt%) but is easily hydrolyzed by acid to water-soluble sugars. Cellulose is relatively resistant to oxidising agents.

1.2.4.2 Hemicelluloses

Hemicellulose is not a form of cellulose at all. It comprises a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed. The hemicellulose differs from cellulose in three important aspects [15]. In the first place, they contain several different sugar units, whereas cellulose contains only 1,4-β-D-glucopyranose units. Secondly, they exhibit a considerable degree of chain branching, whereas cellulose is strictly a linear polymer. Thirdly, the degree of polymerization of native cellulose is 10–100 times higher than that of hemicellulose. Unlike cellulose, the constituents of hemicellulose differ from plant to plant [15, 30].

1.2.4.3 Lignins

Lignins are complex hydrocarbon polymers with both aliphatic and aromatic constituents [31, 32]. Their chief monomer units are various ring-substituted phenyl propanes linked together in ways that are still not fully understood. Their mechanical properties are lower than those of cellulose. Lignin is totally amorphous and hydrophobic in nature. It is the compound that gives rigidity to the plants. Lignin is considered to be a thermoplastic polymer, exhibiting a glass transition temperature of around 90°C and melting temperature of around 170°C. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidised and easily condensable with phenol [33].

1.2.4.4 Pectins and Waxes

Pectin is a collective name for heteropolysaccharides, which consist essentially of polygalacturon acid. Pectin is soluble in water only after a partial neutralisation with alkali or ammonium hydroxide. It provides flexibility to plants. Waxes make up the last part of fibres and they consist of different types of alcohols, which are insoluble in water as well as in several acids.

1.2.5 Cellulose from Plant Fibres

A single fibre of all plant-based natural fibres consists of several cells. These cells are formed out of cellulose-based crystalline microfibrils, which are connected to a complete layer by amorphous lignin and hemicellulose. Multiples of such cellulose–lignin–hemicellulose layers in one primary and three secondary cell walls stick together to form a multiple layer composite. The fibre strength increases with increasing cellulose content and decreasing spiral angle with respect to fibre axis.

Cellulose is found not to be uniformly crystalline. However, the ordered regions are extensively distributed throughout the material, and these regions are called crystallites. The threadlike entity, which arises from the linear association of these components, is called the microfibril. It forms the basic structural unit of the plant cell wall. These microfibrils are found to be 10–30 nm wide, less than this in width, indefinitely long containing 2–30,000 cellulose molecules in cross section. Their structure consists of predominantly crystalline cellulose core. Individual cellulose nanocrystals (Fig. 1.3) are produced by breaking down the cellulose fibres and isolating the crystalline regions [34]. These are covered with a sheath of para-crystalline polyglucosan material surrounded by hemicelluloses [35].

In most natural fibres, these microfibrils orient themselves at an angle to the fibre axis called the microfibril angle. The ultimate mechanical properties of natural fibres are found to be dependent on the microfibrillar angle. Gassan et al. [36] have done calculations on the elastic properties of natural fibres. Cellulose exists in the plant cell wall in the form of thin threads with an indefinite length. Such threads are cellulose microfibrils, playing an important role in the chemical, physical and mechanical properties of plant fibres and wood. Microscopists' and crystallographers' studies have shown the green algae Valonia to be excellent material for the ultrastructural study of the cellulose microfibril [37]. A discrepancy in the size of the crystalline regions of cellulose, obtained by X-ray diffractometry and electron microscopy, led to differing concepts on the molecular organisation of micro-fibrils. David et al. [38] regarded the microfibril itself as being made up of a number of crystallites, each of which was separated by a para-crystalline region and later termed "elementary fibril". The term "elementary fibril" is therefore applied to the smallest cellulosic strand. Electron micrograph studies of the disintegrated microfibrils,

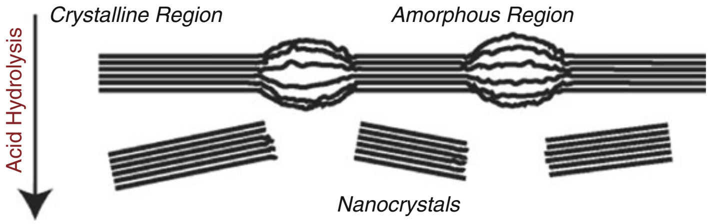


Fig. 1.3 Acid hydrolysis breaks down disordered (amorphous) regions and isolates nanocrystals [34]

showing the crystalline nature of cellulose microfibrils (Magnfn 100 nm) taken by diffraction contrast in the bright field mode, are given in Fig. 1.4. Reports on the characterisation and the make-up of the elementary fibrils and on their association while establishing the fibre structure – usually called fibrillar or fringed fibril structure are there in the literature [39]. According to this concept, the elementary fibril is formed by the association of many cellulose molecules, which are linked together in repeating lengths along their chains. In this way, a strand of elementary crystallites is held together by parts of the long molecules reaching from one crystallite to the next, through less ordered inter-linking regions. Molecular transition from one crystallite strand to an adjacent one is possible, in principle. Apparently, in natural fibres, this occurs only to a minor extent, whereas in man-made cellulosic fibres, such molecular transitions occur more frequently.

The internal cohesion within the elementary fibrils is established by the transition of the long cellulose chain molecules from crystallite to crystallite. The coherence of the fibrils in their secondary aggregation is given either by hydrogen bonds at close contact points or by diverging molecules. Access into this structure is given by large voids formed by the imperfect axial orientation of the fibrillar aggregates, interspaces of nanometre dimensions between the fibrils in the fibrillar aggregations and by the less ordered inter-linking regions between the crystallites within the elementary fibrils. Dufresne has reported on whiskers obtained from a variety of natural and living sources [40]. Cellulose microfibrils and cellulose whisker suspension were obtained from sugar beet root and from tunicin. Typical electron micrographs obtained from dilute suspensions of sugar beet are shown in Fig. 1.5. Individual microfibrils are almost 5 nm in width while their length is of a much higher value, leading to a practically infinite aspect ratio of this filler. They can be used as a reinforcing phase in a polymer matrix.

Fig. 1.4 Electron micrograph of the disintegrated microfibrils [37]

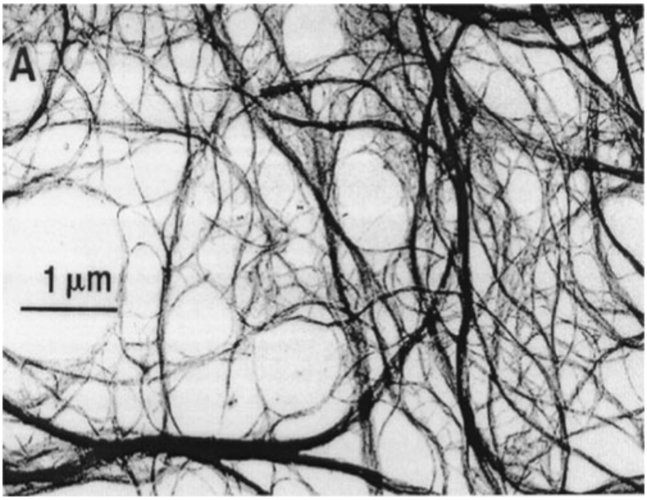


Fig. 1.5 Transmission electron micrograph of a dilute suspension of sugar beet cellulose [40]

1.2.6 Surface Characteristics of Various Plant Fibres

Many natural fibres have a hollow space (the lumen) as well as nodes at irregular distances that divide the fibre into individual cells. The surface of natural fibres is rough and uneven and provides good adhesion to the matrix in a composite structure. The compatibility of fibre surface with the interacting chemicals, such as resin, depends on the smoothness or roughness of the fibre. Rough surfaces increase the number of anchorage points, thus offering a good fibre-resin mechanical interlocking. The presence of waxy substances on the fibre surface contributes immensely to ineffective fibre to resin bonding and poor surface wetting. Also, the presence of free water and hydroxyl groups, especially in the amorphous regions, worsens the ability of plant fibres to develop adhesive characteristics with most binder materials.

Microscopic studies such as optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) can be used to study the morphology of fibre surface and can predict the extent of mechanical bonding at the interface. AFM is a useful technique to determine the surface roughness of fibres [41].

Morphology of Brazilian coconut fibres was studied by Tomczak et al. [42]. The morphological characterization of the fibres was conducted through an optical microscope and scanning electron microscope. The degree of crystallinity of the fibres was calculated from X-ray diffractograms. It was found that fibre consists of different types of regularly arranged cells, with a large lacuna at the centre of the fibre. Figure 1.6 shows the photomicrograph of transverse section of coir fibre. The cells are almost circular, similar to those reported for coir fibres of other countries. The X-ray diffraction spectrum of the coir fibres (Fig. 1.7) showed peak associated

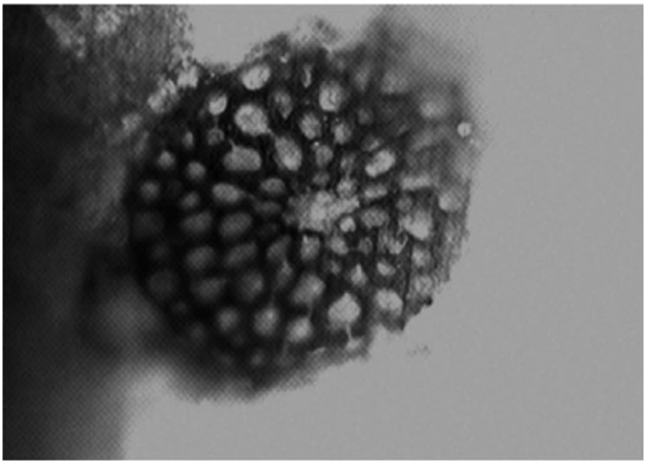


Fig. 1.6 Photomicrograph of transverse section of coir fibre [42]

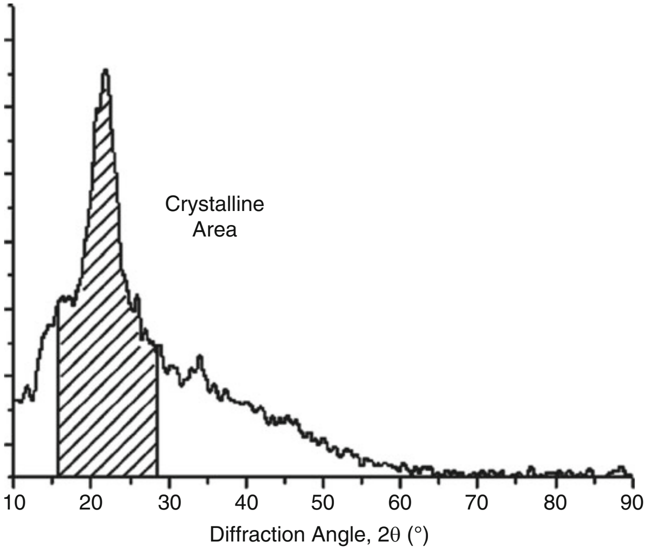


Fig. 1.7 X-ray spectrum of Brazilian coir fibres [42]

with the crystalline part at $2\theta = 22^\circ$. The crystallinity index of coir fibres calculated was 57%, and the microfibrillar angle was found to be 51°.

AFM characterization of the surface wettability of hemp fibre was reported by [41]. These images detailed the rough primary cell wall, which is characteristic of the hemp fibre. The fibres showed lower adhesion force and were presumably hydrophobic. Surface roughness averages of the fibre samples were measured to be between 10 and 20 nm on 1 mm^2 areas, which were significantly rougher than the model surfaces used for the calibration, with surface roughness averages of 0.5–2 nm measured on 1 mm^2 areas. The AFM results were complimented by examination of the contact angle of the fibres. Morphology of hemp fibre surface detailing the rough primary cell wall is shown in (Fig. 1.8). Panels (a) and (b) shown in the above figure are deflection images taken at low and high magnifications, while (c) is a friction map taken from an area similar to that shown in (b), resolving fibres (f) embedded in an amorphous matrix (m). High contact angle was evident for hemp fibres, which showed its hydrophobicity (Fig. 1.9).

Bessadok et al. [43] studied the surface characteristics of agave fibres by means of microscopic analysis, infrared spectroscopy and surface energy. Cross-section of an Agave leaf fibre is shown in Fig. 1.10. Infrared spectroscopy revealed the presence of the major absorbance peaks reflecting the carbohydrate backbone of cellulose. The surface energy analysis showed that surface energy of the fibre was high due to the roughness of the fibre.

Fluorescent microscopic images of the fibre (Fig. 1.11) showed how the fibre was able to fix calcofluor, a fluorescent probe well-known to have high affinity with polysaccharides such as cellulose, hemicellulose and pectins. From the figure, it

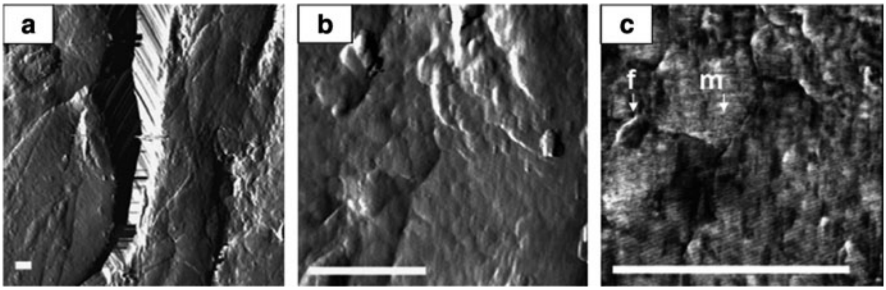


Fig. 1.8 Morphology of hemp fibre surface detailing the rough primary cell wall [41]

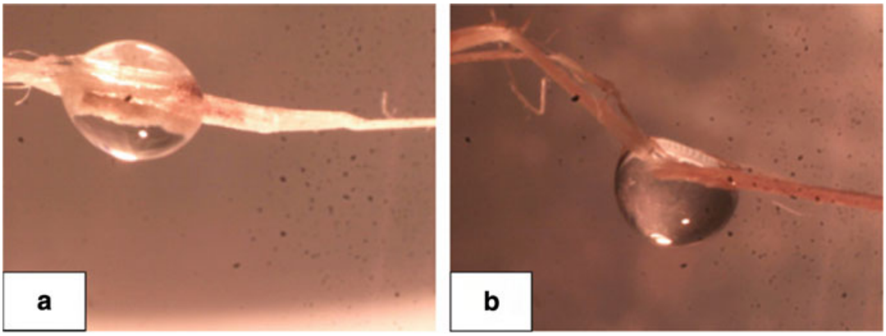


Fig. 1.9 Interaction of water with hemp fibre demonstrating the hydrophobic nature of hemp fibre [42]

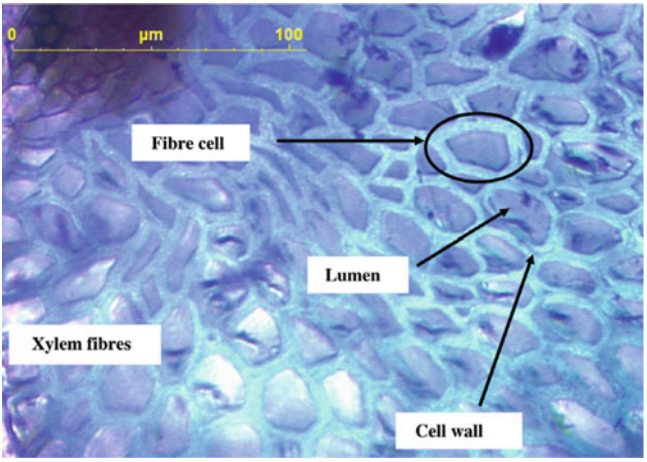


Fig. 1.10 Cross-section of an Agave leaf coloured with Carmin-green [43]

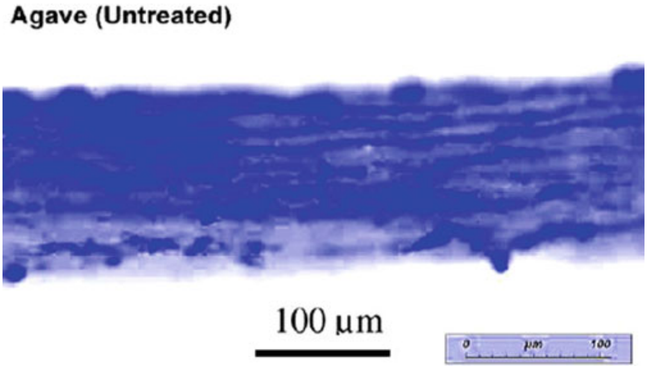


Fig. 1.11 Fluorescent microscopy images of agave fibre [43]

is clear that the fibre is sensitive to calcofluor due to the presence of cellulose, hemicellulose and pectic substances. The study was further supported by SEM studies. SEM studies revealed that agave fibres gathered in a bundle form and constituted spiral tracheids, well-known as water transport materials.

In an innovative study, nanoscale characterization of natural fibres using contact-resonance force microscopy (CR-FM) was reported by Sandeep et al. [44]. This method was used to evaluate the cell wall layers of natural fibres for studying the elastic properties of cell walls. The cell wall layer experiments involved samples collected from a 45-year-old red oak. The studies revealed that there is a thin region between the S1 and S2 layers with apparently lower modulus than that of other secondary layers. Figure 1.12 shows schematic representation of cell wall layers of wood fibre. Figure 1.13 shows images for the topography and indentation modulus. Contrasts in modulus between the compound middle lamellae (CML) and S1 and S2 layers are clearly visible. Mean values of the indentation

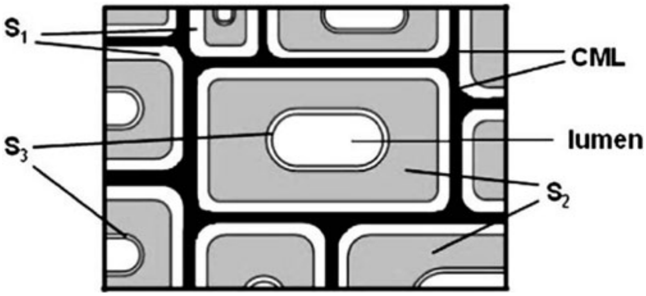


Fig. 1.12 Schematic representation of cell wall layers of wood fibre [44]

modulus for the CML and S1 and S2 layers were obtained from the area enclosed within the box plots, as shown in Fig. 1.13. The average values of indentation modulus obtained for different cell wall layers within a fibre were found to be 22.5–28.0 GPa, 17.9–20.2 GPa, and 15.0–15.5 GPa for the S2 and S1 layers and the CML, respectively. Characterization of natural fibre surfaces of kenaf, hemp and henequen were reported by Sgriccia et al. [45]. The ESEM images of hemp fibre showed the presence of interfibrillar material, hemicellulose and lignin. XPS studies revealed that hemp is more hydrophobic than kenaf as indicated by lower O/C ratio. XPS spectra also revealed that all fibres contained carbon and oxygen, while nitrogen, calcium, silicon and aluminium were detected in some samples. Cellulose, hemicellulose and pectin have an O/C ratio of 0.83 while lignin has a ratio of 0.35. Since the O/C of fibres is found to be less than 0.83, it was concluded that the fibre surface must have a greater proportion of lignin and waxes.

Morphological characterization of okra fibre was studied by Maria et al. [46]. Microscopic examinations of the cross section and longitudinal surface of okra fibres are depicted in Fig. 1.14a and b, respectively. Typically, the structure of an okra fibre consists of several elementary fibres (referred also to as ultimate fibres or cells) overlapped along the length of the fibres and bonded firmly together, by pectin and other non-cellulosic compounds that give strength to the bundle as a whole. However, the strength of the bundle structure is significantly lower than that of elementary cell. The region at the interface of two cells is termed middle lamella (Fig. 1.14a). In common terminology, the bundles of elementary fibres are referred to as technical fibres or single fibres. In longitudinal view, the fibres appear as in Fig. 1.14b, which shows the overlapping of the cells.

Furthermore, the presence of some impurities on the surface of the okra fibre can also be seen, and the fibres are cemented in non-cellulosic compounds. In particular, the cross-sectional shape of okra fibre shows a polygonal shape that varies notably from irregular shape to reasonably circular, as depicted in Fig. 1.15. Their diameter considerably vary in the range of about 40–180 μm. Furthermore, each ultimate cell is roughly polygonal in shape, with a central hole, or lumen like other natural plant fibres, as shown in Fig. 1.15. The cell wall thickness and lumen diameter vary typically between 1–10 μm and 0.1–20 μm, respectively. As a consequence of it,

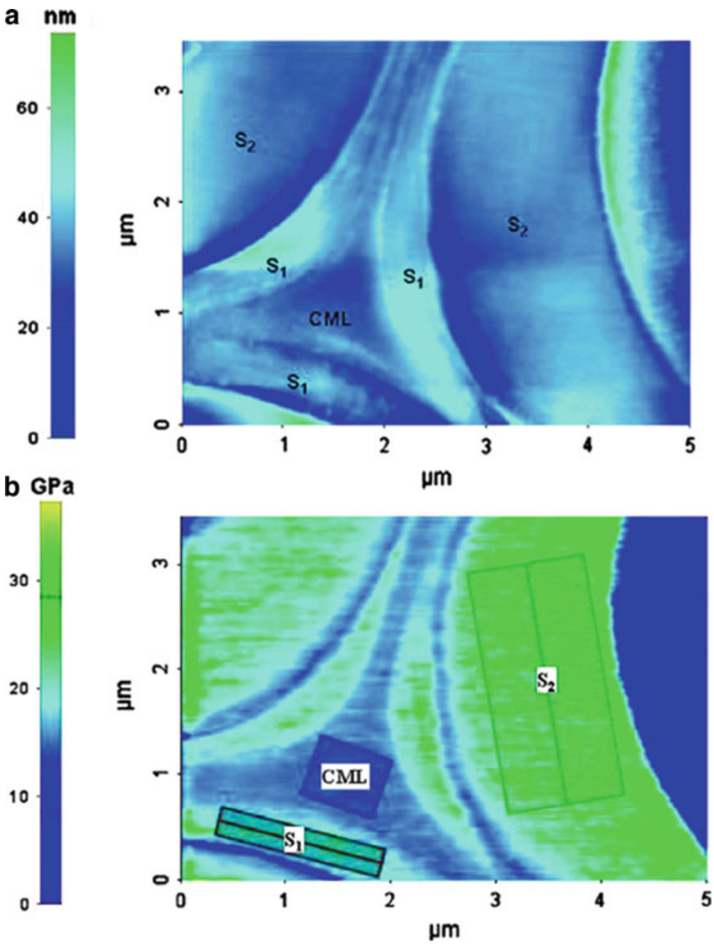


Fig. 1.13 Images of: (**a**) topography and (**b**) box plot analysis of indentation modulus image of various cell wall layers [44]

the considerable difference of the diameter values of the single fibre and lumen and their rough shape strongly affect mechanical and dimensional properties of okra fibres.

In another study, surface morphology of curaua fibres was reported by Spinacé et al. [47]. SEM studies revealed that curaua fibre has a smooth and compact surface, with no fibrillation. The X-ray diffractograms of curaua fibres show three peaks at $2\theta = 16$; 22.6 and 34.7°. These are characteristic of the crystal polymorph I of cellulose. For fibres with higher cellulose content, such as cotton or flax, two peaks around 16° are observed, but for curaua fibres, only one broad peak was observed due to the presence of amorphous materials like lignin, hemicelluloses and amorphous cellulose, which cover the two peaks. In an interesting study, the investigation of surface characterization of banana, sugarcane bagasse and sponge gourd fibres of Brazil was reported by Guimarãesa et al. [48]. It can be seen that the

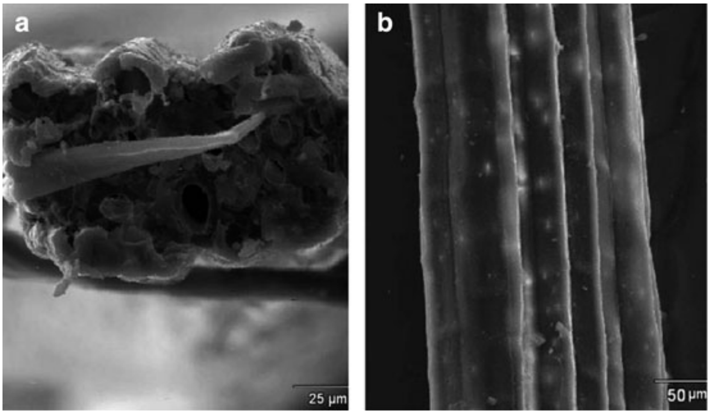


Fig. 1.14 SEM micrographs of (**a**) cross section and (**b**) longitudinal view of okra fibre [46]

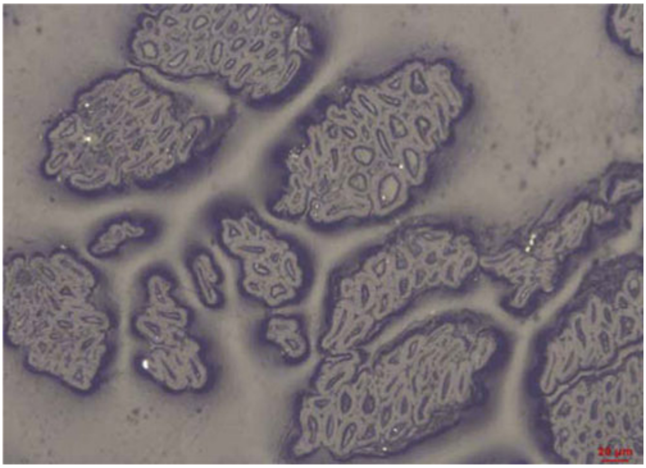


Fig. 1.15 Optical micrograph showing cross section of several okra fibres [46]

three fibres studied (Fig. 1.16) show variations in their structure, namely, different sizes, shape and arrangement of their cells as well as nature of lumen. Cells are non-spherical rather irregular in shape, and cell walls are thick in banana and sponge gourd fibres, while they are almost spherical, compactly arranged and thin walled in the case of bagasse fibre. The central lumen is elliptical (or nearly spherical) and of higher diameter in the case of bagasse fibre compared to other two fibres, which show very narrow and elongated lumen. At higher magnifications, all the fibres show helical winding of microfibrils attached to each other by a binding material (lignin). The interior of these microfibrils show longitudinal array in some cases. The lacuna is present in bagasse fibres, while it seems to be absent in other two fibres. X-ray diffraction patterns of the three fibres exhibited mainly cellulose type I

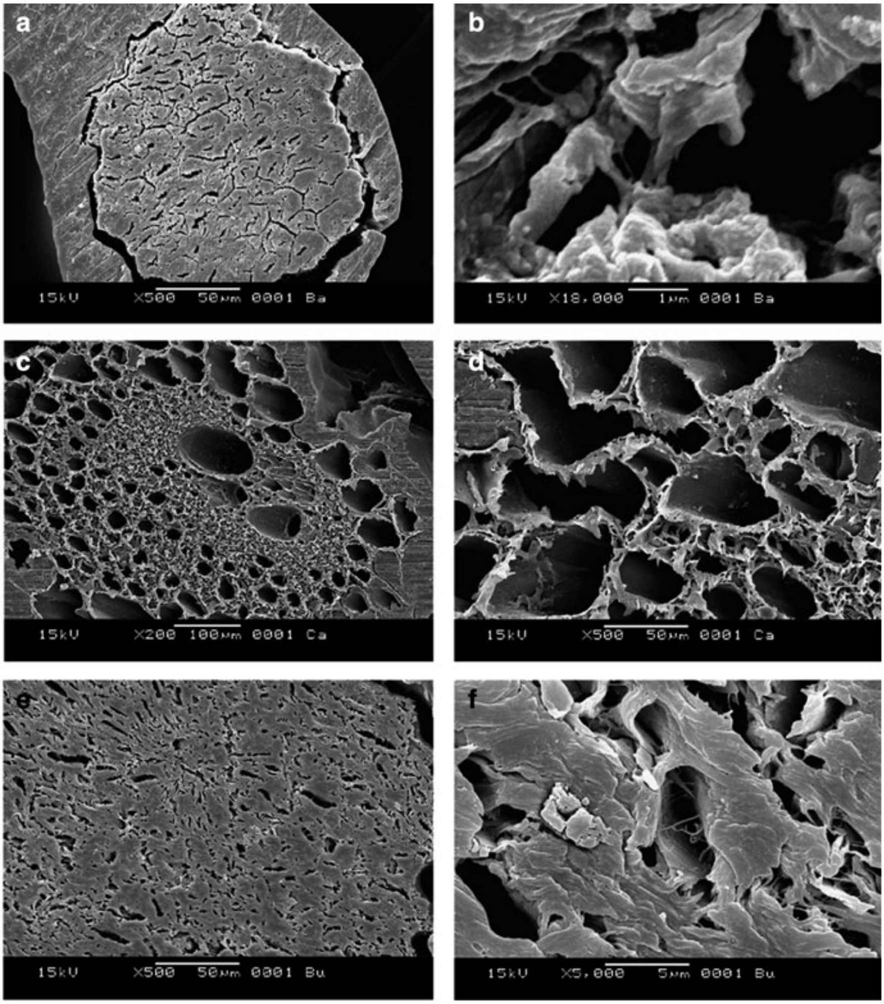


Fig. 1.16 Scanning electron micrographs of cross-sections of fibres (**a** and **b**) banana [**a**: 500×; **b**: 18,000×]; (**c** and **d**) bagasse [**c**: 200×; **d**: 500×;] and (**e** and **f**) sponge gourd [**e**: 500×; **b**: 5000×] [48]

structure with the crystallinity indices of 39%, 48% and 50% for banana, bagasse and sponge gourd fibres, respectively.

In a novel study, Zou et al. [49] reported nanoscale structural and mechanical characterization of the cell wall of bamboo fibres. They reported the discovery of cobble-like polygonal cellulose nanograins with a diameter of 21–198 nm in the cell wall of bamboo fibres. These nanograins are basic building blocks that are used to construct individual bamboo fibres. Nanoscale mechanical tests were carried out on individual fibre cell walls by nanoindentation. It was found that the nanograin structured bamboo fibres are not brittle in nature but somewhat ductile. Figure 1.17a

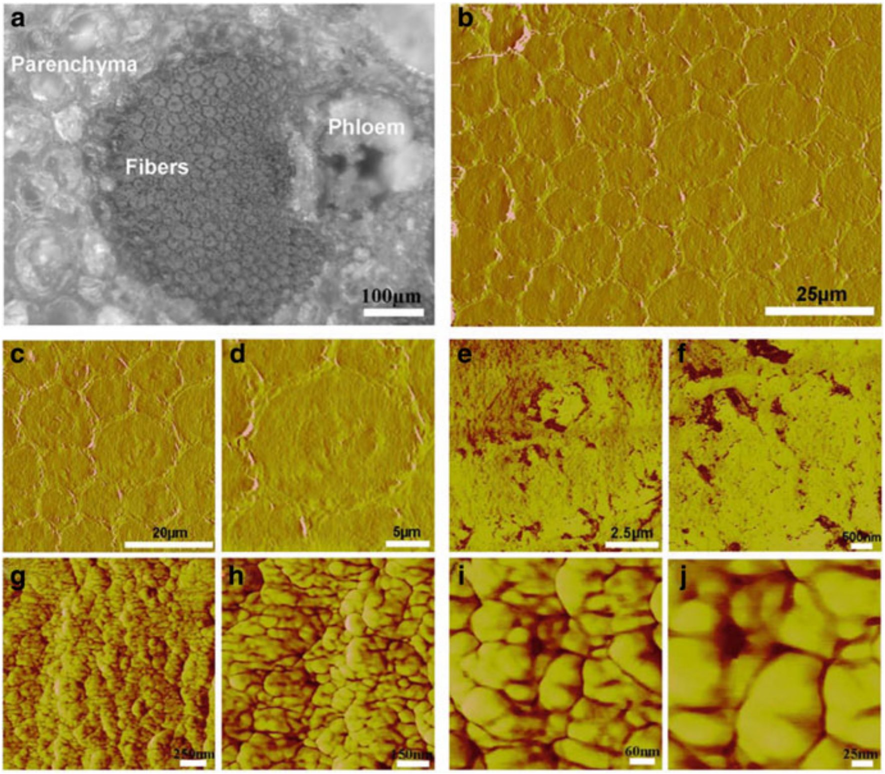


Fig. 1.17 Cross-sectional micrographs of a phloem fibre cap in a vascular bundle of a bamboo culm. (**a**) Optical micrograph of a fibre cap. (**b**)–(**d**) AFM phase images of bamboo fibres. (**e**)–(**j**) AFM phase images of the nanoscale structure in the fibre cell wall [49]

shows a representative optical image of the cross-section of bamboo fibres. It can be seen that a fibre cap with bundles of fibres is embedded among ground parenchyma (Pa) cells with connection to a phloem (Ph). AFM observations (Fig. 1.17b–d) show that these fibres are approximately 5–20 μm in diameter and densely packed within the cap.

Surface characterization of wheat straw fibres using X-ray photoelectron spectroscopy (XPS) was reported by Sain and Panthapulakkal [4]. Elemental surface composition and oxygen to carbon ratio (O/C) of the fibres illustrated that there is more lignin-type surface structure for the fibres. However, slightly higher ratio of oxygen to carbon in the retted fibre indicated a more carbohydrate-rich fibre than the un-retted fibre. The surface chemistry and morphology of spruce (*Picea abies*) mechanical pulps were investigated by Electron spectroscopy for chemical analysis (ESCA) and AFM [50]. As determined by ESCA, the content of lignin was slightly higher on the pulp surface than in the whole pulp. The AFM studies showed that the surfaces of mechanical pulp fibres are very heterogeneous, i.e., different cell wall layers are exposed along the fibre surface.

1.2.7 Applications of Natural Fibres

1.2.7.1 Natural Fibre-Based Composites

Natural fibres possess sufficient strength and stiffness but are difficult to use in load bearing applications by themselves because of their fibrous structure. Most plastics themselves are not suitable for load bearing applications due to their lack of sufficient strength, stiffness and dimensional stability [51]. In natural fibre reinforced composites, the fibres serve as reinforcement by giving strength and stiffness to the structure while the plastic matrix serve as the adhesive to hold the fibres in place so that suitable structural components can be made. The matrix for the natural fibres includes thermosets, thermoplastics and rubber. Different plant fibres and wood fibres are found to be interesting reinforcements for rubber, thermoplastics and thermosets [52–58].

In recent years, a new class of fully biodegradable “green” composites [59–63] have been made by combining natural fibres with biodegradable resins. The major attraction of green composites is that they are fully degradable and sustainable, that is, they are truly “green”. Green composites may be used effectively in many applications with short lifecycles or products intended for one-time or short-term use before disposal. A number of natural biodegradable matrices are also available for use in such green composites. Some of them are polysaccharides (starch, cellulose, chitin), proteins (casein, albumin, fibrogen, silks), polyesters (polyhydroxy alkanoates) and other polymers, which include lignin, lipids, natural rubber and shellac [64–66]. These natural biodegradable polymers show a range of properties and can compete with non-biodegradable polymers in different industrial field.

To fabricate advanced green composites having high strength, Netravali et al. [67] used cellulose fibres spun using liquid crystalline (LC) solutions prepared by dissolving cellulose in phosphoric acid. The dry-jet wet spinning technique similar to what is used to spin aramid fibres such as Kevlar was used in spinning these fibres. The strengths of these LC cellulose fibres were in the range of 1,700 MPa, which is by far the highest strength achieved for cellulose-based fibres. In another study, to make advanced composites, Huang and Netravali [68] developed soy protein concentrate-based resins that were modified using a cross-linking polycarboxylic acid to form interpenetrating network-like resin systems with excellent mechanical properties.

1.2.7.2 Natural Fibres in Automobiles

The automotive industry is the prime driver of “green composites” because the industry is faced with issues for which green materials offer a solution [69]. Many components for the automotive sector are now made from natural fibre composite materials [70]. Natural fibres have intrinsic properties like mechanical strength, low weight and low cost, ecological sustainability, low energy requirements for production, end of life disposal and carbon dioxide neutrality – that have made them particularly attractive to the automobile industry. In Europe, car makers are using mats made from abaca, flax and hemp in press-moulded thermoplastic panels for door liners, parcel shelves, seat backs, engine shields and headrests. Daimler Chrysler, already a major user of natural fibre composites in the interior trim components such as dash boards and door panels using polypropylene and natural fibres, has increased its research and development investment in flax/polyester composite for exterior or semi-exterior applications [70, 71].

For consumers, natural fibre composites in automobiles provide better thermal and acoustic insulation than fibre glass and reduce irritation of the skin and respiratory system. The low density of plant fibres also reduces vehicle weight, which cuts fuel consumption [72]. Alves et al. [73] studied the life cycle assessment (LCA) analysis of the replacement of glass fibres by jute fibres as reinforcement of composite materials to produce automotive structural components in the structural frontal bonnet of an off-road vehicle (Buggy).

1.2.7.3 Natural Fibres in Construction

Natural fibre composites offer vast opportunities for an increasing role as alternate materials, especially wood substitutes in the construction market [74]. Various natural fibre-based composites products such as laminates, panels, partitions, door frames, shutters, and roofing have been produced as an alternative to existing wood materials. Production of jute pultruded door frames, coir/cement roofing sheets, sisal/glass fibre-epoxy shutting plate and sisal/polyester roofing sheets were reported by Singh and Gupta [74]. Composite doors can be made by bonding the jute/sisal laminate face sheets with rigid foam cores [75]. Prospects for natural fibre-reinforced concretes in construction application were studied by Aziz et al. [76]. The studies revealed that natural fibre-reinforced concrete products like sheets (both plain and corrugated) and boards are light in weight and are ideal for use in roofing, ceiling and walling for the construction of low cost houses. Performance of “Agave lecheguilla” natural fibre in Portland cement composites exposed to severe environment conditions was reported by Juárez et al. [77]. In another study, fracture and fatigue of natural fibre-reinforced cemetitious composites was reported by Savastano et al. [78]. They enumerated the results of an experimental study of resistance-curve behaviour and fatigue crack growth in cementitious matrices reinforced with eco-friendly natural fibres. Study of window frame fabrication by injection moulding process was carried out by Rahman et al. [79]. Rice husk filled high-density polyethylene was used as the raw material. Solid and hollow designs were created to compare the pros and cons of each design. The investigations were carried out on flowing, packing, cooling and costing of injection-moulded window frame. From the analysis, they concluded that window frame with hollow design is preferable, since hollow design has the advantage of filling, packing, and cooling properties. The hollow design also costs less than solid design of window frame. However, high injection pressure and clamping tonnage are unfavourable for hollow design.

Durability of compression-moulded sisal fibre reinforced mortar laminates were reported by Toledo et al. [80].

1.2.7.4 Natural Fibres in Soil Conservation

Natural fibres possess a distinctive characteristic, which makes them excellent materials for soil conservation. Coir fibre has very good application in erosion control markets for landscaping. The mesh of woven coir matting acts as miniature dams and prevents the seeds from washing away by rain and wind and facilitates the growth [81] Geotextiles are promising new outlet for natural fibre producers. Originally developed in the Netherlands for the construction of dykes, geotextile nets made from hard natural fibres strengthen earthworks and encourage the growth of plants and trees, which provide further reinforcement. Unlike plastic textiles used for the same purpose, natural fibre nets – particularly those made from coir – decay over time as the earthworks stabilise. Mwasha [82] reported the use of environmentally friendly geotextiles for soil reinforcement. The studies demonstrated the potential for the use of sustainable biodegradable vegetable fibres over man-made polymeric materials in ground improvement. Utilisation of palm-leaf geotextile mats to conserve loamy sand soil in the United Kingdom was reported by Bhattacharyya et al. [83]. The studies recommended to cover palm-mat geotextiles as buffer strips for soil and water conservation on erodible moderate slopes.

Subaida et al. [84] reported the beneficial use of woven coir geotextiles as reinforcing material in a two-layer pavement section. The test results indicated that the inclusion of coir geotextiles enhanced the bearing capacity of thin sections. Placement of geotextile at the interface of the subgrade and base course increased the load carrying capacity significantly at large deformations. Datye and Gore [85] presented a review of the development of natural geotextiles and related materials such as wood and bamboo for a wide range of applications. The geotextile is used in conjunction with reinforced soil constructions, where small-dimensioned timber and bamboo were used as reinforcement in the form of cribs.

1.3 Nanofibres from Natural Fibres

Nanofibres are fibres that have diameter equal to or less than 100 nm. One of most significant characteristic of nanofibres is the enormous availability of surface area per unit mass. The high surface area of nanofibres provides a remarkable capacity for the attachment or release of functional groups, absorbed molecules, ions, catalytic moieties and nanometre scale particles of many kinds.

In recent years, considerable research has been done on the isolation of nanofibres from plants to use them as fillers in biocomposites [86–90]. Agricultural crop residues are one of the most valuable sources of natural cellulose nanofibres. It should be noted that in agricultural fibres, the cellulose microfibrils are less tightly wound in the primary cell wall than in the secondary wall in wood, thus fibrillation to produce nanocellulose should be less energy demanding [91]. Cellulose nanofibres can be extracted from agricultural by-products of different plants such as flax, hemp, sisal, corn, wheat, rice, sorghum, barley, sugar cane, pineapple, banana and coconut crops.

The nanostructure of cellulose can play a significant part in papermaking and manufacture of high quality nanocomposites, as well as in technology of promising health care nano products [92]. The small dimensions of cellulose fibrils enable direct contact between cellulose and matrix polymers, allowing for a large contact surface and thus excellent adhesion. Cellulose nanofibres can be used as a rheology modifier in foods, paints, cosmetics and pharmaceuticals [91]. It seems that among various applications, use of nanocellulose and its derivatives in health care areas will be especially promising due to their high strength and stiffness combined with low weight, biocompatibility and renewability.

1.3.1 Cellulose as a Nanostructured Polymer

Cellulose is the most eminent representative of nanostructures occurring in wood, cotton, hemp, flax and other plant-based materials and serving as the dominant reinforcing phase in plant structures. Cellulose is also synthesised by algae, tunicates, and some bacteria [93–95]. Cellulose fibres are bundles of microfibrils where the cellulose molecules are always biosynthesized in the form of nanosized fibrils. Up to 100 glucan chains are grouped together to form elementary fibrils, which aggregate together to form cellulose nanosized microfibrils or nanofibres [96]. Fibrils have diameters in the nanometre and lengths in the micrometre scale. The production of nanoscale cellulose fibres and the application of cellulose nanofibres in polymer reinforcement is a relatively new research field. Plant-based cellulose nanofibres have great reinforcing potential because of their sustainability, easy availability, and the related characteristics such as a very large surface to volume ratio, high tensile strength, high stiffness, high flexibility and good dynamic mechanical, electrical and thermal properties as compared to other commercial fibres [97, 98]. These nanofibre-reinforced polymer composites give improved properties compared to the neat polymer and micro composites based on the same fibres. The use of cellulose nanofibres as reinforcing elements in the polymer matrix has been predicted to create the next generation of value-added novel eco-friendly nanocomposites.

1.3.2 Extraction Methods for Obtaining Nanocellulose from Natural Fibres

Many studies have been done on extracting cellulose nanofibrils from various sources and on using them as reinforcement in composite manufacturing. The nano architecture of the cellulose promotes isolation of nanofibrils from initial fibres by various methods that facilitate breaking up of the glycosidic bonds in the disordered nanodomains of nanofibrils and cleaving of interfibrillar contacts [92].

Several sources of cellulose have been used to obtain cellulose nanofibres including banana residues [87, 90], soybean source [99], cotton [100], wheat straw [86], bacterial cellulose [101–104], sisal [88, 105], hemp [89, 106], sugar beet pulp [107, 108], potato pulp [109], bagasse [110], stems of cacti [111] and algae [112].

Cellulose nanofibres can be extracted from the cell walls by different types of isolation processes: simple mechanical methods [113], a combination of chemical and mechanical methods [109, 114] or an enzymatic approach [115] etc. Depending upon the raw materials and fibrillation techniques, the cellulose degree of polymerization, morphology and nanofibre aspect ratio may vary [116]. A purely mechanical process can produce refined fine fibrils having a web-like structure. The chemical treatment mainly involves the hydrolysis of cellulose, followed by mechanical disintegration or ultrasound sonification. The combination of acid hydrolysis and high pressure disintegration permits isolation of nano crystalline particles having lengths of 100–200 nm and widths of 20–40 nm. The enzymatic pre-treatment of cellulose fibres, followed by mechanical splitting in water by means of special high-shear mills or refiners, lead to the formation of nanofibrillated cellulose with average diameters of the nano-bundles about 100 nm and length greater than 1 μm. Repeated milling of the pulp in water over a long period of time permits complete fibrillation of the cellulose nanofibrils and turn these into nanofibrils. Dissolving methods and cryocrushing process of hydrolysed cellulose have also been used for the extraction of nanocellulose [92].

Cryocrushing is an alternative method for producing nanofibres in which fibres are frozen using liquid nitrogen and high shear forces are then applied [117]. When high impact forces are applied to the frozen fibres, ice crystals exert pressure on the cell walls, causing them to rupture and thereby liberating microfibrils. The cryocrushed fibres may then be dispersed uniformly into water suspension using a disintegrator before high pressure fibrillation [91]. Several researchers adopted cryocrushing method to extract cellulose nanofibres from soybean stock [99], chemically treated flax and hemp fibres [106] and wheat straw fibres [86]. Various methods used for the preparation of cellulose nanofibres are shown in Table 1.2.

1.3.3 Characterisation Techniques for Nanofibres

Detailed structural examination is essential to investigate the potential of cellulose nanofibre as reinforcement in polymer composites. Several characterization techniques were used to study the ultrastructure of cellulose obtained from various sources. Various techniques such as TEM, field emission scanning electron microscopy (FESEM), SEM, AFM and wide-angle X-ray scattering (WAXS) have been used to characterise the morphology of cellulose nanofibres. TEM and AFM aid

Table 1.2 Examples of cellulose nanofibre preparation procedures

Method	Raw material	Procedure	Nanofibre dimension
Mechanical treatment	Bleached potato pulp	Disintegration in a Waring blender;	~5 nm in width
	Cladodes of Opuntia ficus indica	Homogenisation by 15 passes through a laboratory homogeniser, operated at 500 bars and 90–95°C	
	Kraft pulp	Passing 2–30 times through a refiner with a gap of 0.1 mm, subsequently passing through a high pressure homogeniser 2–30 times	ND
		Passing through a refiner with a gap of 0.1 mm 30 times, subsequently passing through a high pressure homogeniser up to 30 times and finally grinder treatments up to 10 times	
		Cryocrushing followed by 20 passes through a defibrillator at 500–1,000 bar	50–100 nm in width and several nm in length
		Beating and refining in a PFI mill; 20 passes through a defibrillator at 500–1,000 Pa	
	Soybean stock	Cryocrushing followed by fibrillation using a Cramer disintegrator at 2,000 rpm; homogenization by 20 passes through a laboratory defibrillator at pressure above 300 bar	50–100 nm in width and several nm in length
	Wheat straw	Microfibrillation by super-grinder	20–120 nm in width, the majority around 30–40 nm
		Cryocrushing followed by high shear homogenisation	
	Wood pulps, Tunicin cellulose, chitosan, collagen	Disintegration by means of an Ultra-Turrax mixer at 24,000 rpm followed byhomogenisation by a high-pressure laboratory homogeniser at 300 bar for 10–15 passes	20–90 nm in width
	Hemp fibre, spring flax, bleached kraft pulp, Rutabaga		5–80 nm in width, the majority around 10–60 nm
	Dried sugar beet pulp chips		30–100 nm and a length of several nm
	Never-dried bleached sulfite/kraft pulp		Few nanometre in width

(*continued*)

Table 1.2 (continued)

Method	Raw material	Procedure	Nanofibre dimension
Chemical treatment		TEMPO-mediated oxidation, followed by disintegration in a Waring blender	
	Sugar beet pulp	Disintegration in a Waring blender; homogenisation by 15 passes through a laboratory homogeniser, operated at 500 bars and 90–95°C; TEMPO mediated oxidation	ND
	Banana fibre, Pine apple leaf fibre (PALF)	Acid treatment coupled with high pressure defibrillation	Banana fibre having 4–5 nm in diameter and 200–250 nm in length PALF having 5–60 nm in diameter and 200–300 nm in length
Enzymatic pretreatment	Bleached kraft pulp	Enzymatic pre-treatment by fungus OS1 (isolated from infected Elm trees), followed by high shear refining, cryocrushing and dispersion in water by a disintegrator	10–250 nm in width, the majority is around 25–75 nm
	Bleached sulfite softwood cellulose pulp	Refining to increase the accessibility of the cell wall to the subsequent monocomponent endoglucanase treatment; enzymatic treatment; second refining stage; high-pressure homogenising	5–30 nm in diameter
	Softwood sulfite pulp	Beating in a PFI-mill; enzymatic treatment with endoglucanase (Novozyme 476); second beating;	5–30 nm in diameter
	Softwood dissolving pulp	High-pressure homogenisation	

Siró and David [91]

the interpretation of structures from the nanometre to the micrometre size scale. Typical information obtained from conventional TEM is length, aspect ratio, shape and the aggregated or isolated state of fibres. AFM has also been used to examine plant cell walls at a similar resolution to that of the TEM. This type of microscopy has the important advantage of reducing the risks of introducing artefacts resulting from the preparative techniques. These techniques were applied to study the cellulose nanofibres obtained from various sources such as banana, cotton, hemp, sisal ramie, wheat straw, soybean stock, bacterial cellulose, sugar beet, etc. In the literature, there are reports of cellulose nanofibre characterisations using various techniques such as AFM, TEM, SEM, etc.

Teixeira et al. [100] extracted cellulose nanofibres from white and naturally coloured cotton (brown, green and ruby) by acid hydrolysis method. The yields of the various cotton nanocelluloses were around 65 wt% for white nanofibres and 52 wt% for others. Morphological study of several cotton nanofibres by scanning transmission electron microscopy (STEM) and AFM analyses revealed that the nanofibres had a length of the 85–225 nm and diameter of 6–18 nm. The micrographs also indicated that there were no significant morphological differences among the nanostructures from different cotton fibres. The thermal studies showed that the coloured nanofibres were thermally more stable in isothermal oxidising conditions at 180°C than white nanofibres. Figures 1.18 and 1.19 show the TEM and AFM images of white cotton fibres.

Menezes et al. [118] also extracted cellulose nanocrystals or whiskers of ramie fibres by acid hydrolysis. Acid hydrolysis of native ramie cellulose fibres leads to aqueous suspensions of elongated nanocrystals with high aspect ratio. The geometric average length and diameter were around 134 ± 59 nm and 10.8 ± 4.5 nm, respectively, giving rise to an aspect ratio around 12. A minimum of 228 and 70 measurements were used to determine the length and the diameter, respectively, of ramie whiskers. They noticed that more than 50% of the

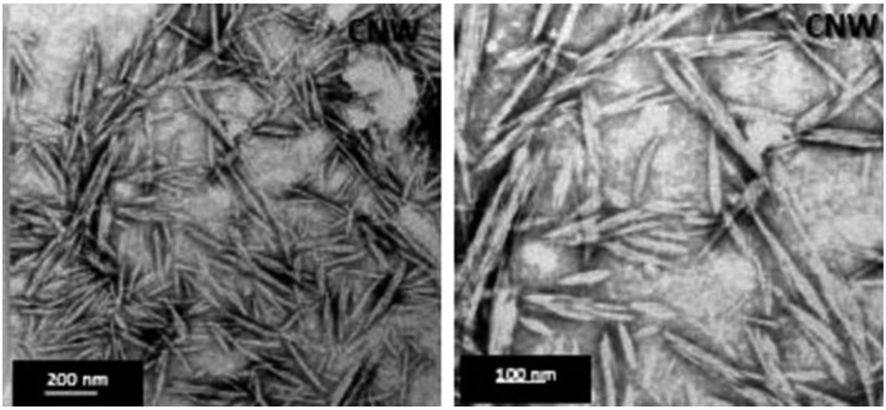


Fig. 1.18 Transmission electron micrographs of nanofibres of white cotton fibres at two magnifications [100]

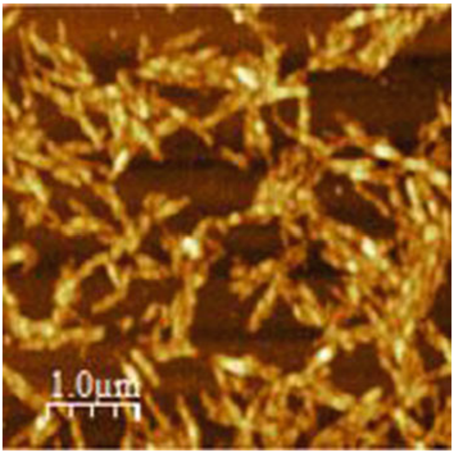
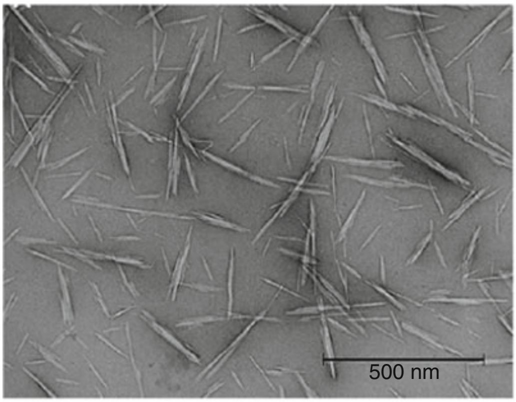


Fig. 1.19 AFM images of nanofibres of white cotton fibres [100]



Length: 134 nm ± 59 nm (228 measurements)	Diameter: 10.8 nm ± 4.5 nm (70 measurements)

Fig. 1.20 Transmission electron micrograph of ramie cellulose whiskers [118]

nanoparticles have a length lower than 100 nm. Figure 1.20 shows the transmission electron micrograph of ramie cellulose whiskers

Alemdar and Sain [86] extracted Cellulose nanofibres of wheat straw and soy hulls, by a chemi-mechanical technique. They analysed the morphology and physical properties of the nanofibres by scanning and transmission electron microscopy. The wheat straw nanofibres have diameters in the range of 10–80 nm and lengths of a few thousand nanometres, and the soy hull nanofibres have diameters in the range of 20–120 nm and shorter lengths than the wheat straw nanofibres. Fig. 1.21a and b shows the TEM pictures of the wheat straw and soy hull nanofibres. The image shows the separation of the nanofibres from the micro-sized fibres. The thermal properties of the nanofibres were studied by the TGA technique and found that the

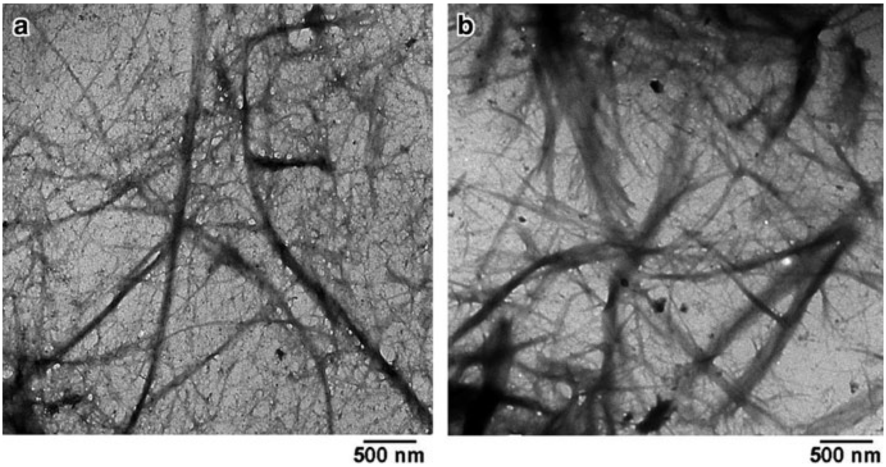


Fig. 1.21 Transmission electron micrographs of the (**a**) wheat straw and (**b**) soy hulls nanofibres [86]

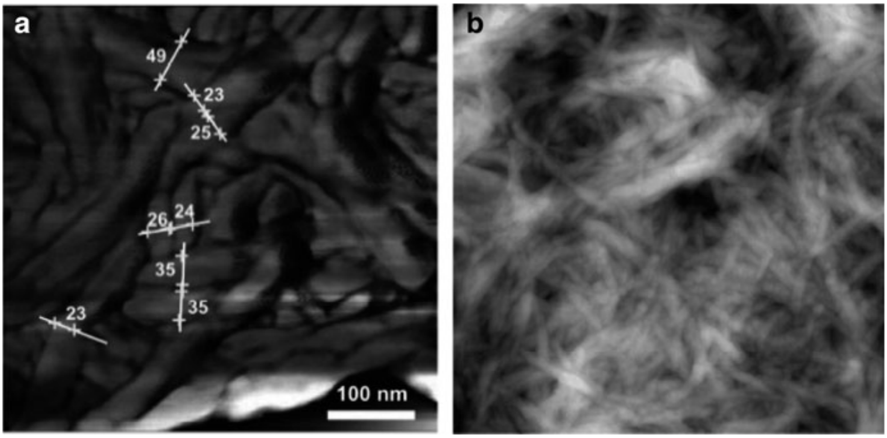
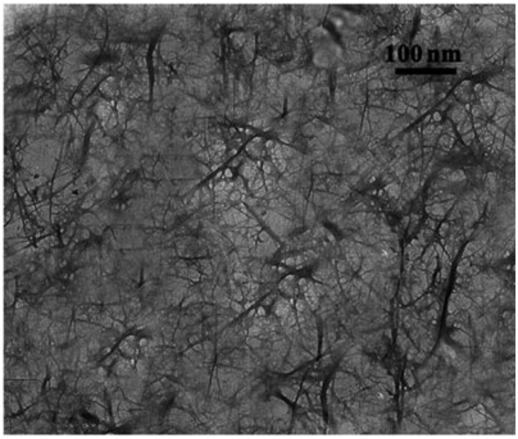


Fig. 1.22 SFM pictures of banana nanofibres [87]

processed fibres shows higher thermal stability. The degradation temperature of both nanofibre types reached beyond 290°C.

Cherian et al. [87] extracted cellulose nanofibres from the pseudo stem of the banana plant by using acid treatment coupled with high pressure defibrillation. Characterization of the fibres by (Scanning Force Microscopy) SFM and TEM showed that there is reduction in the size of banana fibres to the nanometre range (below 40 nm). The average length and diameter of the developed nanofibrils were found to be between 200–250 nm and 4–5 nm, respectively. Figures 1.22a, b and 1.23 show the SFM and TEM pictures of banana nanofibres, respectively.

Fig. 1.23 Transmission electron micrographs of the banana nano fibres [87]



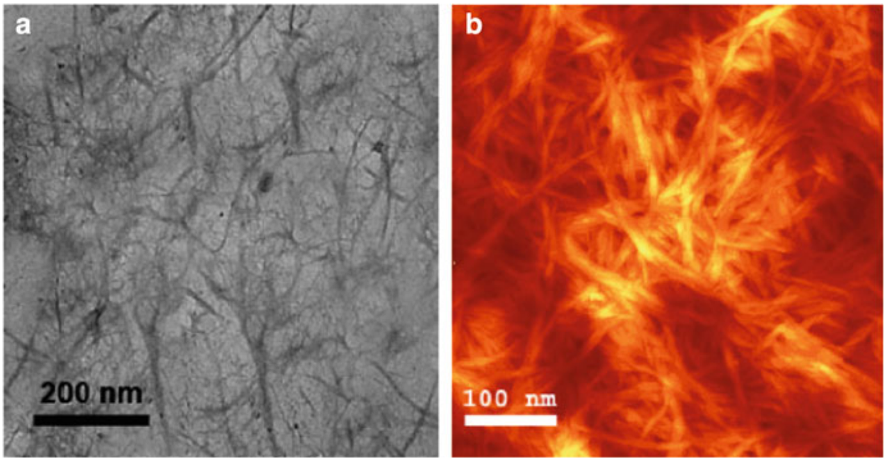


Fig. 1.24 (**a**) Atomic force micrographs of cellulose nanofibres of PALF (**b**) TEM of cellulose nanofibres of PALF [119]

Cherian et al. [119] also extracted cellulose nanofibres from pineapple leaf fibres using acid-coupled steam treatment. The structural and physicochemical properties of the pineapple leaf fibres were studied by environmental scanning electron microscopy (ESEM), AFM and TEM and X-ray diffraction (XRD) techniques. The acid-coupled steam explosion process resulted in the isolation of PALF nanofibres having a diameter range of 5–60 nm. Figure 1.24a and b shows the AFM and TEM images of nano fibres obtained from pineapple leaf fibres. AFM and TEM support the evidence for the isolation of individual nanofibres from PALF.

Wang et al. [89] extracted the cellulose nanofibres of hemp fibre by a chemi-mechanical process, and the structural details were studied with SEM, TEM and

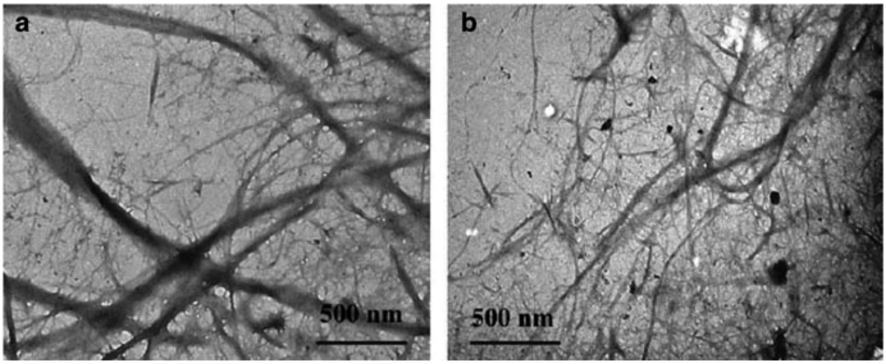
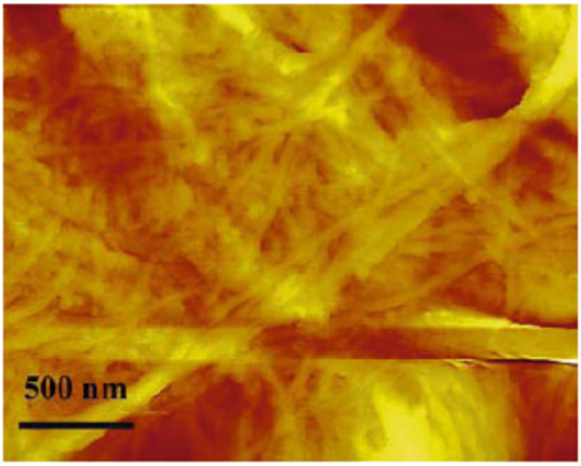


Fig. 1.25 Transmission electron micrographs of (**a**) unbleached, (**b**) bleached hemp nanofibres [89]

Fig. 1.26 Atomic force micrographs of unbleached hemp nanofibres [89]



AFM. The widths of unbleached nanofibres of hemp were estimated between 50 and 100 nm, and most of them had a diameter range of 70–100 nm. Bleached nanofibres of hemp produced smaller widths (30–100 nm) compared with that of unbleached nanofibres, and most of the bleached nanofibres had a diameter range of 30–50 nm. Aspect ratios of the extracted cellulose nanofibres were estimated from transmission electron micrographs. The aspect ratio of the bleached and unbleached nanofibres were found to be 82 and 88, respectively. TEM and AFM images of hemp nanofibres are shown in the Figs. 1.25 and 1.26, respectively. TEM and AFM images showed that the high-pressure defibrillation leads to individualization of the cellulose nanofibres from the cell wall.

Wang and Sain [99] extracted cellulose nanofibres from a soybean source by combining chemical and mechanical treatments. Isolated nanofibres were shown to have diameter between 50 and 100 nm and the length in micrometre scale, which

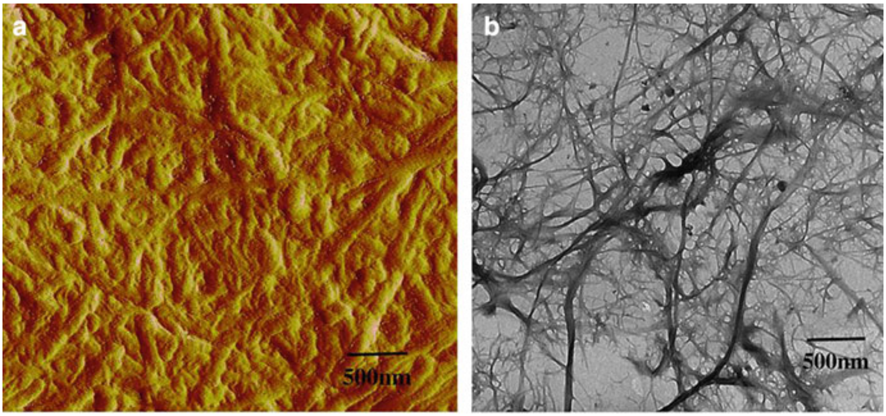


Fig. 1.27 (**a**) Atomic force micrographs of SBN (**b**) TEM of diluted suspension of SBN in water (Wang and Sain 2007)

results in very high aspect ratio. The nanofibres were characterised by using SEM, AFM and TEM analysis. AFM was used to investigate the size of the dispersed nanofibres. The atomic force micrograph (Fig. 1.27a) shows the size of the nanofibres within the range of 50–100 nm in width and several nm in length. Figure 1.27b shows the TEM picture of soybean nanofibres in water suspension.

Besides microscopic techniques, the extent of fibrillation can be assessed indirectly by other measurements. Degree of cellulose polymerization (DP) is reported to correlate strongly with the aspect ratio of the nanofibres; longer fibrils are associated with higher cellulose DP [91]. The DP for the raw material (sulfite pulp) is often reported to be around 1,200–1,400, while mechanical isolation of nanofibres may result in about 30–50% decrease in DP [93]. Depending on the nature of the starting material, the DP of microfibrillated cellulose may be even lower. For example, Iwamoto et al. [94] reported that the DP of microfibrillated cellulose decreased from about 770 to 525 after 9 passes through a grinder. High cellulose DP is desirable for microfibrillated cellulose nanofibres since this is correlated with increased nanofibre tensile strength [93].

1.4 Conclusion

“Back to Nature” is the present day mantra of the modern world. The current trend is to find out new materials based on natural substances. Increased environmental awareness and the current economic situations tempt the modern man to make use of Natural fibres in developing new composite materials. Natural fibres are extracted from various parts of plants, and several extraction procedures are in vogue. The fibre properties depend on the part of the plant from which the fibres are obtained and the extraction methods used.

Nowadays, researchers are increasingly acknowledging the importance of Nanomaterials because of their exciting properties due to their high surface area. Natural fibres serve as a very good source for cellulose, which is the most abundant bio polymer and nanomaterial. As a result of its sustainability, biocompatibility and biodegradability, cellulose is gaining more and more importance nowadays. Nanofibre-reinforced polymer composites give improved properties compared to the neat polymer and micro composites based on the same fibres. Nanofibre-reinforced polymer composites are likely to become the next generation of value-added novel eco-friendly composites.

References

1. Bismarck A, Mishra S, Lampke T et al (2005) Plant fibres as reinforcement for green composites. In: Mohanty AK, Misra M, Drzal LT (eds) Natural fibres biopolymers and biocomposites. CRC, Boca Raton, p 37
2. Bogoeva-Gaceva G, Avella M, Malinconico M, Buzarovska A, Grozdano A, Gentile G, Errico ME et al (2007) Natural fibre eco-composites. Polym Compos 28:98–107
3. Anandjiwala RD (2006) The role of research and development in the global competitiveness of natural fibre products. Proceedings, Natural fibres vision 2020, New Delhi 8–9th December
4. Sain M, Panthapulakkal S (2006) Bioprocess preparation of wheat straw fibres and their characterization. Ind Crops Prod 23:1–8
5. Morton WE, Hearle JWS (1993) Physical properties of textile fibres. The Textile Institute, Manchester, UK
6. Weisman S, Haritos VS, Church JS et al (2010) Honeybee silk: recombinant protein production, assembly and fiber spinning. Biomaterials 1–6 DOI:10.1016/j.biomaterials.2009.12.021
7. Kelsall RW, Hamley IW, Geoghegan M (2005) Handbook of textile fibres II. Man-made fibres. Wiley, UK
8. Matthew’s MH (1954) Textile fibres: their physical, microscopic, and chemical properties. John Wiley and Sons Inc., New York
9. Press J (1959) Man-made textile encyclopedia. Textbook Publishers Inc., London
10. Shi J, Lua S, Du N, Liu X, Song J et al (2008) Identification, recombinant production and structural characterization of four silk proteins from the Asiatic honeybee Apis cerana. Biomaterials 29:2820–2828
11. Sutherland TD, Weisman S, Trueman HE, Sriskantha A, Trueman JWH, Haritos VS et al (2007) Conservation of essential design features in coiled coil silks. Mol Biol Evol 24:2424–2432
12. Poole AJ, Church JS, Huson MG et al (2009) Environmentally sustainable fibers from regenerated protein. Biomacromolecules 10:1–7
13. Bledski AK, Gassan J (1999) Composites reinforced with cellulose-based fibres. Prog Polym Sci 24:221–274
14. Franco PHJ, Valadez-Gonzalez M (2005) Fibre-matrix adhesion in natural fibre composites. In: Mohanty AK, Misra M, Drzal LT (eds) Natural fibres, biopolymers and biocomposites. CRC, Boca Raton, p 37
15. Nevell TP, Zeronian SH (1985) Cellulose chemistry and its applications. Wiley, New York
16. Toumis GT (1991) Structure, properties and utilization. Science and technology of wood. Van Nostrand Reinhold, New York, p 494
17. Zimmermann T, Pohlerand E, Geiger T (2004) Cellulose fibrils for polymer reinforcement. Adv Eng Mater 6, No. 9

18. Rong MZ, Zhang MQ, Liu Y, Yang GC, Zeng HM et al (2001) Effect of fibre treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. Compos Sci Technol 61:1437–1447
19. Murali MRK, Mohana RK (2007) Extraction and tensile properties of natural fibres: Vakka, date and bamboo. Compos Struct 77:288–295
20. Foulk JA, Akin DE, Dodd RB et al (2001) Processing techniques for improving enzyme-retting of flax. Ind Crops Prod 13:239
21. Yu H, Yu C (2007) Study on microbe retting of kenaf fibre. Enzyme Microb Technol 40:1806–1809
22. Goodman AM, Ennos AR, Booth I et al (2002) A mechanical study of retting in glyphosate treated flax stems. Ind Crops Prod 15:169
23. Heinemann O (1997) Standroste vonFlachs-Innovation in derFlachserntetechink in VDI/ MEG Kolloquium Agrartechink:Erzeugung, Aufbereitung und Verarbeitung von Naturfasern fur nichttextile Zwecke. 22 Bonn:101
24. Terentie P, Neacsu H (1995) Die Gewinnung von Textilfasern aus Hanfstengeln, Proceedings Biorhstoff Hanf-Resource Hemp, Reader zum Technologisch-wis senschaftlichen Symposium. Nova-Institut (Hrsg.), Frankfurt, March 2–5:278
25. Katalyse-Institut furangewandte Umweltforschung (Hrsg.) Hanf & Co. (1995) Die Renaissance der heimischen Faserpflanzen, Verlag Die Werkstatt, Gottingen
26. Folster Th, Michaeli W (1993) Flachs-eine nachwachsende Verstarkungsfaser fur Kunststoffe? Kunststoffe 83:687
27. Kessler RW, Kohler BU, Rgoth B et al (1998) Steam explosion of flax- a superior technique for upgrading fibre value. Biomass Bioenergy 14:237–249
28. Kohler R, Kessler RW (1999) Designing Natural fibres for advanced materials. Proceedings of the 5th International Conference on wood fibre plastic composites, Madison, may 26–28: 29–36
29. Wurster J, Daul D (1988) Flachs, eine durch Forschung moderene alte Kulturpflanze. Melliland Textilber 12:551
30. Rowell RM, Han JS, Rowell JS et al (2000) Characterization and factors effecting fibre properties in natural polymers and agro fibres based composites. In: Frollini E, Leao AL, Mattoso LH (eds) Natural polymers and biobased composites, USP, Unesp, Embrapa, Brazil p 115–135
31. Gassan J, Bledzki AK (1995) Internationales Techtexil Symposium, Frankfurt, 20–22 June
32. Kritschewsky GE (1985) Chemische technology von textil materialien. Moskau, Legprombitisdat
33. Sadov F, Korchagin M, Matetsky A et al (1978) Chemical technology of fibrous materials. Mir Publishers, Moscow
34. Oke IW (2010) Nanoscience in nature: Cellulose nanocrystals. Studies by undergraduate researchers at Guelph, Winter 3:77–80
35. Whistler RL, Richards EL (1970) Carbohydrates, vol 2A. Academic, New York
36. Gassan J, Chate A, Bledzki AK et al (2001) J Mater Sci 36:3715
37. David N, Hon S, Shiraishi N et al (1991) Wood and cellulose chemistry. Marcel Dekker, New York
38. Frey-Wyssling A (1954) The fine structure of cell micro-fibrils. Science 119:80
39. Krassig HA (1992) Cellulose. Gordon and Breach Science Publishers, New York
40. Dufresne A (1998) In recent research developments in macromolecules. Pandalai SG (eds) Research Signpost 3:455–474
41. Pietak A, Korte S, Tan E, Downard A, Staiger MP et al (2007) Atomic force microscopy characterization of the surface wettability of natural fibres. Appl Surf Sci 253:3627–3635
42. Tomczak F, Deme´trio Sydenstricker TH, Satyanarayana KG et al (2007) Studies on lignocellulosic fibres of Brazil Part II: morphology and properties of Brazilian coconut fibres. Compos Part A 38:1710–1721

43. Bessadok A, Marais S, Roudesli S, Lixon C, Me´tayer M et al (2008) Influence of chemical modifications on water-sorption and mechanical properties of agave fibres. Compos Part A 39:29–45
44. Sandeep SN, Wanga S, Hurley DC et al (2010) Nanoscale characterization of natural fibres and their composites using contact-resonance force microscopy. Compos: Part A 41:624–631
45. Sgriccia N, Hawley MC, Misra M et al (2008) Characterization of natural fibre surfaces and natural fibre composites. Compos Part A 39:1632–1637
46. Maria DRI, Kenny JM, Puglia D, Santulli C, Sarasini F et al (2010) Morphological, thermal and mechanical characterization of okra (Abelmoschus esculentus) fibres as potential reinforcement in polymer composites. Compos Sci Technol 70:116–122
47. Spinacé MAS, Lambert CS, Fermoselli KKG, De Paoli MA et al (2009) Characterization of lignocellulosic curaua fibres. Carbohydr Polym 77:47–53
48. Guimarãesa JL, Frollini E, da Silva CG, Wypychc F, Satyanarayanac KG et al (2009) Characterization of banana, sugarcane bagasse and sponge gourd fibres of Brazil. Ind Crop Prod 30:407–415
49. Zou L, Jin H, Lu WY, Li X et al (2009) Nanoscale structural and mechanical characterization of the cell wall of bamboo fibres. Mater Sci Eng 29:1375–1379
50. Koljonen K, Österberg M, Johansson LS, Stenius P et al (2003) Surface chemistry and morphology of different mechanical pulps determined by ESCA and AFM. Colloids Surf A: Physicochem Eng Asp 228:143–148
51. Mohanty AK, Misra M, Drzal LT, Selke SE, Harte BR, Hinrchsen G et al (2005) Natural fibres, biopolymers, and bio composites an introduction. In: Mohanty AK, Misra M, Drzal LT (eds) Natural fibres, biopolymers and biocomposites. CRC, Boca Raton, p 37
52. Bax B, Mussig J (2008) Impact and tensile properties of PLA/Cordenka and PLA/flax composites. Compos Sci Technol 68:1601–1607
53. Beckermann GW, Pickering KL (2008) Engineering and evaluation of hemp fibre reinforced polypropylene composites: fibre treatment and matrix modification. Compos Part A 39: 979–988
54. Bledzki AK, Mamun AA, Jaszkiewicz A, Erdmann K et al (2010) Polypropylene composites with enzyme modified abaca fibre. Compos Sci Technol 70:854–860
55. Sangthong S, Pongprayoon T, Yanumet N et al (2009) Mechanical property improvement of unsaturated polyester composite reinforced with admicellar-treated sisal fibres. Compos Part A 40:687–694
56. Towo AN, Ansell MP (2008) Fatigue of sisal fibre reinforced composites: constant-life diagrams and hysteresis loop capture. Compos Sci Technol 68:915–1924
57. Wang ZF, Peng Z, Li SD, Lin H, Zhang KX, She XD, Fu X et al (2009) The impact of esterification on the properties of starch/natural rubber composite. Compos Sci Technol 69:1797–1803
58. Yao F, Wu Q, Lei Y, Xu Y et al (2008) Rice straw fibre-reinforced high-density polyethylene composite: effect of fibre type and loading. Ind Crops Prod 28:63–72
59. Huang X, Netraval AN (2009) Biodegradable green composites made using bamboo micro/nano-fibrils and chemically modified soy protein resin. Compos Sci Technol 69:1009–1025
60. Lee BH, Kim HS, Lee S, Kim HJ, Dorgan JR et al (2009) Bio-composites of kenaf fibres in polylactide: role of improved interfacial adhesion in the carding process. Compos Sci Technol 69:2573–2579
61. Shih YF, Huang CC, Chen PW et al (2009) Biodegradable green composites reinforced by the fibre recycling from disposable chopsticks. Mater Sci Eng 527:1516–1521
62. Suryanegara L, Nakagaito AN, Yano H et al (2009) The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites. Compos Sci Technol 69:1187–1192

63. Wu CS (2009) Renewable resource-based composites of recycled natural fibres and maleated polylactide bioplastic: Characterization and biodegradability. Polym Degrad Stab 94:1076–1084
64. Ma X, Chang PR, Yu J, Stumborg M et al (2009) Properties of biodegradable citric acid-modified granular starch/thermoplastic pea starch composites. Carbohydr Polym 75:1–8
65. Netravali AN, Chabba S (2003) Composites get greener. Mater Today 6:22–29
66. Zhu H, Shen J, Feng X, Zhang H, Guo Y, Chen J et al (2010) Fabrication and characterization of bioactive silk fibroin/wollastonite composite scaffolds. Mater Sci Eng 30:132–140
67. Netravali AN, Huang X, Mizuta K et al (2007) Advanced green composites. Adv Compos Mater 16:16269–16282
68. Huang X, Netravali AN (2006) Characterization of Nano-clay reinforced phytagel modified soy protein concentrate. Biomacromolecules 7:2783–2789
69. Hill S (1997) Cars that grow on trees. New Scientist Feb 3–39
70. Suddell BC, Evans WJ (2005) Natural fibre composites in automotive applications. In: Mohanty AK, Misra M, Drzal LT (eds) Natural fibres, biopolymers and biocomposites. CRC, Boca Raton, p 37
71. Mohanty AK, Khan MA, Hinrichsen G et al (2000) Surface modification of jute and its influence on performance of biodegradable jute-fabric/Biopol composites. Compos Sci Technol 60:1115–1124
72. Lea˜o AL, Rowell R, Tavares N et al (1998) Applications of natural fibres in automotive industry in Brazil – thermoforming process. In: Prasad PN (ed) Science and technology of polymers and advanced materials. Plenum, New York
73. Alves C, Ferra˜o PMC, Silva AJ, Reis LG, Freita LB, Rodrigues M, Alves DE et al (2010) Ecodesign of automotive components making use of natural jute fibre composites. J Clean Prod 18:313–327
74. Singh B, Gupta M (2005) Natural fibre composites for building applications. In: Mohanty AK, Misra M, Drzal LT (eds) Natural fibres, biopolymers and biocomposites. CRC, Boca Raton, p 37
75. Singh B, Gupta M (2003) Proceedings of the advances in polymeric building materials. Poly Built -2003, Roorke, March 6–7: 5
76. Aziz MA, Paramasivam P, Lee SL et al (1981) Prospects for natural fibre reinforced concretes in construction. Int J Cement Compos Lightweight Concrete 3:123–132
77. Juárez C, Durán A, Valdez P, Fajardo G et al (2007) Performance of "Agave lecheguilla" natural fibre in Portland cement composites exposed to severe environment conditions. Build Environ 42:1151–1157
78. Savastano H Jr, Santos SF, Radonjic M, Soboyejo WO et al (2009) Fracture and fatigue of natural fibre-reinforced cementitious composites. Cement Concr Compos 31:232–243
79. Rahman WA, Tin SL, Razak RA et al (2008) Injection moulding simulation analysis of natural fibre composite window frame. J Mater Process Technol 197:22–30
80. Toledo FRD, Andrade SF, Fairbairn EMR, Melo FA et al (2009) Durability of compression molded sisal fibre reinforced mortar laminates. Construct Build Mater 23:2409–2420
81. Pillai MS (2006) Applications of natural coir fibre, proceedings, natural fibres vision 2020, New Delhi 8–9th December
82. Mwasha A (2009) Using environmentally friendly geotextiles for soil reinforcement: a parametric study. Mater Des 30:1798–1803
83. Bhattacharyya R, Fullen DK, Booth CA et al (2009) Utilizing of palm-leaf geotextile mats to conserve loamy sand soil in the United Kingdom. Agric Ecosyst Environ 130:50–58
84. Subaida EA, Chandrakaran S, Sankar N et al (2009) Laboratory performance of unpaved roads reinforced with woven coir geotextiles. Geotextiles Geomembr 27:204–210
85. Datye KR, Gore VN (1994) Application of natural geotextiles and related products. Geotextiles Geomembr 13:371–388
86. Alemdar A, Sain M (2008) Isolation and characterization of nanofibres from agricultural residues-wheat straw and soy hulls. Bioresour Technol 99:1664–1671

87. Cherian BM, Pothan LA, Nguyen-Chung T, Mennig G, Kottaisamy M, Thomas S et al (2008) A novel method for the synthesis of cellulose nanofibril whiskers from banana fibres and characterization. J Agric Food Chem 56:5617–5627
88. Morán JI, Alvarez VA, Cyras VP, Vázquez A et al (2008) Extraction of cellulose and preparation of nanocellulose from sisal fibres. Cellulose 15:149–159
89. Wang B, Sain M, Oksman K et al (2007) Study of structural morphology of hemp fibre from the micro to the nanoscale. Appl Compos Mater 14:89–103
90. Zuluaga R, Putaux JL, Restrepo A, Mondragon I, Gañán P et al (2007) Cellulose microfibrils from banana farming residues: isolation and characterization. Cellulose 14:585–592
91. Siró I, David P (2010) Microfibrillated cellulose and new nanocomposite materials: a review. Cellulose. doi:10.1007/s10570-010-9405-y
92. Ioelowich M (2008) Cellulose as a nano structured polymer: a short review. Bioresources 3(4):1403–1418
93. Henriksson M, Henriksson G, Berglund LA, Lindström T et al (2007) An environmentally friendly method for enzyme assisted preparation of microfibrillated cellulose (MFC) nanofibres. Eur Polym J 43:3434–3441
94. Iwamoto S, Nakagaito AN, Yano H (2007) Nano-fibrillation of pulp fibres for the processing of transparent nanocomposites. Appl Phys A-Mater Sci Process 89:461–466
95. Klemm D, Schumann D, Kramer F, Hessler N, Hornung M, Schmauder HP, Marsch S et al (2006) Nanocelluloses as innovative polymers in research and application. Polysaccharides 205:49–96
96. Fahmy TYA, Mobarak F (2008) Nanocomposites from natural cellulose fibres filled with kaolin in presence of sucrose. Carbohydr Polym 72:751–755
97. Roohani M, Habibi Y, Belgacem NM, Ebrahim G, Karimi AN, Dufresne A et al (2008) Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. J Eur Polym 44:2489–2498
98. Seydibeyoğlu MO, Oksman K (2008) Novel nanocomposites based on polyurethane and micro fibrillated cellulose. J Compos Sci Technol 68:908–914
99. Wang B, Sain M (2007) Isolation of nanofibres from soybean source and their reinforcing capability on synthetic polymers. Compos Sci Technol 67:2521–2527
100. Teixeira EM, Correâ AC, Manzoli A, Leite FL, Oliveira CR, Mattoso LHC et al (2010) Cellulose nanofibres from white and naturally colored cotton fibres. Cellulose. doi:10.1007/s10570-010-9403-0
101. Grande CJ, Torres FG, Gomez CM, Troncoso OP, Canet-Ferrer J, Martinez-Pastor J et al (2008) Morphological characterization of bacterial cellulose–starch nanocomposites. Polym Compos 16:181–185
102. Iguchi M, Yamanaka S, Budhiono A et al (2000) Bacterial cellulose – a masterpiece of nature's arts. J Mater Sci 35:261–270
103. Juntaro J, Pommet M, Kalinka G, Mantalaris A, Shaffer MSP, Bismarck A et al (2008) Creating hierarchical structures in renewable composites by attaching bacterial cellulose onto sisal fibres. Adv Mater 20:3122–3126
104. Nakagaito AN, Iwamoto S, Yano H et al (2005) Bacterial cellulose: the ultimate nano-scalar cellulose morphology for the production of high-strength composites. Appl Phys A Mater Sci Process 80:93–97
105. De Rodriguez NLG, Thielemans W, Dufresne A et al (2006) Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. Cellulose 13:261–270
106. Bhatnagar A, Sain M (2005) Processing of cellulose nanofibres-reinforced composites. J Reinf Plas Compos 24:1259–1268
107. Goussé C, Chanzy H, Cerrada ML, Fleury E et al (2004) Surface silylation of cellulose microfibrils: preparation and rheological properties. Polymer 45:1569–1575
108. Habibi Y, Vignon MR (2008) Optimization of cellouronic acid synthesis by TEMPO-mediated oxidation of cellulose III from sugar beet pulp. Cellulose 15:177–185

109. Dufresne A, Dupeyre D, Vignon MR et al (2000) Cellulose micro-fibrils from potato tuber cells: processing and characterization of starch–cellulose microfibril composites. J Appl Polym Sci 76:2080–2092
110. Bhattacharya D, Germinario LT, Winter WT et al (2008) Isolation, preparation and characterization of cellulose microfibres obtained from bagasse. Carbohydr Polym 73:371–377
111. Malainine ME, Mahrouz M, Dufresne A et al (2005) Thermoplastic nanocomposites based on cellulose microfibrils from Opuntia ficus-indica parenchyma cell. Compos Sci Technol 65:1520–1526
112. Imai T, Putaux JL, Sugiyama J et al (2003) Geometric phase analysis of lattice images from algal cellulose microfibrils. Polymer 44:1871–1879
113. Nakagaito AN, Yano H (2004) Novel high-strength biocomposites based on microfibrillated cellulose having nano-order-unit web-like network structure. Appl Phys A 80:155–159
114. Dinand E, Chanzy H, Vignon MR et al (1999) Suspensions of cellulose micro- fibrils from sugar beet pulp. Food Hydrocolloid 13:275–283
115. Wan YZ, Hong L, Jia SR, Huang Y, Zhu Y, Wang YL et al (2006) Synthesis and characterization of hydroxyapatite–bacterial cellulose nanocomposites. Compos Sci Technol 66 (11–12):1825–1832
116. Svagan AJ, Samir MASA, Berglund LA et al (2008) Biomimetic foams of high mechanical performance based on nanostructured cell walls reinforced by native cellulose nano- fibrils. Adv Mater 20:1263–1269
117. Chakraborty A, Sain M, Kortschot M et al (2005) Cellulose microfibrils: a novel method of preparation using high shear refining and cryocrushing. Holzforschung 59:102–107
118. Menezes AJ, Siqueira G, Curvelo AAS, Dufresne A (2009) Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites. Polymer 50:4552–4563
119. Cherian BM, Leão AL, Souza SF, Thomas S, Pothan LA, Kottaisamy M (2010) Isolation of nanocellulose from pineapple leaf fibres by steam explosion. Carbohydr Polym 81:720–725

Chapter 2
Chemical Functionalization of Cellulose Derived from Nonconventional Sources

V. K. Varshney and Sanjay Naithani

Abstract Chemical functionalization of cellulose aims to adjust the properties of macromolecule for different purposes, particularly, as a chemical feedstock for production of cellulose derivatives for a variety of applications. The conventional sources of cellulose include cotton linters and wood pulp which now-a-days are discouraged on account of the cost of the former and environment conservative regulations associated with the latter. Further, renewable raw materials are gaining considerable importance because of the limited existing quantities of fossil supplies. In this regard, cellulose-rich biomass derived from the nonconventional sources such as weeds, fibers, bamboos, and wastes from agriculture and forests, etc. acquires enormous significance, as alternative chemical feedstock, since it consists of cellulose, hemicellulose, and lignin, which contain many functional groups suitable to chemical functionalization. Etherification of cellulose through methylation, carboxymethylation, cynaoethylation, hydroxypropylation, single or mixed, is one of the most important routes of cellulose functionalization. Chemical composition and rheological characteristics make possible the selection of the modified cellulose to serve special applications. Prompted by above facts, possibility for chemical functionalization of cellulose rich biomass derived from bamboo, *Dendrocalamus strictus* (DCS), and noxious weeds – *Lantana camara* (LC) and *Parthenium hysterophorus* (PH) for their utilization was examined and results are reported. Proximate analysis of these materials was conducted and processes were standardized for production of α-cellulose on 1 kg batch scale. The percent yield, Av. DP, and the percentage of α-cellulose content of the obtained celluloses were found in the range of 35–40, 400–825, >90 (Brightness 80% ISO), respectively. Processes were optimized for production of water-soluble carboxymethyl cellulose (DCS, LC, and PH), cyanoethyl cellulose (DCS) and water-soluble hydroxypropyl cellulose (DCS and PH). The optimized products were characterized by IR spectra. Rheological studies of 1% and 2% aqueous solutions of the optimized carboxymethyl celluloses and hydroxypropyl celluloses showed their non-Newtonian

---

V.K. Varshney (✉)
Chemistry Division, Forest Research Institute, Dehra Dun 248 006, India
e-mail: varshney2000@yahoo.com

S. Kalia et al. (eds.), *Cellulose Fibers: Bio- and Nano-Polymer Composites*,
DOI 10.1007/978-3-642-17370-7_2,

pseudoplastic behavior. Thus, abundantly available biomass from *Dendrocalamus strictus* bamboo and the weeds – *Lantana camara* and *Parthenium hysterophorus* seem to be a potential feedstock for production of α-cellulose and its subsequent functionalization into cellulose derivatives for variety of applications. This was also demonstrated that these noxious weeds could also be managed by their utilization into products of commercial importance.

Keywords Bamboo · Cellulose · Cellulose ethers · Chemical functionalization · Lantana · Parthenium

Contents

Abbreviations

AGU	Anhydroglucose unit
AN	Acrylonitrile
CEC	Cyanoethylcellulose
CMC	Carboxymethyl cellulose
CMHEC	Carboxymethylhydroxyethylcellulose
DCS	Dendrocalamus strictus
DP	Degree of Polymerization
DS	Degree of Substitution
HDP	Hypochlorite/Chlorine dioxide/Peroxide
HEC	Hydroxyethylcellulose
HP	Hydroxypropoxyl content
HPC	Hydroxypropyl cellulose
HPMC	Hydroxypropylmethylcellulose
IR	Infra Red

ISO	International organization for standardization
LC	Lantana camara
MC	Methylcellulose
MCA	Monochloroacetic acid
MS	Molar Substitution
PH	Parthenium hysterophorus
PO	Propylene oxide

2.1 Introduction

2.1.1 Cellulose and Its Sources

Cellulose, the most abundant renewable and biodegradable polymer, is the promising feedstock for the production of chemicals for their applications in various industries. Annual production of cellulose in nature is estimated to be 10^{11}–10^{12} t in two forms, partially in a pure form, for example seed hairs of the cotton plant, but mostly as hemicelluloses in cell wall of woody plants (Klemm et al. 1998). The versatility of cellulose has been reevaluated as a useful structural and functional material. The environmental benefits of cellulosics have become even more apparent (Hon 1996a). Cellulose is revered as a construction material, mainly in the form of intact wood but also in the form of natural textile fibers like cotton or flax, or in the form of paper and board. The value of cellulose is also recognized as a versatile starting material for subsequent chemical transformation in production of artificial cellulose-based threads and films as well as of a variety of cellulose derivatives for their utilization in several industries such as food, printing, cosmetic, oil well drilling, textile, pharmaceutical, etc. and domestic life.

Cellulose can be derived from a variety of sources such as woods, annual plants, microbes, and animals. These include seed fiber (cotton), wood fibers (hardwoods and softwoods), bast fibers (flax, hemp, jute, ramie), grasses (bagasse, bamboo), algae (*Valonica ventricosa*), and bacteria (*Acetobacter xylinum*) (Nevell and Zeronian 1985). *A. xylinum* can synthesize extracellular pellicles of cellulose from glucose. Some simple marine animals such as tunicates deposit cellulose in their cell walls (Coffey et al. 1995). Besides cellulose, these materials also contain hemicelluloses, lignin, and a comparable small amount of lignin. Wood and cotton are the raw materials for commercial production of cellulose. Cellulose serves as a structural material within the complex architecture of the plant cell walls with variation in its content. In wood, it constitutes about 40–50%; in leaf fibers: sisal fibers (55–73%), in bast fibers: flax 70–75%, hemp 75–80%, jute 60–65%, ramie 70–75%, kenaf 47–57%, in canes: bamboo 40–55%, baggase 33–45%, and in cereal straw: barley 48%, oat 44–53%, rice 43–49%, rye 50–54%, wheat 49–54%. Cotton seed hairs, the purest source, contain 90–99% of cellulose (Hon 1996b; Han and Rowell 1996).

2.1.2 Chemical Functionalization of Cellulose

Among the polysaccharides, the structure of cellulose is unique and simple. However, this influences its chemical reactions significantly. Cellulose being rigid, highly crystalline, and insoluble in common organic solvents is an ideal structural engineering material (Hon 1996b; Mathur and Mathur 2001). Cellulose is a polydisperse, linear, syndiotactic polymer. Its basic monomeric unit is D-glucose (anhydroglucose unit, AGU), which links successively through a β-configuration between carbon 1 and carbon 4 of adjacent units to form a long chain 1,4 glucans (Mathur and Mathur 2001). Two glucose molecules react to form a cellobiose which is the basic chemical unit of a cellulose molecule. The pyranose rings are in the $^4C_1$ conformation, which means that the –CH_2OH and –OH groups as well as glycosidic bonds are all equatorial with respect to the mean planes of the rings. The hydroxyl groups at both ends of the cellulose chain show different behavior. The C-1 end has reducing properties, while the glucose end group with a free C-4 hydroxyl group is nonreducing.

When the cellulose molecule is fully extended it takes the form of a flat ribbon with hydroxyl groups protruding laterally and capable of forming both inter- and intramolecular hydrogen bonds. Intramolecular hydrogen bonding between adjacent anhydroglucose rings enhances the linear integrity of the polymer chain and affects the reactivity of the hydroxyl groups, particularly of the C-3 hydroxyl group, which hydrogen binds strongly to the ring oxygens on adjacent anhydroglucose units. The surface of ribbons consists mainly of hydrogen atoms linked directly to carbon and is therefore hydrophobic. These two features of cellulose are responsible for its supramolecular structure, and this in turn determines many of its chemical and physical properties. In the fully extended molecule adjacent chain units are oriented with their mean planes at an angle of 180° to each other. Thus the repeating unit in cellulose is the AGU and the number of repeating units per molecule is half the Degree of Polymerization (DP) (Nevell and Zeronian 1985).

The size of cellulose molecule occurring in nature is indicated by its chain length or DP, which is average value of the number of monomer units. The DP of cellulose can be determined by various physical methods such as intrinsic viscosity measurements, light scattering, etc. DP of cellulose is heavily dependent on source. For example, cellulose obtained from cotton fibers, cotton linters, baggase, and wood fibers have DP 8,000–14,000; 1,000–6,500; 700–900; and 8,000–9,000, respectively. The DP or molecular weight distribution in many cases profoundly influences the mechanical, solution, biological, and physiological properties of cellulose and has given very useful clues for the designing of effective cellulose derivatives (Hon 1996b).

The abundance of hydroxyl groups and concomitant tendency to form intra- and intermolecular hydrogen bonds results in the formation of linear aggregates. In the solid state, highly ordered crystalline areas are interspersed between less ordered amorphous zones. These amorphous zones are regions in which the hydroxyl groups are more readily available for reaction than in the more highly ordered crystalline areas, which are less reactive (Coffey et al. 1995). The ratio of amorphous cellulose to crystalline cellulose is called degree of crystallinity which depends upon the species and pretreatment of the sample (Fink et al. 1995). For instance, the degree of crystallinity of cellulose derived from bacteria, cotton, and *Valonia* algae is about 75%, 40–45%, and 93%, respectively (Kulshreshtha and Dweltz 1973; Yamamoto and Horii 1993; Osullivan 1997).

Degree of crystallinity plays an important role in chemical functionalization of cellulose. Cellulose contains 31.48% by weight of hydroxyl groups (one primary and two secondary per AGU), accessibility of these present enormous opportunities for preparing useful derivatives. Reactivity of these hydroxyl groups varies according to the reaction medium in which functionalization is done. For example, the order of reactivity for etherification performed in an alkaline medium is $2 > 6 > 3$ while the primary hydroxyl group (OH-6) is the most active in esterification (Hon 1996b). The type, distribution, and uniformity of substituents groups determine the properties of derivatives. (Nicholson and Meritt 1985). The average number of hydroxyl groups replaced by the substituents is the degree of substitution (DS); the maximum is three. For example, in a cellulose ether with a DS 1.5, 50% of the hydroxyl groups are etherified and 50% are free, to average 1.5 substituent moieties per anhydroglucose unit. When the side chain formation is possible, as for example in hydroxypropylation, molar substitution (MS) is used to denote the length of the side chain, and the value can exceed three. If the DS value is known for a substitution, the average chain length of the ether side chain can be calculated from the ratio of MS to DS (Hon 1996b).

In 1838, Payen recognized cellulose as a definitive substance and coined the name cellulose (Zugenmaier 2008). The functionalization of cellulose was utilized extensively, even when its polymeric nature was not determined and understood, as evidenced from the discovery of cellulose nitrate by Schonbein (1846), the preparation of Schweizer's reagent, that is, a cuprammonium hydroxide solution, the first cellulose solvent (Schweizer 1857) in 1857, the synthesis of an organosoluble cellulose acetate by Schutzenberger in 1865 (Cross and Bevan 1907), and artificial fibers in 1892 (Menachem 2006). The partially nitrated ester of cellulose is well known among the first polymeric materials used as a "plastic" under the trade name of celluloid. Cellulose nitrates of higher N-content have been used extensively for military purposes. Cellulose nitrate is the only inorganic cellulose ester of commercial interest (Balser et al. 1986). Other derivatives such as methyl-, ethyl-, hydroxyalkyl ethers, mixed ethers/esters like ethylhydroxyethyl, hydroxypropyl methyl cellulose, cellulose acetopropionates, and acetobutyrates are still important, many decades after their discovery.

Chemical functionalization of cellulose include reactions of hydroxyl groups such as esterification, etherification, intermolecular crosslinking reactions, and macrocellulosic free radical reactions, particularly in the formation of graft cellulose copolymers (Arthur 1986) to increase the usefulness of cellulose by altering its properties. These cellulose derivatives are grouped according to the processes and substituents, for instance, esters- cellulose acetate through esterification and ethers-methyl cellulose/cyanoethyl cellulose/carboxymethyl cellulose (CMC) via etherification. Chemical functionalization continue to play a dominant role in improving the overall utilization of cellulosic polymers. The accessibility to hydroxyl groups and their reactivity open prospects for preparation of specific molecular structures for future applications. Broader and more specialized applications of advanced and trend setting materials based on this unique and renewable macromolecule will increase the demand for more diverse synthesis paths and derivatives (Heinze and Liebert 2001).

The esters of cellulose with inorganic and organic acids were the first chemically modified cellulosics (Klemm et al. 1998). Among the more than 100 cellulose esters developed, only a few of them including nitrates, acetates, and mixed esters of acetic acid and propionic acid, acetic acid and butyric acid, and acetic acid and phthalic acid have industrial applications (Hon 1996b). Cellulose acetate is extensively used in fibers, plastics, and coatings and thus becomes the universally recognized and the most important organic ester of cellulose.

2.1.3 Applications of Cellulose Derivatives

Cellulose derivatives, being of natural origin, have diverse physicochemical properties because of the kind of substituents, DS, molecular weights and DP and are revered for their large scale use mainly as additives of fine/special chemicals in textile, pharmaceutical, cosmetic, food, and packaging industries (Balser et al. 1986; Barndt 1986). Cellulose derivatives of commercial importance belong to water or organic solvents such as soluble ethers or esters (Table 2.1). Nevertheless, cross linked and graft copolymers of cellulose are also of significant industrial importance.

Despite the large variety of cellulose derivatives that have been made, there is continuous expansion in the worldwide market of cellulose ethers because of their availability, economic efficiency, easy handling, low toxicity, and great variety of types. Combined effects of flow control, stabilization, water retention, film formation, etc. provided by cellulose ethers are not generally obtainable by the use of fully synthetic polymers. Cellulose ethers such as CMC, hydroxypropyl cellulose (HPC), cyanoethylcellulose (CEC), ethylcellulose (EC), methylcellulose (MC), hydroxyethylcellulose (HEC), hydroxypropylmethylcellulose (HPMC), carboxymethylhydroxyethylcellulose (CMHEC), etc. have gained their position in the market due to their multifunctional properties. The worldwide annual production of cellulose ethers is estimated to be over 300,000 metric ton (Schweizer and Sorg 1995). They exhibit useful properties of thickening, thermal gelation, surfactancy, film formation, and adhesion. Further they are kinetically and thermodynamically more stable and appear easy to prepare and characterize. These characteristics earn them applications in areas such as pharmacy, cosmetics, food, oil drilling, paper, paint, textiles, construction, and adhesives (Davidson 1980; Whistler and BeMiller 1973; Nicholson and Meritt 1985). Among cellulose derivatives, cellulose ethers constitute the only food allowed group of modified celluloses.

Crosslinking of cellulose, in heterogeneous systems, with formaldehyde or formaldehyde adducts of urea, melamine, or carbamates impart dimensional stability to cellulosic textile and paper products (Nicholson and Meritt 1985). A range of polymers, to obtain a better balance of properties for the commercial application of

Table 2.1 Some commercially marketed cellulose esters and ethers (Arthur Jr 1986)

Cellulose derivatives	DS range	Solubility	Product applications
Cellulose esters			
Nitrate	1.5–3.0	MeOH, $PhNO_2$, ethanol-ether	Films, fibers, explosives
Acetate	1.0–3.0	Acetone	Films, fibers, coatings, heat and rot resistant fabrics
Cellulose ethers			
Methyl	1.5–2.4	Hot H_2O	Food additives, films, cosmetics, greaseproof paper
Carboxymethyl	0.5–1.2	H_2O	Food additives, fibers, coatings, oil-well drilling muds, paper size, paints, detergents
Ethyl	2.3–2.6	Organic solvents	Plastics, lacquers
Hydroxyethyl	Low DS	H_2O	Films
Hydroxypropyl	1.5–2.0	H_2O	Paints
Hydroxypropylmethyl	1.5–2.0	H_2O	Paints
Cyanoethyl	2.0	Organic solvents	Products with high dielectric constants, fabrics with heat and rot resistances

polymeric materials, can be synthesized by graft copolymerization of cellulose. By minimizing degradation, copolymerization reactions of cellulose could result in retaining of the desirable properties of the natural molecule giving it additional properties through the added polymer. Cellulose graft copolymers find a wide array of applications in construction (wood plastic composites), furniture and industrial parts, sporting goods, woodcarving, textiles, and pulp and paper. They are also used as thickeners, absorbents, and in making ion exchange fibers and extrudable composites (Hebeish and Guthrei 1981).

2.2 Status of Research on Chemical Functionalization of Cellulose Derived from Nonconventional Sources

Renewable raw materials are gaining considerable importance because of the limited existing quantities of fossil supplies, escalating cost and problem of nonbiodegradability of petroleum-based polymers, and the recent environment-conservative regulations. The chemical industry is estimated to meet about 10% of its raw material needs from the renewable raw materials (Clasen and Kulicke 2001). Natural polymers are of renewable nature, hence, environment-friendly and cost-effective technologies can be developed by functionalization of these polymers In this regard, cellulose rich biomass acquires enormous significance as chemical feedstock, since it consists of cellulose, hemicellulose, and lignin, which contain many functional groups suitable to chemical functionalization (Barkalow and Young 1985). The limitation of insolubility of cellulose in water can be overcome and spectrum of its industrial applications can be widened by functionalized to water-soluble forms. Various polymer analogous reactions could be used to modify the cellulose and its derivatives can be used as substitutes of petrochemicals in getting some important polymers including thermoplastics.

The conventional sources of cellulose are wood pulp and cotton linters. However, global efforts are going on to search for cellulose biomass from other sources as a feedstock as an alternative to expensive cotton linters, and wood pulp which now-a-days are discouraged due to environment conservative regulations. Annual plants are considered as potential resource because of their higher yield of cellulose than wood (McDougall et al. 1993; Atchison 1996; Han 1998), lower lignin contents, looser fibril structure than wood, consumption of less pulping chemicals and energy (McDougall et al. 1993; Han and Rowell 1996; Oggiano et al. 1997), have same main chemical components as woody plants, i.e., cellulose, hemicellulose, lignin, and extractives, ease of cultivation, harvesting and transportation (McDougall et al. 1993). Under the consideration of the economical objective, the environment influence, the sufficient supply, and the higher yield of cellulose, annual plants are now gradually substituting woods as alternative resources of cellulosic products. Investigations have shown that annual plants such as *Miscanthus sinensis, Cynara cardunculus*, flax, hemp, jute, sisal, and abaca could be used as new alternative sources for production of methyl cellulose (Daiyong 2005).

Agricultural wastes, for example, rice straw, sugarcane bagasse, saw dust, cotton stables (Hebeish, et al. 1984), orange mesocarp (Akaranta and Osugi 1997), and weeds, *Eichoria crassipes* (Barai et al. 1997), have been used as a base material for production of CMC differing in their DS and properties using different set of reaction conditions depending upon the DP and composition of the cellulosic material. Reactivity of fibers of *Agave lechuguilla* and *Agave fourcroydes* toward chemical functionalization such as carboxymethylation, sulfation, acetylation, tritylation, and subsequent carboxymethylation as well as oxidation and grafting has been studied, which has demonstrated the suitability of the agave fibers as a potential feedstock for producing cellulose derivatives for a variety of applications (Vieira et al. 2002; Ramos et al. 2005; Cruz et al. 1999). Graft copolymerization of acrylonitrile and methyl methacrylate onto jute fibers and pineapple leaf fibers has been examined (Patra and Singh 1994; Patnaik et al. 1989; Ghosh and Ganguly 1994; Samal and Bhuyan 1994). Low-quality woods as well as industrial wastes of wood have been utilized to produce a thermoplastic material through cyanoethylation (Khalil and El-Wakil 2000). The goal of these functionalizations is to increase the utilization of this abundantly available cellulose biomass from nonconventional sources.

2.3 Chemical Functionalization of Cellulose Derived from Nonconventional Biomass *Dendrocalamus strictus* (DCS) and Noxious Weeds *Lantana camara* (LC) and *Parthenium hysterophorus* (PH)

Identification of biopolymers from different plant sources, their isolation, and subsequent chemical functionalization for varied applications has been one of the research programs of the Chemistry Division, Forest Research Institute, Dehra Dun

(Sharma 2003; Gupta 2005; Bhatt 2004; Bansal 2005; Rana 2006; Sharma 2007; Pandey 2008; Goyal 2008). A technology for production of α-cellulose of high DP (800–3,000), high purity (>95%), and high brightness (>80%) derived from cotton linters, bamboo, eucalyptus, and bagasse was developed.

L. camara L. (Verbenaceae) and *P. hysterophorus* L., (Helianthae: Asteraceae) are noxious weeds, which have imposed a great threat to land productivity, grazing livestock, human health, biodiversity, and consequently to the overall ecology (Sharma et al. 1988; Pass 1991; Evans 1997). Attempts to manage these weeds using mechanical, chemical, and biological means have been made but met with limited success on account of their inbuilt limitations such as high cost, impracticability, environmental safety, temporary relief, etc (Sharma 2004; Jayanth 1987; Jayakumar et al. 1989). Alternatively, luxuriant growth and vigorous survival make these weeds of potential economic value for utilization of their abundantly available biomass into value added products offering thereby an efficient and effective method for their management. During the last few years, research has been conducted to utilize the lantana biomass for development of furniture products, baskets, mulch, compost, drugs, and other biologically active agents (Sharma and Sharma 1989; Inada et al. 1997; Sharma 2004).

Bamboo, belonging to the grass family Poaceae, is an abundant renewable natural resource capable of producing maximum biomass per unit area and time as compared to counterpart timber species (Tewari 1995). The chemical composition of *D. strictus* has been studied, which was found to contain Cross and Bevan cellulose 68.0% and lignin 32.20% (Singh et al. 1991). Its hemicellulose (18.8%) has also been shown to consist of xylose 78.0%, arabinose 9.4%, and uronic acid 12.8% (Tewari 1995).

Driven by the challenges to explore and increase the usefulness of cellulosic biomass from nonconventional sources, possibility for chemical functionalization of cellulose rich biomass derived from bamboo, *D. strictus* (DS) and noxious weeds – *L. camara* (LC) and *P. hysterophorus* (PH) for their utilization was examined.

2.3.1 Proximate Analysis of Biomass

L. camara and *P. hysterophorus* used in the study were collected from the field of the institute's campus. All the chemicals used were of laboratory grade. Plant materials were reduced to chips of 1–2 in. size and air dried. Chips were reduced to dust, and the dust passing through 40 mesh and retained on 60 mesh were taken for studies. Proximate chemical composition of the plant material was studied using the standard methods to assess the quality and solubility of raw material for further processing and results of the analysis are presented in Table 2.2.

Table 2.2 Proximate chemical composition of *Lantana camara* (LC) and *Parthenium hysterophorus* (PH)

Sl. No.	Parameters	Value%		Method used
		LC	PH	
1	Hot water solubility	7.0	11.25	APPITA P 4 M-61
2	1% NaOH solubility	18.0	22.5	APPITA P 5 M-61
3	Alcohol–benzene solubility	4.45	5.89	APPITA P 7 M-70
4	Holocellulose	71.34	78.0	TAPPI 9 m-54
5	α-cellulose	64.91	65.0	TAPPI T-203 OM 88
6	Pentosans	13.0	15.86	TAPPI T-203 OM 84
7	Lignin	27.25	17.2	TAPPI T-222 OM 88
8	Ash	1.8	2.1	APPITA P3 M-69

2.3.2 Isolation of α-Cellulose

The air-dried chips were subjected to following treatments. The conditions at each stage were optimized and 1 Kg production of α-cellulose [yield 35% (DCS), 38.76% (LC), and 37.4% (PH) and Brightness 80% (DS), 81.0% (LC), and 80.0% (PH) ISO] was carried out under optimized conditions.

2.3.2.1 Water Prehydrolysis

The chips were prehydrolyzed in autoclave keeping bath ratio 1:4 at 100°C for 30.0 min (DCS and LC)/1:5 at 100°C for 30.0 min (PH). The yield after prehydrolysis was 96.5%, 95.5%, 92.2%, respectively.

2.3.2.2 Alkali Hydrolysis

Water prehydrolyzed chips were treated with 2% alkali as NaOH. The bath ratio was maintained 1:4 (DCS)/1:4 (LC)/1:5 (PH) and heated in autoclave to 130°C (DCS)/120°C (LC)/130°C (PH) for 60 min. The yield was 94.4%, 85.9%, and 87.4%, respectively.

2.3.2.3 Pulping

The pulping of alkali hydrolyzed chips was carried out with 20% (DCS)/20% (LC)/18% (PH) alkali as NaOH at 170°C for 120 min (DCS)/90.0 min (LC)/60 min (PH). The kappa number of the pulp was 24, 26, 23 and pulp yield was 45.8%, 48%, and 45.6% with 3.2–3.8%, 1.2% screen rejects, respectively.

2.3.2.4 Bleaching

Bleaching was carried out using HDP sequence.

Table 2.3 Characteristics of the cellulose isolated from *Dendrocalamus strictus* (DCS), *Lantana camara* (LC), and *Parthenium hysterophorus* (PH)

Characteristics of cellulose	Value (%)			Method used
	DCS	LC	PH	
α-cellulose	90.09	94.80	90.82	TAPPI T2003 OM-88
β-cellulose	3.9	2.5	3.2	
γ-cellulose (by difference)	5.0	1.42	1.2	
Lignin	0.44	0.80	4.0	TAPPI T-222
Ash	0.56	0.48	0.98	APPITA P3 M-69
Av. DP	816	430	661.5	SCAN 15

Cellulose obtained as above was characterized for its DP and composition and are presented in Table 2.3 DP was determined by CED viscosity method using following formula:

$DP^{0.905} = 0.75\ (\eta)$, where η is intrinsic viscosity.

2.3.3 *Etherification of α-Cellulose*

2.3.3.1 Carboxymethylation

A typical carboxymethylation method involving given below two competitive reactions was followed.

$$\underset{\text{Cellulose}}{\text{Cell-OH}} + \underset{\text{Monochloroacetic acid}}{ClCH_2COOH} + NaOH \rightarrow \underset{\text{Sodium carboxymethyl cellulose}}{\text{Cell-OCH}_2\text{COONa}} + NaCl + H_2O \tag{2.1}$$

$$ClCH_2COOH + NaOH \rightarrow \underset{\text{Sodium glycolate}}{HOCH_2COONa} + NaCl \tag{2.2}$$

Carboxymethylation was conducted in two steps alkalization and etherification under heterogeneous conditions and the process was optimized with respect to DS by varying the reaction parameters such as concentration of NaOH, monochloroacetic acid (MCA), temperature, and duration of reaction. Each of these parameters was varied one by one keeping the remaining parameters constant as shown in Table 2.4. The alkalization consisted of addition of varied amount of aqueous NaOH to vigorously stirred slurry of α-cellulose (3 g) in iso-propanol (80 ml)/12.5% aq. iso-propanol (in case of PH) over a period of 30 min. Stirring was continued for another 60 min. Then varied amount of monochloro acetic acid dissolved in 10 ml iso-propanol was added under continuous stirring and the reaction mixture was heated upto the desired temperature and stirred at that temperature for fixed duration. After neutralizing the excess alkali with acetic acid, the CMC samples were filtered, washed with 70% aq. methanol, followed by absolute methanol, and dried at 60°C in oven. Yield: 110–124% (DCS), 110–133% (LC), and 140–150% (PH). Using the optimized set of reaction conditions as presented in Table 2.5,

Table 2.4 Reaction parameters for carboxymethylation of α-cellulose isolated from *Dendrocalamus strictus* (DCS), *Lantana camara* (LC), and *Parthenium hysterophorus* (PH)

Reaction parameters	DCS	LC	PH
Aq. NaOH concentration, temp. (°C)	2.5–12.5M 28	3.24 (mol/AGU); 10–40%; 25	3.89 (mol/AGU); 18–70% 25
MCA (mol/AGU)	1.80–2.55	1.55–2.30	0.98–2.48
Temperature of carboxymethylation (°C)	35–65	35–65	45–65
Duration of carboxymethylation (h)	1.5–5.5	1.5–4.5	3–6

Table 2.5 Optimized reaction parameters for preparing CMC from α-cellulose isolated from *Dendrocalamus strictus* (DCS), *Lantana camara* (LC), and *Parthenium hysterophorus* (PH)

Reaction parameters	DCS	LC	PH
Aq. NaOH concentration, temp. (°C)	10M	3.24 (mol/AGU); 20%	3.89 (mol/AGU); 60%
MCA (mol/AGU)	1.80	2.05	1.98
Temperature of carboxymethylation (°C)	4.5	3.5	5.0
Duration of carboxymethylation (h)	55	55	55

water-soluble Na-CMC of degree of substitution 0.98 (DCS), 1.22 (LC), and 1.33 (PH) could be prepared (Varshney et al. 2005; Khullar et al. 2007).

2.3.3.2 Cyanoethylation

A typical cellulose etherification involving Michael addition of an activated C=C bond of acrylonitrile (AN) to a partially anionized cellulosic hydroxyls in an aqueous alkaline medium represented below was employed.

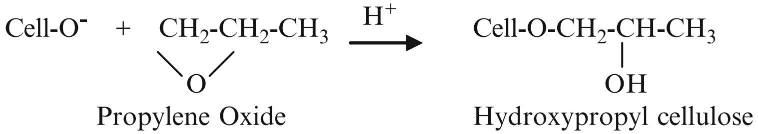
$$\underset{\text{AN}}{\text{Cell-OH} + \text{CH}_2 = \text{CH-CN}} \xrightarrow{\text{NaOH}} \underset{\text{Cyanoethyl cellulose}}{\text{Cell-O-CH}_2\text{-CH}_2\text{-CN}}$$

Cellulose (2 g) obtained from bamboo was cyanoethylated by first converting it into alkali cellulose using 20 ml of aqueous sodium hydroxide solution (8–14% by weight) for 1 h at temperature varying between 20 and 40°C followed by squeezing alkali from alkali cellulose up to three times the weight of the cellulosic material. The alkali cellulose was then dispersed in a large excess of acrylonitrile (70–90 mol/AGU) and reacted at a certain temperature for a fixed duration varying from 45 to 60°C and 0.5 to 1.25 h, respectively. During this reaction, the cyanoethylcellulose is dissolved in an excess of acrylonitrile to yield a homogenous solution. Each of these parameters was altered one by one keeping the remaining parameters constant in the reaction in order to optimize the reaction conditions for the production of CEC of maximum degree of substitution. The reaction was stopped by adding an excess of 10% aqueous acetic acid and was subsequently precipitated from this still homogenous reaction mass by an excess of ethanol/water mixture (1:1, v/v), filtered, washed first with hot and then with cold water followed by drying in vacuum at 60°C (Yield: 124–145%). Using the optimized set of conditions, viz aqueous NaOH concentration 12%, alkalization temperature 20°C, acrylonitrile concentration 90 mol/AGU, cyanoethylation time 0.75 h, and temperature 55°C, an organosoluble CEC of DS 2.2 could be prepared (Khullar et al. 2008).

2.3.3.3 Hydroxypropylation

A typical hydroxypropylation reaction shown below was used.

$$\text{Cell-OH} \xrightleftharpoons{\text{NaOH}} \text{Cell-O}^- + \text{H}^+ \tag{2.3}$$



$$\text{Cell-O}^- + \underset{\text{O}}{\text{CH}_2\text{-CH}_2\text{-CH}_3} \xrightarrow{\text{H}^+} \text{Cell-O-CH}_2\text{-}\underset{\text{OH}}{\text{CH}}\text{-CH}_3 \tag{2.4}$$

The reaction was carried out in two steps – alkalization and etherification of cellulose under heterogeneous conditions and the process was optimized with respect to percent hydroxypropoxyl content (% HP) by varying the process parameters such as concentration of NaOH and propylene oxide (PO), temperature, and duration of reaction and studying their effect on the hydroxypropoxyl content. Each of these parameters was varied one by one keeping the remaining parameters constant in the reaction as shown in Table 2.6. The alkalization was carried out by adding varying amount of aqueous NaOH to slurry of finely pulverized cellulose (1.0 g) in iso-propanol (10 ml) at ambient temperature, with continuous stirring for 1 h (DS), while in case of PH for 0.5 h. Alkali cellulose thus formed was pressed to remove alkali and transferred to a three-necked round-bottom flask of capacity 250 ml, fitted with a coiled condenser and nitrogen inlet. Ice-cold water was circulated in the condenser throughout the reaction. Varied amount of propylene oxide (PO) in iso-propanol (50 ml) and water (2 ml) were added and the reaction was allowed to proceed at desired temperature for fixed duration. After neutralizing the excess alkali with acetic acid, the synthesized HPC samples were dissolved in water and precipitated in acetone, filtered and washed in acetone, and dried at 60°C in oven [Yield: 110–130% (DCS), 105–144% (PH)]. The standardized reaction

Table 2.6 Reaction parameters for hydroxypropylation of α-cellulose isolated from *Dendrocalamus strictus* (DCS) and *Parthenium hysterophorus* (PH)

Reaction parameters	DCS	PH
Aq. NaOH concentration (w/v%)	14–26	18 (0.5–2.0 mol/AGU)
Propylene oxide (mol/AGU)	11.6–29	11.6–38.9
Temperature of hydroxypropylation (°C)	30–60	60–80
Duration of hydroxypropylation (h)	2–5	2–4