# Handbook of Polymer Nanocomposites. Processing, Performance and Application

## Volume C: Polymer Nanocomposites of Cellulose Nanoparticles

Jitendra K. Pandey • Hitoshi Takagi
Antonio Norio Nakagaito • Hyun-Joong Kim
Editors

# Handbook of Polymer Nanocomposites. Processing, Performance and Application

## Volume C: Polymer Nanocomposites of Cellulose Nanoparticles

With 251 Figures and 55 Tables

Springer

*Editors*
Jitendra K. Pandey
University of Petroleum and Energy Studies (UPES)
Bidholi Campus Office Energy Acres
Dehradun, India

Antonio Norio Nakagaito
Department of Mechanical Engineering
Graduate School of Engineering
The University of Tokushima
Tokushima, Japan

Hitoshi Takagi
Advanced Materials Division
Institute of Technology and Science
The University of Tokushima
Tokushima, Japan

Hyun-Joong Kim
College of Agriculture and Life Sciences
Seoul National University
Seoul, Republic of Korea

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# Contents

# Contributors

**H. P. S. Abdul Khalil** School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia

**E. Abraham** Department of Chemistry, Bishop Moore College, Mavelikara, Kerala, India

Department of Chemistry, C.M.S. College, Kottayam, Kerala, India

Robert H. Smith Faculty of Agriculture, Food and Environment Hebrew University, Jerusalem, Israel

**A. Abu Bakar** Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Penang, Malaysia

**S. H. Ahn** School of Mechanical & Aerospace Engineering, Seoul National University, Seoul, Korea

**Ramesh Atmakuru** Department of Analytical Chemistry, International Institute of Biotechnology and Toxicology (IIBAT), Padappai, Kancheepuram, Tamilnadu, India

**Henriette Monteiro C. Azeredo** Embrapa Agroindústria Tropical, Fortaleza, CE, Brazil

**A. H. Bhat** Department of Fundamental and Applied Sciences, Universiti Teknologi Petronas, Perak, Malaysia

**Qingzheng Cheng** Forest Products Development Center, Auburn University, Auburn, AL, USA

Agricultural & Biological Engineering, University of Florida, Gainesville, FL, USA

**Craig M. Clemons** USDA Forest Products Laboratory, Madison, WI, USA

**Viviana P. Cyras** Facultad de Ingeniería, Instituto de Investigación en Ciencia y Tecnología de Materiales (INTEMA), Universidad de Mar del Plata, Mar del Plata, Argentina

**Y. Davoudpour** School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia

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

Department of Chemistry, C.M.S. College, Kottayam, Kerala, India

**Hong Dong** Macromolecular Science and Technology Branch, U.S. Army Research Laboratory, Aberdeen, MD, USA

**Rani F. Elhajjar** College of Engineering & Applied Science, University of Wisconsin, Milwaukee, WI, USA

**Waleed K. El-Zawawy** Cellulose and Paper Department, National Research Center, Giza, Egypt

**Clea Brito de Maria Figueirêdo** Embrapa Agroindústria Tropical, Fortaleza, CE, Brazil

**M. Laura Foresti** Instituto de Tecnología en Polímeros y Nanotecnología (ITPN), Engineering Faculty, University of Buenos Aires, National Research Council (CONICET), Las Heras, Buenos Aires, Argentina

**Toru Fujii** Department of Mechanical Engineering and Systems, Doshisha University, Kyotonabe, Kyoto, Japan

**Mohamed H. Gabr** Department of Mechanical Engineering and Systems, Research and Development Center, Kanazawa Institute of Technology, Ishikawa, Kyoto, Japan

Faculty of Industrial Education, Sohag University, Sohag, Egypt

**Raed Hashaikeh** Materials Science and Engineering Program, Masdar Institute of Science and Technology, Abu Dhabi, United Arab Emirates

**Mohammad L. Hassan** Cellulose and Paper Department & Advanced Materials and Nanotechnology Group, Centre of Excellence for Advanced Sciences, National Research Centre, Cairo, Egypt

**Noriko Hayashi** Forestry and Forest Products Research Institute (FFPRI), Tsukuba, Ibaraki, Japan

**Maha M. Ibrahim** Cellulose and Paper Department, National Research Center, Giza, Egypt

**Shinsuke Ifuku** Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, Tottori, Japan

**Syed H. Imam** Bioproduct Chemistry & Engineering Research, WRRC, ARS-USDA, Albany, CA, USA

**Yukiko Ishikura** Local Independent Administrative Agency, Hokkaido Research Organization, Forest Research Department, Forest Products Research Institute, Asahikawa, Japan

**P. Jain** Central Institute for Research on Cotton Technology, Matunga, Mumbai, India

**M. Jawaid** Department of Biocomposite Technology, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, Serdang, Selangor, Malaysia

**Sera Jeon** Laboratory of Adhesion & Bio-Composites, Program in Environmental Materials Science, Seoul National University, Seoul, Republic of Korea

**Mehdi Jonoobi** Department of Engineering Sciences and Mathematics, Lulea University of Technology, Lulea, Sweden

**Hyun-Joong Kim** College of Agriculture and Life Sciences, Seoul National University, Seoul, Republic of Korea

**Tetsuo Kondo** Biomaterial Design Laboratory, Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, Fukuoka, Japan

**Rekha Rose Koshy** Department of Chemistry, Bishop Moore College, Mavelikara, Kerala, India

**Parakalan Krishnamachari** Materials Science and Engineering Program, Masdar Institute of Science and Technology, Abu Dhabi, United Arab Emirates

**Hyeok-Jin Kwon** Laboratory of Adhesion & Bio-Composites, Program in Environmental Materials Science, Seoul National University, Seoul, Republic of Korea

**Hyun Taek Lee** School of Mechanical & Aerospace Engineering, Seoul National University, Seoul, Korea

**Haiqing Liu** Fujian Provincial Key Laboratory of Polymer Materials, College of Materials Science and Technology, Fujian Normal University, Fuzhou, China

**Ruilai Liu** Fujian Provincial Key Laboratory of Polymer Materials, College of Materials Science and Technology, Fujian Normal University, Fuzhou, China

**Thiripura Sundari Marimuthu** Department of Analytical Chemistry, International Institute of Biotechnology and Toxicology (IIBAT), Padappai, Kancheepuram, Tamilnadu, India

**M. Misra** Department of Plant Agriculture, or, School of Engineering, University of Guelph, Guelph, ON, Canada

**Juan I. Moran** Facultad de Ingeniería, Instituto de Investigación en Ciencia y Tecnología de Materiales (INTEMA), Universidad de Mar del Plata, Mar del Plata, Argentina

**Antonio Norio Nakagaito** Department of Mechanical Engineering, Graduate School of Engineering, The University of Tokushima, Tokushima, Japan

**Diego M. do Nascimento** Embrapa Agroindústria Tropical, Fortaleza, CE, Brazil

**Kazuya Okubo** Department of Mechanical Engineering and Systems, Doshisha University, Kyotonabe, Kyoto, Japan

**Jitendra K. Pandey** University of Petroleum and Energy Studies (UPES), Bidholi Campus Office Energy Acres, Dehradun, India

**Ji-Won Park** Laboratory of Adhesion & Bio-Composites, Program in Environmental Materials Science, Seoul National University, Seoul, Republic of Korea

**Krishna M. Pillai** College of Engineering & Applied Science, University of Wisconsin, Milwaukee, WI, USA

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

**Morsyleide F. Rosa** Embrapa Agroindústria Tropical, Fortaleza, CE, Brazil

**Enih Rosamah** Faculty of Forestry, Mulawarman University, Kelua Samarinda, East Kalimantan, Indonesia

**Ronald C. Sabo** USDA Forest Products Laboratory, Madison, WI, USA

**D. R. Saini** Department of Polymer Science and Engineering, National Chemical Laboratory, Pune, India

**Yarjan Abdul Samad** Materials Science and Engineering Program, Masdar Institute of Science and Technology, Abu Dhabi, United Arab Emirates

**P. Satyamurthy** Central Institute for Research on Cotton Technology, Matunga, Mumbai, India

**Klanarong Sriroth** Kasetsart Agricultural and Agro-Industrial Product Improvement Institute, Department of Biotechnology, Kasetsart University, Bangkok, Thailand

**Jackapon Sunthornvarabhas** Laboratory of Adhesion & Bio–Composites, Program in Environmental Materials Science, Seoul National University, Seoul, Republic of Korea

Cassava and Starch Technology Research Unit, National Center for Genetic Engineering and Biotechnology, Bangkok, Thailand

**Pitt Supaphol** The Petroleum and Petrochemical College (PPC) and The Center of Excellence on Petrochemical and Materials Technology (PetroMAT), Chulalongkorn University, Pathumwan, Bangkok, Thailand

**Orawan Suwantong** School of Science, Mae Fah Luang University, Muang, Chiang Rai, Thailand

**Paridah Md. Tahir** Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia (UPM), Serdang, Selangor, Malaysia

**Hitoshi Takagi** Advanced Materials Division, Institute of Technology and Science, The University of Tokushima, Tokushima, Japan

**Chunyi Tang** College of Biological and Chemical Engineering, Guangxi University of Science and Technology, Liuzhou, China

**Kalsang Tharpa** Department of Chemistry, University of Mysore, Manasagangothri, Mysore, Karnataka, India

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

International and InterUniversity Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam, Kerala, India

**Zhaohui Tong** Agricultural & Biological Engineering, University of Florida, Gainesville, FL, USA

**A. Vazquez** Instituto de Tecnología en Polímeros y Nanotecnología (ITPN), Engineering Faculty, University of Buenos Aires, National Research Council (CONICET), Las Heras, Buenos Aires, Argentina

**N. Vigneshwaran** Central Institute for Research on Cotton Technology, Matunga, Mumbai, India

**Siqun Wang** Center for Renewable Carbon, University of Tennessee, Knoxville, TN, USA

**Masakazu Yoshikawa** Department of Biomolecular Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto, Japan

**I. S. M. Zaidul** Faculty of Pharmacy, International Islamic University Malaysia, Kuala Lumpur, Malaysia

**Lukmanul Hakim Zaini** Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia (UPM), Serdang, Selangor, Malaysia

# Cellulosic Nanocomposites from Natural Fibers for Medical Applications: A Review

# 25

H. P. S. Abdul Khalil, A. H. Bhat, A. Abu Bakar, Paridah Md. Tahir, I. S. M. Zaidul, and M. Jawaid

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H.P.S. Abdul Khalil (✉)
School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia
e-mail: akhalilhps@gmail.com

A.H. Bhat
Department of Fundamental and Applied Sciences, Universiti Teknologi Petronas, Perak, Malaysia
e-mail: bhataamir@gmail.com

A. Abu Bakar
Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Penang, Malaysia
e-mail: azhar@eng.usm.my

P.M. Tahir
Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia (UPM), Serdang, Selangor, Malaysia
e-mail: parida.introp@gmail.com

I.S.M. Zaidul
Faculty of Pharmacy, International Islamic University Malaysia, Kuala Lumpur, Malaysia
e-mail: zaidul@iium.edu

M. Jawaid
Department of Biocomposite Technology, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, Serdang, Selangor, Malaysia
e-mail: akhalilhps@gmail.com

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## Abstract

The nanocellulose and its composites have been covered in this chapter which is confirmed to be a very versatile material having the wide range of medical applications, including cardiovascular implants, scaffolds for tissue engineering, repair of articular cartilage, vascular grafts, urethral catheters, mammary prostheses, penile prostheses, adhesion barriers, and artificial skin. These implants were produced from bioresorbable and/or biodegradable materials.

Nanocellulose, such as that produced other than microfibrillated cellulose and cellulose nanowhiskers, is also produced by the bacteria (bacterial cellulose, BC) which is also an emerging biomaterial with great potential as a biological implant, wound and burn dressing material, and scaffolds for tissue regeneration. Moreover, the nanostructure and morphological similarities with collagen make cellulose attractive for cell immobilization and cell support. This article describes current and future applications of cellulosic nanofibers in the biomedical field.

Cellulose micro-/nanofibril as a reinforcing material for composites is becoming more and more attractive to researchers in composite science because of its potential lightweight and high strength. In the present article, we have reviewed the nanocellulosic fibers-based nanocomposites for medical applications. Processing methods, properties, and various applications of cellulosic composites are also discussed in this article. However, the separation of cellulose nanofibers along with the manufacture of cellulose nanocomposites is still challengeable. The aim of this chapter is to demonstrate the current state of development in the field of cellulose nanofibril-based nanocomposite research and application through examples.

**Keywords**
Nanocellulose • Composites • Nanofibers • Cellulose

## 1 Introduction

The hydrophilic nature of MFC has led most of the studies to be focused on nanocomposites based on hydrophilic matrices. For example, Nakagaito and Yano [1, 2]) impregnated microfibrillated Kraft pulp with a phenol–formaldehyde resin and then compressed the resulting material under high pressure to produce high-strength cellulose nanocomposites.

This study was also designed to clarify how the degree of fibrillation of pulp fibers affects the mechanical properties of cellulose composites. It was found that fibrillation that only influences the fiber surfaces is not effective in improving composite strength but that a complete fibrillation of the bulk of the fibers is required. In the study by Nakagaito and Yano [2], this was achieved by 16–30 passes through a refiner, followed by high-pressure homogenization. The resulting nanocomposites had Young's modulus and bending strength values of 19 GPa and 370 MPa, respectively, as determined by a three-point bending test [1]. More recently, the same authors used aqueous sodium hydroxide-treated MFC and phenolic resin to produce nanocomposites. The tensile properties of MFC–resin nanocomposites were compared with those of wood pulp–resin composites, and it was shown that the tensile strength of the MFC composites was significantly higher than that of the pulp composites, regardless of the treatment or resin content. In contrast, the Young's modulus values were practically the same. These authors thus confirmed the advantage of nanostructured composites over microstructured composites in terms of obtaining high strength and ductility.

Tensile tests showed that strong alkali-treated MFC nanocomposites with resin content around 20 wt% had strain at fracture values twice as high as those of untreated MFC nanocomposites based on the same resin.

In this review we describe various approaches to the synthesis of nanofibers from plant resources. Potential use of nanofibers as reinforcing material for the development of polymer composites specifically for medical applications with enhanced properties of these composites in various biomedical fields is also discussed.

## 2 Cellulose Fibers

Cellulose fibers are being used as potential reinforcing materials because of so many advantages such as abundantly available, low weight, biodegradable, cheaper, renewable, low abrasive nature, and interesting specific properties, since these are waste biomass and exhibit good mechanical properties [3–5]. Cellulose fibers also have some disadvantages such as moisture absorption, quality variations,

**Table 25.1** The family of nanocellulose materials classified in three main subcategories (Table 25.1)

| Type of nanocellulose | Selected references and synonyms | Typical sources | Formation and average size |
|---|---|---|---|
| Microfibrillated cellulose (MFC) | Microfibrillated cellulose [85], nanofibrils and microfibrils, nanofibrillated cellulose | Wood, sugar beet, potato tuber, hemp, flax | Delamination of wood pulp by mechanical pressure before and/or after chemical or enzymatic treatment diameter: 5–60 nm length, several micrometers |
| Nanocrystalline cellulose (NCC) | Cellulose nanocrystals, crystallites [89], whiskers [90], rodlike cellulose microcrystals [151] | Wood, cotton, hemp, flax, wheat straw, mulberry bark, ramie, Avicel, tunicin, cellulose from algae, and bacteria | Acid hydrolysis of cellulose from many sources diameter: 5–70 nm length; 100–250 nm (from plant celluloses); 100 nm to several micrometers (from celluloses of tunicates, algae, bacteria) |
| Bacterial nanocellulose (BNC) | Bacterial cellulose [38], microbial cellulose [48], biocellulose [48] | Low-molecular-weight sugars and alcohols | Bacterial synthesis diameter: 20–100 nm; different types of nanofiber networks |

low thermal stability, and poor compatibility with the hydrophobic polymer matrix [6, 7]. On the basis of their dimensions, functions, and preparation methods, which in turn depend mainly on the cellulosic source and on the processing conditions, nanocellulosics are classified into three main subcategories as shown in Table 25.1.

## 2.1 Chemistry of Cellulose

Cellulose is the most abundant form of living terrestrial biomass [8] and finds applications in many spheres of modern industry. The existence of cellulose as the common material of plant cell walls was first recognized by Anselme Payen in 1838. Cellulose has been shown to be a long-chain polymer with repeating units of D-glucose, a simple sugar. It occurs in almost pure form in cotton fiber [9].

However, in wood, plant leaves, and stalks, it is found in combination with other materials, such as lignin and hemicelluloses. Although generally considered a plant material, some bacteria are also found to produce cellulose. Cellulose is a natural polymer, a long chain made by the linking of smaller molecules. The links in the cellulose chain consist of sugar, β-D-glucose [10]. The sugar units are linked when water is eliminated by combining the H and –OH group. Linking just two of these sugars produces a disaccharide called cellobiose. In the cellulose chain, the glucose units are in 6-membered rings, called pyranoses. They are joined by single oxygen atoms (acetal linkages) between the C-1 of one pyranose ring and the C-4 of the next ring. Since a molecule of water is lost due to the reaction of an alcohol and a hemiacetal to form an acetal, the glucose units in the cellulose polymer are referred to as anhydroglucose units.

The spatial arrangement or stereochemistries of these acetal linkages are very important. The pyranose rings of the cellulose molecule have all the groups larger than hydrogen sticking out from the periphery of the rings (equatorial positions). The stereochemistry at carbons 2, 3, 4, and 5 of the glucose molecule is fixed, but in pyranose form, the hydroxyl at C-4 can approach the carbonyl at C-1 from either side, resulting in two different stereochemistries at C-1. When the hydroxyl group at C-1 is on the same side of the ring as the C-6 carbon, it is said to be in the configuration. In cellulose, the C-1 oxygen is in the opposite or β-configuration (i.e., cellulose is poly [β-1, 4-ᴅ-anhydroglucopyranose]. This β-configuration, with all functional groups in equatorial positions, causes the molecular chain of cellulose to extend in a more or less straight line, making it a good fiber-forming polymer [164].

Because of the equatorial positions of the hydroxyls on the cellulose chain, they protrude laterally along the extended molecule and are readily available for hydrogen bonding. These hydrogen bonds cause the chains to group together in a highly ordered structure. Since the chains are usually longer than the crystalline regions, they are thought to pass through several different crystalline regions, with areas of disorder in between ("fringed-micelle" model) [11]. The interchain hydrogen bonds in the crystalline regions are strong, giving the resultant fiber good strength and insolubility in most solvents. They also prevent cellulose from melting (non-thermoplastic). In the less ordered regions, the chains are further apart and more available for hydrogen bonding with other molecules, such as water. Most cellulose structures can absorb large quantities of water (hygroscopic). Thus, cellulose swells but does not dissolve in water [164].

The cellulose molecule contains three different kinds of anhydroglucose units, the reducing end with a free hemiacetal (or aldehyde) group at C-1, the nonreducing end with a free hydroxyl at C-4, and the internal rings joined at C-1 and C-4. But because of long-chain length, the chemistry of the alcohol groups of the internal units predominates, so long as the chains are not cleaved by the reaction conditions. However, unlike simple alcohols, cellulose reactions are usually controlled by steric factors than would be expected on the basis of the inherent reactivity of the different hydroxyl groups. C-2, C-3, and C-6 hydroxyls and C-H groups are active sites in cellulose for the incorporation of polymeric chains through grafting. In grafting it has been reported that the reactivity of hydroxyl group at C-6 is far less than those at C-2 and C-3 [164].

## 2.2 Chemical Composition, Structure, and Properties of Cellulose Fibers

Cellulose fibers can be classified according to their origin and grouped into leaf, abaca, cantala, curaua, date palm, henequen, pineapple, sisal, and banana; seed, cotton; bast, flax, hemp, jute, and ramie; fruit, coir, kapok, and oil palm; grass, alfa, bagasse, and bamboo; and stalk, straw (cereal) [12]. The bast and leaf (the hard fibers) types are the most commonly used in composite applications [13–15]. Commonly used plant fibers are cotton, jute, hemp, flax, ramie, sisal, coir, henequen, and kapok. The largest producers of sisal in the world are Tanzania and Brazil.

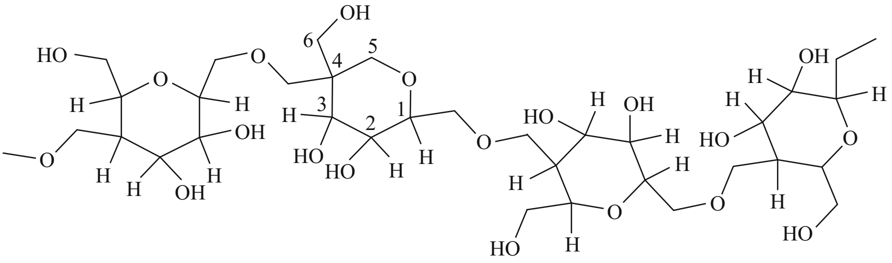


**Fig. 25.1** Cellulosic units joined by glycosidic linkages

Henequen is produced in Mexico whereas abaca and hemp in the Philippines. The largest producers of jute are India, China, and Bangladesh [16, 17].

Plant fibers are constitutes of cellulose fibers, consisting of helically wound cellulose microfibrils, bound together by an amorphous lignin matrix. Lignin keeps the water in fibers and acts as a protection against biological attack and as a stiffener to give stem its resistance against gravity forces and wind.

Hemicellulose found in the natural fibers is believed to be a compatibilizer between cellulose and lignin [17]. The cell wall in a fiber is not a homogenous membrane (Fig. 25.1) [18]. Each fiber has a complex, layered structure consisting of a thin primary wall which is the first layer deposited during cell growth encircling a secondary wall [19]. The secondary wall is made up of three layers and the thick middle layer determines the mechanical properties of the fiber. The middle layer consists of a series of helically wound cellular microfibrils formed from long-chain cellulose molecules. The angle between the fiber axis and the microfibrils is called the microfibrillar angle. The characteristic value of microfibrillar angle varies from one fiber to another. These 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 fiber.

The properties of cellulose fibers are affected by many factors such as variety, climate, harvest, maturity, retting degree, decortications, disintegration (mechanical, steam explosion treatment), fiber modification, textile, and technical processes (spinning and carding) [20]. In order to understand the properties of natural fiber-reinforced composite materials, it becomes necessary to know the mechanical, physical, and chemical properties of natural fibers. Flax fibers are relatively strong fibers as compared to other natural fibers. The tensile strength of elementary fibers is in the region of 1,500 MPa, and for technical fibers a value of circa 800 MPa was observed at 3 mm clamp length [21]. Baley [22] and Lamy and Baley [23] investigated the modulus of flax fibers. The modulus of elementary fibers is dependent on the diameter of fiber, and it ranges from 39 GPa for fibers having diameter approximately 35 μm to 78 GPa for fibers having 5 μm diameter. This variation is related to the variation in relative lumen size between fibers having different diameters. An average Young's modulus of 54 GPa was observed after numerous tensile tests on single flax fibers, and the results are within the range of moduli measured on technical fibers. The mechanical, chemical, and physical properties of plant fibers are strongly harvest dependent, influenced by climate, location, weather conditions, and soil characteristics. These properties are also affected during the processing of fiber such as retting, scotching, bleaching, and spinning [24].

Cellulose fibers have relatively high strength, high stiffness, and low density [25]. The characteristic value for soft-wood-Kraft fibers and flax has been found close to the value for E-glass fibers. Different mechanical properties can be incorporated in natural fibers during processing period. The fiber properties and structure are influenced by several conditions and vary with area of growth, its climate, and age of the plant [26]. Technical digestion of the fiber is another important factor which determines the structure as well as characteristic value of the fiber. The elastic modulus of the bulk natural fibers such as wood is about 10 GPa. Cellulose fibers with moduli up to 40 GPa can be separated from wood by chemical pulping process. Such fibers can be further subdivided into microfibrils within elastic modulus of 70 GPa. Theoretical calculations of elastic moduli of cellulose chain have been given values up to 250 GPa. However, no technology is available to separate these from microfibrils [27]. The tensile strength of natural fibers depends upon the test length of the specimen which is of main importance with respect to reinforcing efficiency. Mieck et al. [28] and Mukherjee and Satyanarayana [29] reported that tensile strength of flax fiber is significantly more dependent on the length of the fiber. In comparison to this, the tensile strength of pineapple fiber is less dependent on the length, while the scatter of the measured values for both is located mainly in the range of the standard deviation. The properties of flax fiber are controlled by the molecular fine structure of the fiber which is affected by growing conditions and the fiber processing techniques used. Flax fibers possess moderately high specific strength and stiffness.

Quality and other properties of fibers depend on factors such as size, maturity, and processing methods adopted for the extraction of fibers. Properties such as density, electrical resistivity, ultimate tensile strength, and initial modulus are related to the internal structure and chemical composition of fibers [25]. Desirable properties for fibers include excellent tensile strength and modulus, high durability, low bulk density, good moldability, and recyclability.

## 2.3 Cellulose Derivatives

Cellulose derivatives are important commercial products for plastics, textiles, packaging, films, lacquers, and explosives. More recently, cellulose derivatives which are soluble in water or dilute alkali have been developed. Researchers are finding ways to use these derivatives as finishing and sizing agents for textiles; as absorbable surgical gauze, protective colloids, and adhesives; as thickening agents for foods, creams, ointments, and pastes; and in pharmaceutical, printing, paper, and other industries.

Wood cellulose is the principal raw material for cellulose derivative products, and several million tons are produced each year. The second source of cellulose for

**Table 25.2** Cellulose derivatives and its properties

| Cellulose derivatives | Properties |
|---|---|
| Cellulose acetate | Can be composted or incinerated |
| | Can be dyed; however, special dyes and pigments are required since acetate does not accept dyes ordinarily used for cotton and rayon (this also allows cross-dyeing) |
| Cellulose propionate | Stiffer than cellulose acetate or cellulose acetate butyrate |
| | Transparent and glossy with better low temperature impact properties than cellulose acetate or cellulose acetate butyrate |
| Cellulose acetate/ butyrate (CAB) | Better weathering characteristics than cellulose acetate or cellulose propionate |
| | Tougher than cellulose acetate |
| Carboxymethyl cellulose (CMC) | Viscosity modifier or thickener and to stabilize emulsions |
| | More cooling capacity than ice |
| Hydroxyethyl cellulose (HEC) | Emulsion stabilizer |
| | Nonionic surfactant stabilizer |
| Hydroxypropyl cellulose (HPC) | HPC is used as a thickener, as a low level binder, and as an emulsion stabilizer |
| | As a disintegrant and a binder |
| Methyl cellulose (MC) | Thickener and emulsifier |
| | Variable viscosity personal lubricant |
| | Substitute for tears or saliva |
| | Bacterial motility inhibitor |
| Ethyl cellulose (EC) | As a thin-film coating material |
| | As a food additive and as an emulsifier |
| Hydroxypropyl methylcellulose (HPMC) | Tile adhesives and renders, rheology modifier, and water retention agent |
| | Inert, viscoelastic polymer used as an ophthalmic lubricant, as well as an excipient and controlled delivery component in oral medicaments |
| Cellulose nitrate | Highly flammable compound |
| | Magician's flash paper leaving no ash |
| | Nitrocellulose lacquer is also used as an aircraft dope |
| | Now declining importance due to its unstable nature |

cellulose derivatives is cotton linters (chemical cotton). Cotton linters find preferred use in certain products such as in cellulose acetate for plastics or high-tenacity rayon. For other applications cellulose acetate is more often made from wood cellulose as shown in Table 25.2.

## 3 Cellulose Nanofibers

Cellulose nanofibers have a high potential to be used in many different areas particularly as reinforcement in the development of nanocomposites. Many studies have been done on isolation and characterization of cellulose nanofibers from various sources. Cellulose nanofibers can be extracted from the cell walls by simple mechanical methods or a combination of both chemical and mechanical methods.

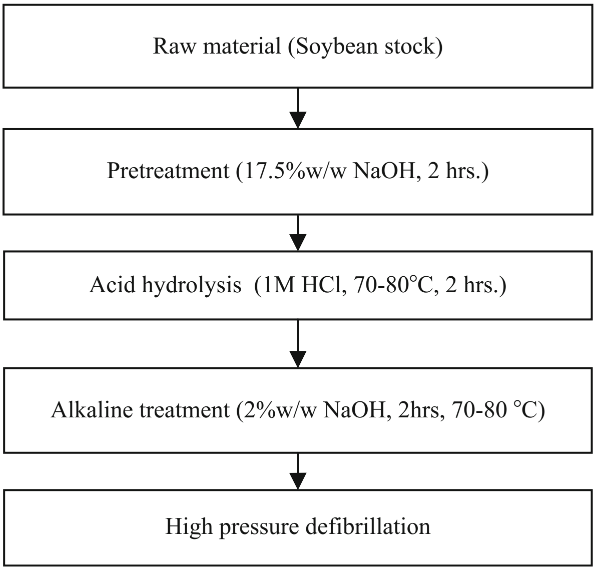


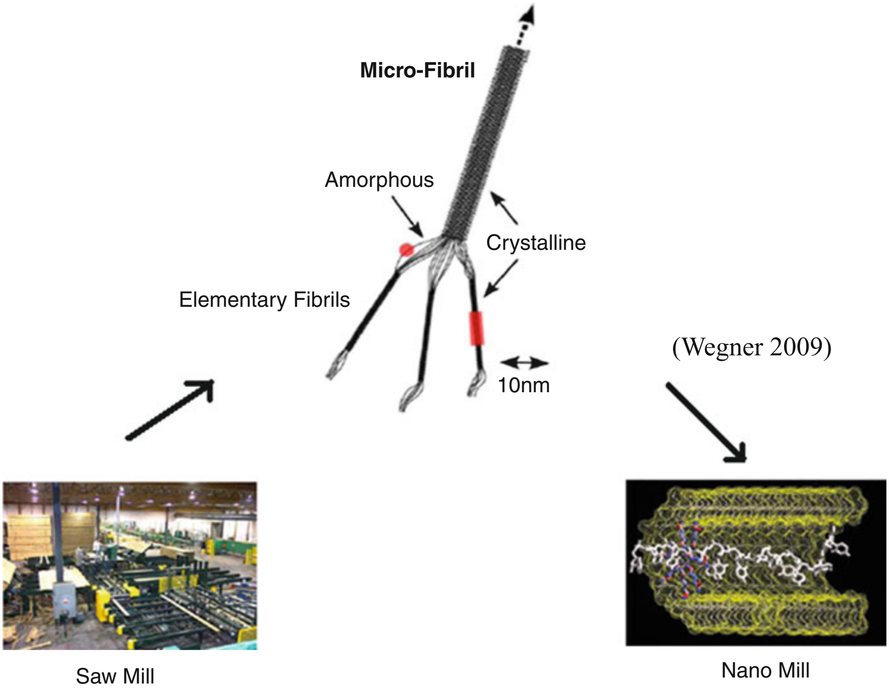
**Fig. 25.2** Isolation of nanofibers by chemomechanical treatment [31]

## 3.1 Synthesis of Cellulose Nanofibers

Alemdar and Sain (2008) have extracted cellulose nanofibers from wheat straw by a chemical treatment, resulting to purified cellulose. To individualize the nanofibers from the cell walls, a mechanical treatment (disintegration and defibrillation steps) was applied to the chemically treated fibers. Cellulose nanofibers were extracted from the agricultural residues, wheat straw, and soy hulls, by a chemomechanical technique (Alemdar and Sain 2008). The wheat straw nanofibers were determined to have diameters in the range of 10–80 nm and lengths of a few thousand nanometers. By comparison, the soy hull nanofibers had a diameter of 20–120 nm and shorter lengths than the wheat straw nanofibers. Zimmermann et al. [30] separated nanofibrillated cellulose (NFC) at the greatest possible lengths and diameters below 100 nm from different starting cellulose materials by mechanical dispersion and high-pressure (up to 1,500 bar) homogenization processes. The treatment resulted in nanoscaled fibril networks.

The cellulose nanofibers were extracted by Wang and Sain [31] from soybean stock by chemomechanical treatments (Fig. 25.2).

The cellulose nanofibrils were extracted from wheat straw using steam explosion, acidic treatment, and high-shear mechanical treatment. Alkaline-treated pulp was soaked in 8 % solution of $H_2O_2$ (v/v) overnight. Bleached pulp was then rinsed with abundant distilled water. Bleached pulp was then treated with 10 % HCl (1 N) solution and mixed using ultrasonicator at temperature around 60 ± 1 °C for 5 h. Finally, the fibers were taken out and washed several times with distilled water in order to neutralize the final pH and then dried. Fibers were suspended in water and continuously stirred with a high-shear homogenizer for 15 min. High-shearing action breaks down the fiber agglomerates and results in nanofibrils (Fig. 25.3) [32].



(Wegner 2009)

**Fig. 25.3** Progress in fiber processing from natural wood to nanofibers

## 3.2 Structure and Properties of Cellulose Nanofibers

Transmission electron microscopy (TEM), scanning electron microscopy (SEM), field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), wide-angle X-ray scattering (WAXS), and NMR spectroscopy have been used to study the structure of cellulose nanofibers [165]. A combination of microscopic techniques with image analysis can provide information about widths of cellulose nanofiber, but it is very difficult to find out the lengths of the nanofiber because of entanglements and difficulties in identifying both ends of individual nanofibers. It is often reported that MFC suspensions are not homogeneous and that they consist of cellulose nanofibers and nanofiber bundles (Siro and Plackett 2010).

Teixeira et al. [33] obtained the suspensions of white and colored nanofibers by the acid hydrolysis of white and naturally colored cotton fibers. Possible differences among them in morphology and other characteristics were investigated. Morphological study of cotton nanofibers showed a length of 85–225 nm and diameter of 6–18 nm. It was found that there were no significant morphological differences among the nanostructures from different cotton fibers. The main differences found were the slightly higher yield, sulfonation effectiveness, and thermal stability under dynamic temperature conditions of the white nanofiber. On the other hand, the colored nanofibers showed a better thermal stability than the white in isothermal conditions at 180 °C.

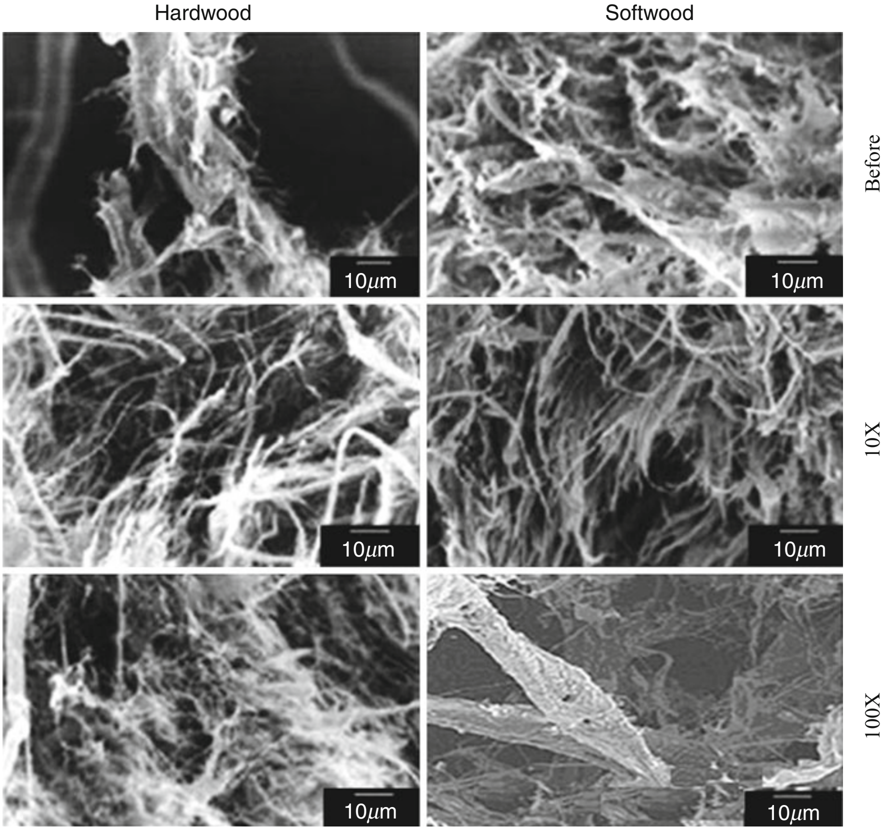


**Fig. 25.4** Scanning electron micrographs of hard- and softwood cellulose fibers, before and after 10 passes through the homogenizer [34]

The structure of the cellulose nanofibers from agricultural residues was investigated by Alemdar and Sain (Alemdar and Sain 2008). FTIR spectroscopic analysis demonstrated that chemical treatment also led to partial removal of hemicelluloses and lignin from the structure of the fibers. PXRD results revealed that this resulted in improved crystallinity of the fibers. Thermal properties of the nanofibers were studied by the TGA technique and were found to increase dramatically.

Stelte and Sanadi [34] have studied the mechanical fibrillation process for the preparation of cellulose nanofibers from two commercial hard- and softwood cellulose pulps. The degree of fibrillation was studied using light microscopy (LM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). SEM images (Fig. 25.4) of hard- and softwood fibers showed that the hardwood fibers that were fibrillated only on the surface during the refining step are now disintegrated into a network of small fibers. AFM images of the final products after high-pressure homogenization showed that the size distribution of the hard- and softwood nanofibers is in the range of 10–25 nm in diameter.

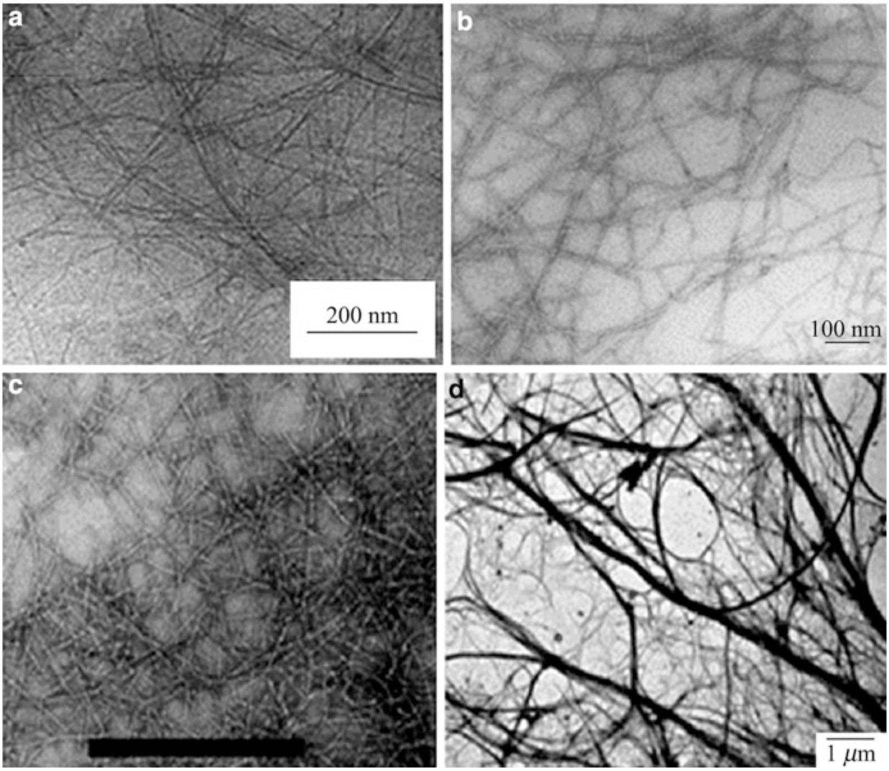


**Fig. 25.5** Transmission electron micrographs from dilute suspension of cellulose nanocrystals from (**a**) ramie [35], (**b**) bacterial [36], (**c**) sisal [37], (**d**) microcrystalline cellulose [38], (**e**) sugar beet pulp [151], (**f**) tunicin [39], (**g**) wheat straw [40], and (**h**) cotton [41]

## 3.3 Cellulose Nanofiber-Reinforced Nanocomposites

The potential of nanocomposites in various sectors of research and application is promising and attracting increasing investments. In the nanocomposite industry, a reinforcing particle is usually considered as a nanoparticle when at least one of its linear dimensions is smaller than 100 nm. Owing to the hierarchical structure and semicrystalline nature of cellulose, nanoparticles can be extracted from this naturally occurring polymer. Native cellulose fibers are built up by smaller and mechanically stronger long thin filaments, the microfibrils consisting of alternating crystalline and noncrystalline domains. Multiple mechanical shearing actions can be used to release more or less individually these microfibrils. This material is usually called microfibrillated cellulose (MFC) as shown in Fig. 25.5.

Longitudinal cutting of these microfibrils can be performed by submitting the biomass to a strong acid hydrolysis treatment, allowing dissolution of amorphous domains. The ensuing nanoparticles occur as rodlike nanocrystals or whiskers with dimensions depending on the source of cellulose and preparation procedure.

**Table 25.3** Geometrical characteristics of cellulose nanocrystals from various sources: length (L), cross section (D), and aspect ratio (L/d)

| Source | L (nm) | D (nm) | L/D |
|---|---|---|---|
| Acacia pulp | 100–250 | 5–15 | – |
| Alfa | 200 | 10 | 20 |
| Algal (*Valonia*) | >1,000 | 10–20 | ∞ |
| Bacterial | 100–several 1,000 | 5–10 × 30–50 | – |
| Banana rachis | 500–1,000 | 5 | – |
| Bioresidue from wood bioethanol production | >100 | 10–20 | – |
| Capim dourado | 300 | 4.5 | 67 |
| Cassava bagasse | 360–1,700 | 2–11 | – |
| *Cladophora* | – | 20 × 20 | – |
| Coconut husk fibers | 80–500 | 6 | 39 |
| Cotton | 100–300 | 5–15 | 10 |
| Cottonseed linter | 170–490 | 40–60 | – |
| Curaúa | 80–170 | 6–10 | 13–17 |
| Date palm tree (rachis/leaflets) | 260/180 | 6.1 | 43/30 |
| Eucalyptus wood pulp | 145 | 6 | 24 |
| Flax | 100–500 | 10–30 | 15 |
| Grass Zoysia | 200–700 | 10–60 | – |
| Hemp | Several 1,000 | 30–100 | – |
| Luffa cylindrica | 242 | 5.2 | 47 |
| MCC | 150–300 | 3–7 | – |
| Mulberry | 400–500 | 20–40 | – |
| Pea hull | 240–400 | 7–12 | 34 |
| Ramie | 350–700 | 70–120 | |
| | (150–250) | 6–8 | |
| Recycled pulp | 100–1,800 | 30–80 | – |
| Sisal | 100–500 | 3–5 | 60/43 |
| | (215) | 5 | |
| Sugar beet pulp | 210 | 5 | 42 |
| Sugarcane bagasse | 200–310 | 2–6 | 64 |
| Tunicin | 100–>1,000 | 10–20 | 67 |
| Wheat straw | 150–300 | 5 | 45 |
| Wood | 100–300 | 3–5 | 50 |

The typical geometrical characteristics for nanocrystals derived from different species and reported in the literature are collected in Table 25.3 [42–45].

Impressive mechanical properties and reinforcing capability, abundance, low weight, and biodegradability of cellulose nanocrystals make them ideal candidates for the processing of polymer nanocomposites (Samir et al. 2005; [46–48]. With a Young’s modulus around 150 GPa and a surface area of several hundred square meters per gram [49], they have the potential to significantly reinforce polymers at low filler loadings.

A broad range of applications of nanocellulose exists even if a high number of unknown remains at date. Tens of scientific publications and experts show its potential even if most of the studies focus on their mechanical properties as reinforcing phase and their liquid crystal self-ordering properties. However, as for any nanoparticle, the main challenge is related to their homogeneous dispersion within a polymeric matrix.

## 4 Extraction of Nanofibrils

### 4.1 Homogenization

The fibrillation of pulp fiber to obtain nano-order-unit weblike network structure, called microfibrillated cellulose, is obtained through a mechanical treatment of pulp fibers, consisting of refining and high-pressure homogenizing processes. The refining process used is common in the paper industry and is accomplished via a piece of equipment called a refiner. In a disk refiner, the dilute fiber suspension to be treated is forced through a gap between the rotor and stator disks, which have surfaces fitted with bars and grooves against which the fibers are subjected to repeated cyclic stresses. This mechanical treatment brings about irreversible changes in the fibers, increasing their bonding potential by modification of their morphology and size. In the homogenization process, dilute slurries of cellulose fibers previously treated by refining are pumped at high pressure and fed through a spring high-pressure-loaded valve assembly.

As this valve opens and closes in rapid succession, the fibers are subjected to a large pressure drop with shearing and impact forces. This combination of forces promotes a high degree of microfibrillation of the cellulose fibers, resulting in microfibrillated cellulose [50]. The refining process is carried out prior to homogenization due to the fact that refining produces external fibrillation of fibers by gradually peeling off the external cell wall layers (*P* and *S*1 layers) and exposing the *S*2 layer and also causes internal fibrillation that loosens the fiber wall, preparing the pulp fibers for subsequent homogenization treatment [51]. Nakagaito and Yano [1] studied how the degree of fibrillation of pulp fibers affects the mechanical properties of high-strength cellulose composites. It was found that fibrillation solely of the surface of the fibers is not effective in improving composite strength, though there is a distinct point in the fibrillation stage at which an abrupt increase in the mechanical properties of composites occurs. In the range between 16 and 30 passes through refiner treatments, pulp fibers underwent a degree of fibrillation that resulted in a stepwise increment of mechanical properties, most strikingly in bending strength. This increase was attributed to the complete fibrillation of the bulk of the fibers. For additional high-pressure homogenization-treated pulps, composite strength increased linearly against water retention values, which characterize the cellulose's exposed surface area, and reached maximum value at 14 passes through the homogenizer (Fig. 25.6).

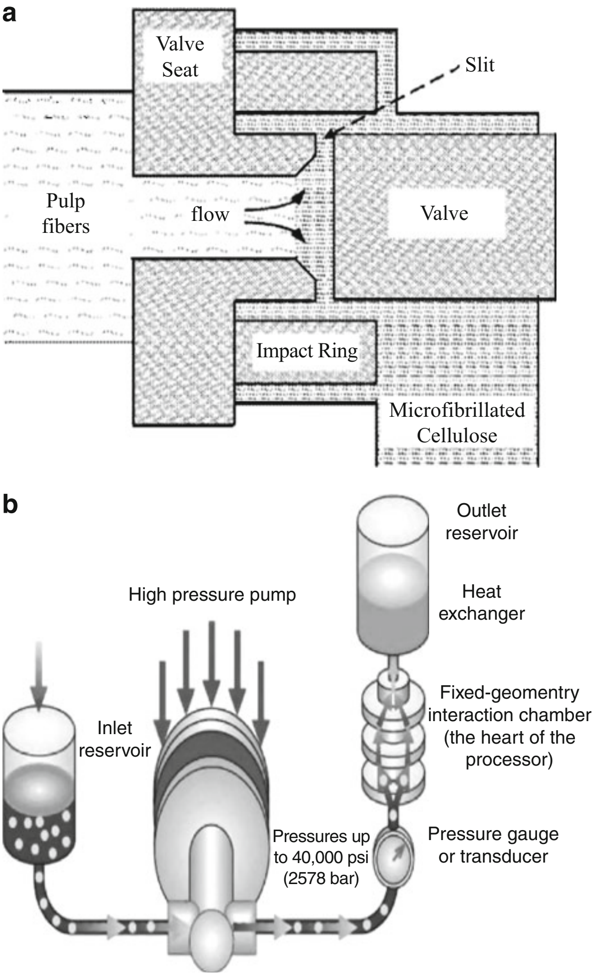


**Fig. 25.6** Schematic representation of (**a**) the homogenizer and (**b**) the microfluidizer

## 4.2 Steam Explosion

Several methods are used to extract highly purified microfibrils from the plant cell wall. They are generally based on successive chemical and mechanical treatments. The steam explosion treatment is currently still being extensively studied as a promising pretreatment method. Lignocellulosic biomass materials can be fractionated into biopolymer constituents by steam explosion technology.

Treating various biomass resources by steam explosion has been studied by many researchers [53–55]. The steam explosion process was first introduced by Mason in 1927 to defibrate wood into fiber for board production [56]. The treatment of lignocellulosic resources with high-pressure steam, for short periods of time, followed by sudden decompression (explosion) represents a simple treatment

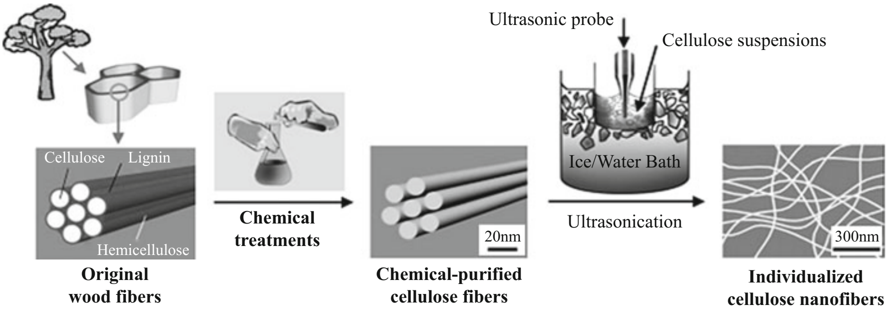


**Fig. 25.7** Procedure for individualizing cellulose nanofibers

for biomass that achieves fiberization or "mulching" by a combination of chemical and mechanical action. During the steam explosion process, the raw material is exposed to pressurized steam followed by rapid reduction in pressure resulting in substantial breakdown of the lignocellulosic structure, hydrolysis of the hemicellulose fraction, depolymerization of the lignin components, and defibrillization [57, 58]. Marchessault mentions that the steam explosion is an auto-hydrolysis process [59]. Effects of this process on biomass are:

i. Cleavage of some accessible glycosidic links
ii. Cleavage of b-ether linkages of lignin
iii. Cleavage of lignin–carbohydrate complex bonds
iv. Minor chemical modification of lignin and carbohydrates

Both the aspect ratio and percentage yield of nanocellulose obtained by this technique have been found to be very high as compared to other conventional methods [60].

## 4.3 High-Intensity Ultrasonication

This process consists of combination of chemical pretreatment and high-intensity ultrasonication (Fig. 25.7). In the chemical pretreatment stage, the wood fibers are being purified to prepare the cellulose fibers according to general methods [61, 62]. First, lignin is removed from the samples using acidified sodium chlorite solution at 75 °C for an hour; this process is then repeated five times until the product became white. Next, the samples are treated in 3 wt% potassium hydroxide at 80 °C for 2 h. and then in 6 wt% potassium hydroxide at 80 °C for 2 h in order to leach hemicellulose, residual starch, and pectin. After a series of chemical treatments, the samples are filtered and rinsed with distilled water until the residues get neutralized. To avoid generating strong hydrogen bonding among nanofibers after matrix removal, the samples are kept in a water-swollen state during the whole chemical process.

After chemical pretreatment, the purified cellulose fibers are soaked in distilled water (concentration: ~0.5 % in mass). About 120 ml of solution containing chemical-purified cellulose fibers are then placed in a common ultrasonic generator of 20–25 kHz in frequency equipped with a cylindrical titanium alloy probe tip of 1.5 cm in diameter. The subsequent ultrasonication is conducted for 30 min to isolate the nanofibers. To investigate the effect of ultrasonic intensity on the nanofibrillation of the chemical-purified cellulose fibers, the output power of the ultrasonication is conducted at different power, viz., 400, 800, 1,000, and 1,200 W, respectively. The ultrasonic treatment is carried out in an ice/water bath, and the ice is maintained throughout the entire ultrasonication time.

## 4.4 Electrospining Technique

Electrospinning technique has received a growing attention because polymer fibers prepared by this technique achieve fiber diameters in the range from micrometers down to a few nanometers straightforwardly and cost-effectively. In a typical process, a polymer solution is forced through a capillary, forming a pendent drop at the tip of capillary. Then a high voltage is applied between the capillary and a grounded collection target. When the electric field strength overcomes the surface tension of the droplet, a polymer solution jet is initiated and accelerated toward the collection target. As the jet travels through the air, the solvent evaporates and a nonwoven polymeric fabric is formed on the target. Because the resulting nonwoven fabrics often resemble the superstructure features of natural extracellular matrix, they have gained a great interest in tissue engineering as scaffold materials for tissue regeneration, immobilized enzymes and catalyst systems, and wound dressing articles. In addition, the high specific surface area and highly porous three-dimensional structure enables their use in high density cell and tissue cultures. The diameter and morphology of the resulting fiber has been shown to be effected by all variables in the electrospinning process including the solution composition, applied voltage, collector distance, and collector type [63].

In many respects, the formation of nano- and microscale fibers from cellulose via electrospinning has mirrored the history of conventional cellulose fiber spinning. Just as cellulose was derivatized to form the first manufactured fiber, it is also reported as the first electrospun fiber with patents dating back to Formhals in 1934. Over the last 50 years, several direct solvents for cellulose have been discovered and utilized in wet spinning or dry-jet wet spinning processes. Some of these solvents including *N*-methyl-morpholine *N*-oxide/water (nNMMO/$H_2O$) [64] and lithium chloride/dimethylacetamide (LiCl/DMAc) have also been investigated for electrospinning cellulose. Additionally, electrospinning cellulose fibers from some more recently developed cellulose solvents such as ionic liquids and ethylene diamine/salt have been reported [65]. The great challenges of spinning cellulose directly from a solvent without derivatization are evident in electrospinning as in wet spinning and dry-jet wet spinning, and many researchers have taken the route of spinning more readily soluble cellulose derivatives and subsequently converting the derivatives back to cellulose.

To date, it has been well established that the ES process allows easy incorporation of particles with different habits, such as 1-dimensional carbon nanotubes, 2-dimensional layered silicates, or 3-dimensional $SiO_2$ nanoparticles and many others, into the nanofibers.

## 4.5 Bacterial Synthesis

Cellulose has traditionally been sourced from plants. However, refining of plant cellulose typically involves harsh, aggressive processing to remove noncellulose materials such as lignin and hemicellulose. Fortunately, an alternative source of cellulose where no chemical or mechanical refining is necessary is available. Bacterial cellulose (hereinafter called BC) has been developed as an alternative to plant cellulose. Due to its high water-holding capacity, high crystallinity, high tensile strength, and fine weblike network structure, which means that it can be formed into any size or shape, BC is being used as a promising nanofiber biomaterial for making composites [66, 67–69, 72, 152].

It is well known that cellulose fiber networks – as in the case of paper – provide good mechanical properties because of the degree of hydrogen bonding obtained between the fibers in the network. The greater the hydrogen bonding, the stronger is the paper material. BC synthesized extracellularly by *Acetobacter xylinum* is of nano-size, as a result of which hydrogen bonding between fibrils is greater than with plant cellulose in normal paper. The hydrogen bonds due to the hydroxyl group give rise to properties such as a high degree of crystallinity, high water-holding capacity, and high tensile strength.

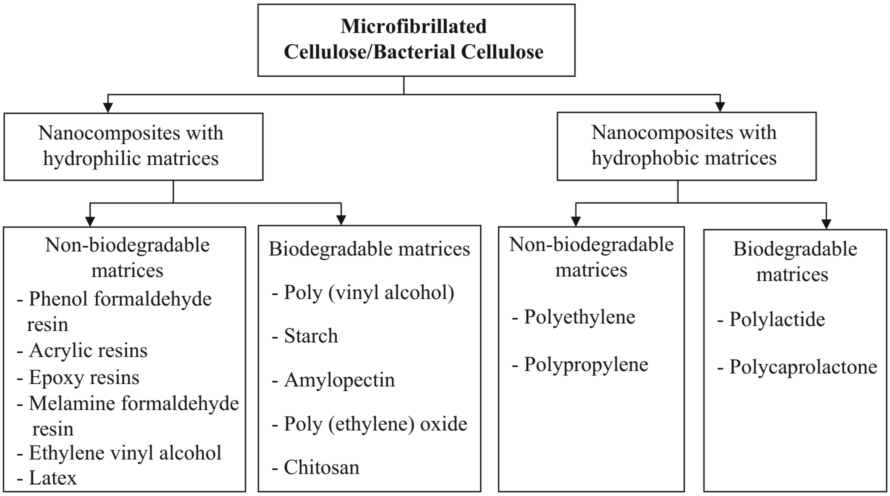
Since BC has unique properties, including high hydrophilicity, as well as having a high water-holding capacity and a fine fiber network which can be easily shaped into three-dimensional structures during synthesis, it is an excellent candidate for use as a scaffold for tissue engineering [70, 71]. The porosity of BC, which is necessary to support cell ingrowths and effective mass transport of tissue such as cartilage, makes it a natural medium for growing cells.

Due to its remarkable mechanical properties, an ability to form homogeneous membrane sheets after drying under certain synthesis conditions and an ultrafine network structure, BC is useful for numerous applications [66, 72]. The relative inertness of BC fibers has led to their use as reinforcing agents in composites [73]. Therefore, the methods of producing BC have been developed with the aims of improving yield, structure, and other desired physical properties [74, 75]. Besides using various production methods, the medium used for culture, the pH level, and the source of nitrogen and phosphate as the main foods for *Acetobacter xylinum* have all been varied [76].

Previous research has focused on ensuring that the *Acetobacter xylinum* does not undergo genetic mutation [77, 154]. Efforts to prevent mutation have included adding 20 wt% malt extract to a medium inoculated with *Acetobacter xylinum* as a cryoprotectant [78]. The implications of mutation occurring are the growth of a wild type organism which can reduce *Acetobacter xylinum*'s ability to produce cellulose. Other side effects include affecting the morphological and physiological properties of BC and a fall in the Young's modulus of the BC sheet produced because of the growth of a byproduct known as acetan [79]. Various biosynthesis-related methods of ensuring a high productivity of BC from the *Acetobacter xylinum* have been used, such as expression of sucrose, in which UDP-glucose is efficiently formed from sucrose [80]; the addition of polyacrylamide-co-acrylic acid [166]; and addition of 1 % ethanol in the medium [167]. The most recent was through cloning of the *Acetobacter xylinum* whereby the resulting yield of BC was far more than that produced by the original bacteria itself [81, 82].

## 5 Nanocomposite Processing

Cellulose nanoparticles are obtained as stable aqueous suspensions and most investigations focused on hydrosoluble (or at least hydrodispersible) or latex-form polymers. The main advantage is that the dispersion state of the nanoparticles is kept when using an aqueous medium for the processing.



After dissolution of the hydrosoluble or hydrodispersible polymer, the aqueous solution can be mixed with the aqueous suspension of cellulosic nanoparticles. The ensuing mixture is generally cast and evaporated to obtain a solid nanocomposite film. It can also be freeze-dried and hot-pressed. The preparation of cellulose nanofiber-reinforced starch [67, 83–86, 160], silk fibroin [87], poly(oxyethylene) (POE) [88–90]; Samir et al. 2005; [91], polyvinyl alcohol (PVA) [92–96], hydroxypropyl cellulose (HPC) [92, 93], carboxymethyl cellulose (CMC) [97], or soy protein isolate (SPI) [68] has been reported in the literature.

The first publication reporting the preparation of cellulose nanocrystal-reinforced polymer nanocomposites was carried out using a latex obtained by the copolymerization of styrene and butyl acrylate (poly($S$-co-BuA)) and tunicin (the cellulose extracted from tunicate – a sea animal) whiskers [98]. The same copolymer was used in association with wheat straw [40, 99] or sugar beet (Samir et al. 2004) cellulose nanocrystals. Other latexes such as poly($\beta$-hydroxyoctanoate) (PHO) [100–102], polyvinylchloride (PVC) [103–106], waterborne epoxy [107], natural rubber (NR) [108–110], and polyvinyl acetate (PVAc) [37] were also used as matrix. Recently, stable aqueous nanocomposite dispersion-containing cellulose whiskers and a poly(styrene-*co*-hexyl-acrylate) matrix were prepared via miniemulsion polymerization [45]. Addition of a reactive silane was used to stabilize the dispersion. Solid nanocomposite films can be obtained by mixing and casting the two aqueous suspensions followed by water evaporation.

The possibility of dispersing cellulosic nanofibers in nonaqueous media has been investigated using surfactants or chemical grafting, and it opens other possibilities for nanocomposites processing. Cellulose nanoparticles possess a reactive surface covered with hydroxyl groups, providing the possibility to extensive chemical modification. Although this strategy decreases the surface energy and polar character of the nanoparticles, improving by the way the adhesion with nonpolar polymeric matrix, a detrimental effect is generally reported for the mechanical performances of the composite. This unusual behavior is ascribed to the originality of the reinforcing phenomenon of polysaccharide nanocrystals resulting from the formation of a percolating network thanks to hydrogen bonding forces. Therefore, grafting of long chains instead of small molecules can be used to preserve the mechanical properties of the material.

Very few studies have been reported concerning the processing of cellulose nanofibers-reinforced nanocomposites by extrusion methods. The hydrophilic nature of cellulose causes irreversible agglomeration during drying and aggregation in nonpolar matrices because of the formation of additional hydrogen bonds between amorphous parts of the nanoparticles. Therefore, the preparation of cellulose whiskers-reinforced PLA nanocomposites by melt extrusion was carried out by pumping the suspension of nanocrystals into the polymer melt during the extrusion process [111]. An attempt to use PVA as a compatibilizer to promote the dispersion of cellulose whiskers within the PLA matrix was reported [112]. Organic acid chlorides-grafted cellulose whiskers were extruded with LDPE [113]. The homogeneity of the ensuing nanocomposite was found to increase with the length of the grafted chains. Polycaprolactone-grafted cellulose nanocrystals obtained by ring-opening polymerization (ROP) of the corresponding lactone were also used as “masterbatches” by melt blending with a PCL matrix [114].

An attempt to use a recently patented concept (dispersed nano-objects protective encapsulation – DOPE process) intended to disperse carbon nanotubes in polymeric matrices was reported. Physically cross-linked alginate capsules were successfully formed in the presence of either cellulose whiskers or microfibrillated cellulose [115]. The ensuing capsules have been extruded with a thermoplastic material.

## 5.1 Interfacial Interactions

Strong interactions between cellulose nanofibers prepared from cottonseed linters and between the filler and the glycerol-plasticized starch matrix were reported to play a key role in reinforcing properties [116]. In nonpercolating systems, for instance for materials processed from freeze-dried cellulose nanocrystals, strong matrix/filler interactions enhance the reinforcing effect of the filler.

This observation was reported using EVA matrices with different vinyl acetate contents and then different polarities [117]. An improvement of matrix/filler interactions by using cellulose whiskers coated with a surfactant was shown to play a major role on the nonlinear mechanical properties, especially on the elongation at break [168]. Grunert and Winter [36] founded a higher reinforcing effect for unmodified cellulose whiskers than for trimethylsilylated whiskers. Apart from the fact that 18 % of the weight of the silylated crystals was due to the silyl groups, they attributed this difference to restricted filler/filler interactions.

## 5.2 Nanocomposite Manufacturing Method

Natural fiber composites are prepared using various composites manufacturing methods such as compression molding, injection molding, resin transfer molding (RTM), and vacuum bagging. The preforms are mostly fibers, fabrics, or nonwovens. Prepregs are also widely used to prepare composites [118]. Where $V_f$ is the fiber volume fraction, $W_f$ is the weight of fiber and Wm is the weight of matrix. $r_f$ and $r_m$ are the densities of the fiber and matrix, respectively. The production of the composites is optimized in relation to temperature, pressure, and molding time. It is often necessary to preheat the natural fibers to reduce the moisture before processing the composites. High temperatures degrade the cellulose, thus negatively affecting the mechanical properties of the composites. Inefficient fiber dispersion in the matrix causes fiber agglomeration which decreases the tensile strength [118]. Most of the previous research on natural fiber composites has focused on reinforcements such as flax, hemp, sisal and jute, and thermoplastic and thermoset matrices. Some of these composites have been produced using matrices made of derivatives from cellulose, starch, and lactic acid to develop fully biodegradable composites or biocomposites [119].

The emerging diversity of applications of natural fiber composites has seen the production of sandwich structures based on natural fiber composite skins. In some cases, these sandwich composites have been produced from paper honeycomb and natural fiber-reinforced thermoplastic or thermoset skins, depending on the applications [149].

The main criteria for the selection of the appropriate process technology for natural-fiber composite manufacture include the desired product geometry, the performance needed, the cost, and the ease of manufacture. The fabrication methods for natural fiber composites are similar to those used for glass fibers [150]. The most commonly used manufacturing processes are introduced in the followings. Although many variants on these techniques exist, this overview gives a good indication of the production possibilities.

### 5.2.1 Hand Laminating

The fibers are placed in a mold and the resin is later applied by rollers. One option is to cure using a vacuum bag, as then excess air is removed and the atmospheric pressure exerts pressure to compact the part. The simplicity, low cost of tooling, and flexibility of design are the main advantages of the procedure. On the other end, the long production time, intensive labor, and low automation potential consist some of the disadvantages [152].

### 5.2.2 Resin Transfer Molding (RTM)

The resin transfer molding technique requires the fibers to be placed inside a mold consisting of two solid parts (close mold technique). A tube connects the mold with a supply of liquid resin, which is injected at low pressure through the mold, impregnating the fibers. The resulting part is cured at room temperature or above until the end of the curing reaction, when the mold is opened and the product removed. Parameters such as injection pressure, fiber content, or mold temperature have a great influence on the development of the temperature profiles and the thermal boundary layers, especially for thin cavities. This technique has the advantage of rapid manufacturing of large, complex, and high performance parts. Several types of resins (epoxy, polyester, phenolic, and acrylic) can be used for RTM as long as their viscosity is low enough to ensure a proper wetting of the fibers. Parameters such as injection pressure, fiber content, or mold temperature have a great influence on the development of the temperature profiles and the thermal boundary layers, especially for thin cavities. Good knowledge of all the operating steps is very important to obtain high-quality parts [118].

An alternative variant of this process is the vacuum injection or vacuum assisted resin transfer molding (VARTM), where a single solid mold and a foil (polymeric film) are used. The VARTM process is a very clean and low-cost manufacturing method: resin is processed into a dry reinforcement on a vacuum bagged tool, using only the partial vacuum to drive the resin. As one of the tool faces is flexible, the molded laminate thickness depends partially on the compressibility of the fiber–resin composite before curing and the vacuum negative pressure [153].

### 5.2.3 Compression Molding

Compression molding is another major technique for the construction of fiber-reinforced polymers, which involves a semifinished composite sheet widely known as sheet molding compound (SMC) that is later molded into the final parts by compression. For the SMC the process consists of a rolling film of resin on which fibers are added. A second film of resin is then added, so as to later be compressed in a composite sheet that may be stored for a few days. To get the final product, the reinforced sheet is then placed into a press to take its desired shape [154].

Advantages of compression molding are the very high volume production ability, the excellent part reproducibility, the short cycle times, and the low crap arising. Processing times of <2 min are reached during the compression molding of three-dimensional components with a high forming degree [155]. It has also been shown that the adhesion of natural fibers and matrix resin is important in order to obtain good mechanical properties of natural fiber composites, and the mechanical properties were improved by the molding condition, molding pressure, and temperature. A big concern with compression molding that needs always to be considered is the maximum pressure before the damage of the fibers and the structure.

### 5.2.4 Injection Molding

Injection molding process is suitable to form complex shapes and fine details with excellent surface finish and good dimensional accuracy for high production rate and low labor cost. In the injection molding, resin granules and short fibers are mixed into a heated barrel and transported to the mold cavity by a spindle. Injection molding is another process among the most important for the manufacturing of plastics/composites and can produce from very small products such as bottle tops to very large car body parts [156].

### 5.2.5 Pultrusion

Pultrusion is a continuous process to manufacture composite profiles at any length. The impregnated fibers are pulled through a die, which is shaped according to the desired cross section of the product. The resulting profile is shaped until the resin is dry. Advantages of this process are the ability to build thin wall structures, the large variety of cross-sectional shapes, and the possibility for high degree of automation.

## 6 Cellulose Fiber-Reinforced Biocomposites

### 6.1 Polyurethane-Based Composites for Medical Applications

PALF-derived nanocellulose-embedded polyurethane has been utilized as an attractive and readily available range of materials for the fabrication of vascular prostheses. The elastic properties of the material, coupled with low thrombogenicity and exceptional physical and mechanical properties, have led to a considerable research effort aimed at the development of nanocellulose polyurethane vascular grafts (Fig. 25.8). Nanocellulose–PU vascular grafts with a wall thickness of 0.7–1.0 mm showed elongation at break of 800–1,200 % and withstood hydraulic pressures up to 300 kPa.

High tensile strength and high strain-to-failure nanocomposites with strongly improved modulus were synthesized based on nanocellulose and polyurethane. The cellulose nanocomposites were prepared by solvent casting, based on dry crystalline cellulose and hydrophilic polyurethane.

Cellulose dissolution was avoided while still allowing successful dispersion of the cellulose nanofibrils present in dry nanoscale cellulose particles. ESEM proves the presence of dispersed cellulose nanofibrils in the developed nanocomposites. The XRD analysis confirms that cellulose nanofibrils in the prepared nanocomposites preserve the original crystalline structure of cellulose (cellulose I) [157]. The composition with 5 wt% cellulose was optimal and showed the highest strain-to-failure. The produced nanocellulose and its composites confirmed to be a very versatile material having the wide range of medical applications, including cardiovascular implants, scaffolds for tissue engineering, repair of articular cartilage, vascular grafts, urethral catheters, mammary prostheses, penile prostheses, adhesion barriers, and artificial skin [158]. These implants were produced from bioresorbable and/or biodegradable materials. Progressive degradation

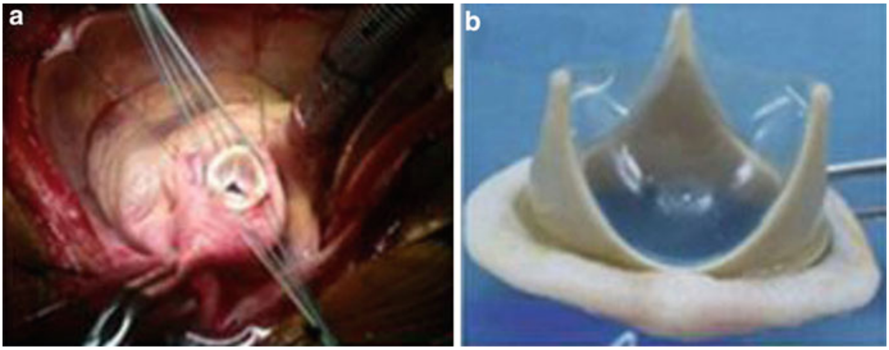


**Fig. 25.8** Nanocellulose–polyurethane prosthetic heart valve: (**a**) valve implant, (**b**) heart valve

of the implant material may then be accompanied by the formation of the new tissues. The developed material can also be utilized for construction of non-latex condoms, breathable wound dressing, surgical gloves, surgical gowns or drapes, medical bags, organ retrieval bags, and medical disposables [159].

The development of PALF nanocellulose–polyurethane valve design (Fig. 25.8) with good biological durability, fatigue resistance, and hemodynamics, and a new generation of biostable polyurethanes which have proven themselves of superior biostability in a demanding 6-month, strained, rat implant model. Thus, anticipate early development of a polyurethane valve which has a good hemodynamic function maintained during long-term implant and which neither fails from biological degradation nor from fatigue-induced material failure while maintaining a low thrombogenic surface. In accelerated fatigue tests, five out of five consecutively produced valves exceeded the equivalent of 12 years cycling without failure. The only failure occurred after the equivalent of approximately 13 years cycling, and three valves have reached 608 million cycles (approximately 15 years equivalent) to date.

## 6.2 Polyvinyl Alcohol-Based Composites for Medical Applications

Polyvinyl alcohol (PVA) is a hydrophilic biocompatible polymer with various characteristics desired for biomedical applications. PVA can be transformed into a solid hydrogel with good mechanical properties by physical cross-linking using freeze-thaw cycles. Hydrophilic nanocellulose fibers of an average diameter of 50 nm are used in combination with PVA to form biocompatible nanocomposites. According to Millon and Wan [120], the resulting nanocomposites possess a broad range of mechanical properties and can be made with mechanical properties similar to that of cardiovascular tissues, such as aorta and heart valve leaflets. On their studies, the stress–strain properties for porcine aorta are matched by at least one type of PVA–nanocellulose nanocomposite in both the circumferential and the axial tissue directions. A PVA–nanocellulose nanocomposite with similar properties as heart valve tissue is also developed. Relaxation properties of all samples, which are important for cardiovascular applications, were also studied and found to relax at a faster rate and to a lower residual stress than the tissues they might replace. So, finally the new PVA–nanocellulose composite is a promising material for cardiovascular soft tissue replacement applications.

## 7 Cellulosic Nanocomposite Applications in Biomedical Field

### 7.1 Pharmaceutical

Cellulose has a long history of use in the pharmaceutical industry. The material has excellent compaction properties when blended with other pharmaceutical excipients so that drug-loaded tablets form dense matrices suitable for the oral administration of drugs. Polysaccharides, natural polymers, fabricated into hydrophilic matrices remain popular biomaterials for controlled-release dosage forms, and use of a hydrophilic polymer matrix is one of the most popular approaches in formulating an extended release dosage forms [121–123]. This is due to the fact that these formulations are relatively flexible, and a well-designed system usually gives reproducible release profiles. Drug release is the process by which a drug leaves a drug product and is subjected to absorption, distribution, metabolism, and excretion (ADME), eventually becoming available for pharmacologic action. Crystalline nanocellulose offers several potential advantages as a drug delivery excipient. Crystalline nanocellulose and other types of cellulose in advanced pelleting systems whereby the rate of tablet disintegration and drug release may be controlled by microparticle inclusion, excipient layering, or tablet coating [124, 125]. The very large surface area and negative charge of crystalline nanocellulose suggests that large amounts of drugs might be bound to the surface of this material with the potential for high payloads and optimal control of dosing.

Other nanocrystalline materials, such as nanocrystalline clays, have been shown to bind and subsequently release drugs in a controlled manner via ion exchange mechanisms and are being investigated for use in pharmaceutical formulations [126]. The established biocompatibility of cellulose supports the use of nanocellulose for a similar purpose. The abundant surface hydroxyl groups on crystalline nanocellulose provide a site for the surface modification of the material with a range of chemical groups by a variety of methods. Surface modification may be used to modulate the loading and release of drugs that would not normally bind to nanocellulose, such as nonionized or hydrophobic drugs. For example, Lonnberg et al. suggested that poly(caprolactone) chains might be conjugated onto nanocrystalline cellulose for such a purpose [127].

Additionally, since crystalline nanocellulose is a low-cost, readily abundant material from a renewable and sustainable resource, its use provides a substantial environmental advantage compared with other nanomaterials.

## 7.2 Medical

Recently nanocellulose has been called as the eyes of biomaterial highly applicable to biomedical industry which includes skin replacements for burnings and wounds; drug releasing system; blood vessel growth; nerves, gum, and dura mater reconstruction; scaffolds for tissue engineering; stent covering; and bone reconstruction [128–132]. Figure 25.9 shows some applications for nanocellulose within biomedical field.

Tissue engineering looks for new material and devices which could interact positively with biological tissues [133], either working as an in vitro basis for cell growth or rearranging and developing tissue about to be implanted. They also aim new classes of degradable biopolymers that are biocompatible and whose activities are controllable and specific [134], more likely to be used as cell scaffolds [135] or in vitro tissue reconstruction.

As mentioned above, a great variety of biomaterials have been developed recently. They have all sorts of properties (physical/chemical and mechanical) depending mostly in the final application (tissue regeneration, medication holding and releasing, tissue grafting, or scaffolding) [132]. The scaffold's success depends much on the cellular adhesion and growth onto the surface; thus, biopolymer's chemical surface can dictate cellular response by interfering in cellular adhesion, proliferation, migration, and functioning. The surface–cell interaction is extremely important in implant effectiveness, including its rejection. Since the interaction is fully understood in a cell level, new biomaterials and products can be easily developed [136]. The problems still arise due to some methods' inefficiency such as cell seeds and sources, scaffolding, ambient, extracellular matrix producing, analysis, and appropriate models [137].

On the other hand, to regenerate tissues, three specific foundations are taken: cells, support, and growth factors. Cells synthesize the matrix for the new tissues, support holds, and keep the ambient proper for the growth, while the growth factors facilitate and promote the cell regeneration [137]. Material used for implants cannot be either rejected or cause inflammatory response; in others, it should be biocompatible. Furthermore, it should promote regeneration and if necessary, be absorbed after a while or be biodegradable [138]. Studies on support cell interactions are crucial to implants viability. Many cell responses are observed out of different materials, so the cell ability to discriminate and adapt to it whether adhere or not to its surface [139]. This is crucial as it will direct further responses as cell proliferation, migration, and viability.

Due to the clinical importance of skin lesions, many laboratories have been aroused to the search for healing products having benefits including immediate pain relief, close adhesion to the wound bed, and reduced infection rate. The nanocellulose developed having huge superficial area gives great water absorption capacity and elasticity. These are characteristics from an ideal healing bandage. On the other hand, it holds no microbial activity. Nanocellulose mats are very effective in promoting autolytic debridement, reducing pain, and accelerating granulation, all of which are important for proper wound healing. These nanobiocellulose membranes can be created in any shape and size, which is beneficial for the treatment of

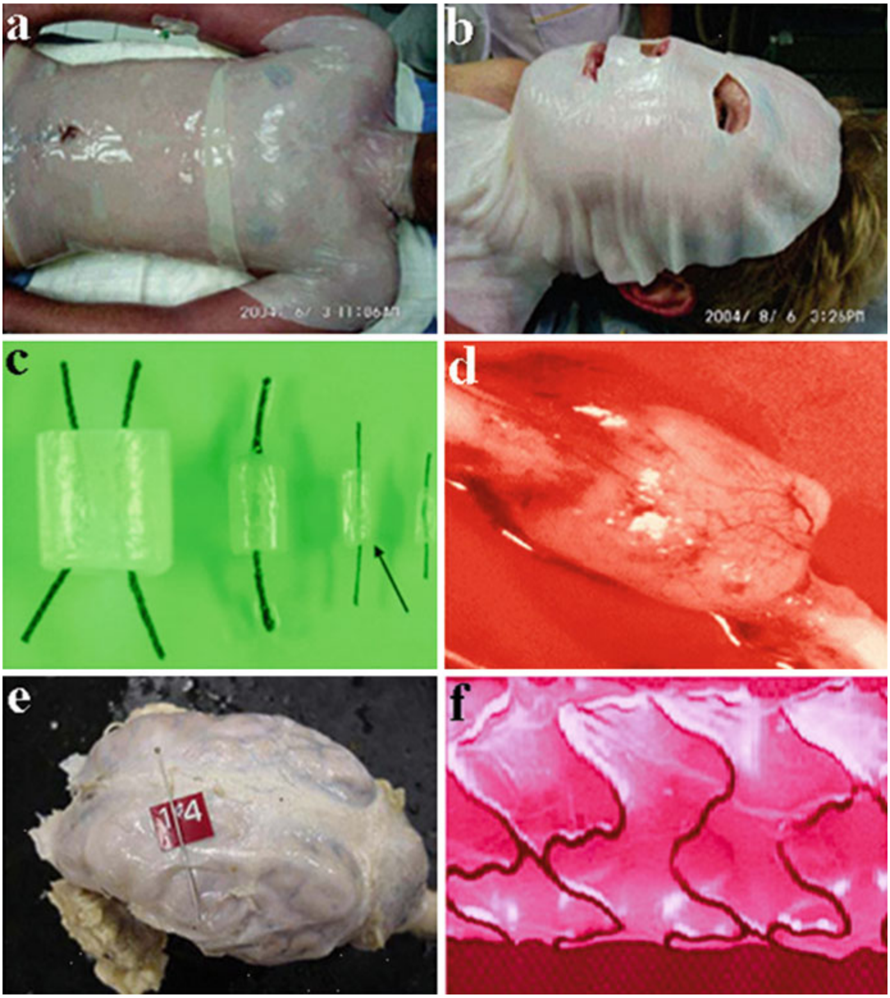


**Fig. 25.9** Biomedical applications of nanocellulose (**a**) and (**b**) never-dried nanocellulose membrane [132]; (**c**) and (**d**) artificial blood vessels [130]; (**e**) dura mater reconstruction [129]; and (**f**) covering stents [131]

large and difficult to cover areas of the body. Barud [140] has developed a biological membrane with bacterial cellulose and standardized extract of propolis. Propolis has many biological properties including antimicrobial and anti-inflammatory activities. All the above mentioned characteristics present, which make the membrane (Fig. 25.9) a good treatment for burns and chronic wounds. Odontology is challenged to find ideal materials to replace the bones in several procedures for bone malformation and maxillary and facial deformities. The biggest challenge is the loss of alveolar bone. Nanocellulose having suitable porosity, which gives the mat an infection barrier, loss of fluids, and painkiller effect, allows medicines to be easily applied, and it also absorbs the purulent fluids during all inflammatory stages, expelling it later on in a controlled and painless manner [141].

## 7.3 Veterinary

In veterinary medicine, the reports consulted about the use of biocellulose produced by the A. xylinum refer to applications for conduit for isolation in reconstruction of peripheral nerves, healing of experimental wounds of bovine mammary teats, healing of experimental tegument wounds in equine and swine, prophylaxis of the formation of membrane post laminectomy in dogs, and healing of incisional experimental lesions of the cornea in dogs. Clinically, gross (brute) membrane was used in healing of natural wounds of dogs.

Biosynthesized nanocellulose membrane was utilized [142] in experimental trochleoplasty in dogs, and it was found that the use of this biomaterial has advantages instead of the conventional treatment for osteochondral injuries. The cellulose membrane was applied in the tissue formation of fibrocartilage ripe obtaining good integration of the newly formed tissue and the adjacent cartilage, allowing its clinical use in dogs.

The membranes were tested through a lateral parapatellar skin incision 5–7 cm, followed by incision of the retinaculum and articular capsule, until the exposure of the knee joint. With the limb in extension, the patella was displaced by promoting the exposure of the femoral trochlea (Fig. 25.10a) [142].

Iamaguti et al. conducted a bent knee and trochleoplasty through the deepening of the trochlear groove with the aid of gouge forceps (Fig. 25.10b). The nanocellulose membrane, the base of cellulose 5 mm thick, was applied inside the limb of the dogs, after the deepening of the groove, and fixed with 4–5 simple points separated the edge of the normal cartilage, with the use of synthetic absorbable suture thread 6-0 (Fig. 25.10c). The patella was repositioned after the extension of the limb, performing the synthesis of the articular capsule and retinaculum in a type of points of suture, with 3-0 monofilament nylon thread (Fig. 25.10d) [142]. After the inclusion of the membrane, a link was obtained between the subcutaneous tissue in simple continuous pattern and skin, using 3-0 monofilament nylon, with simple stitches apart (Fig. 25.10e).

The cartilage that covers the trochlear groove is composed of chondrocytes embedded in a matrix and has the surface layer formed by flattened chondrocytes. The repaired tissue that covers the region of trochleoplasty consisted of more organized tissue, with higher thickness compared to the previous period.

The nanocellulose membranes were used to repair defects of the abdominal wall in humans or animals. Nanocellulose may be used as treatment of great abdominal wall defects to avoid tension during repair. Falcão et al. [143] investigated the incorporation type by host tissue of membranes of nanocellulose produced by the bacteria and of polytetrafluoroethylene (PTFE) in abdominal wall defects of rats. The cellulose membrane was sutured at the level of the musculoaponeurotic defect

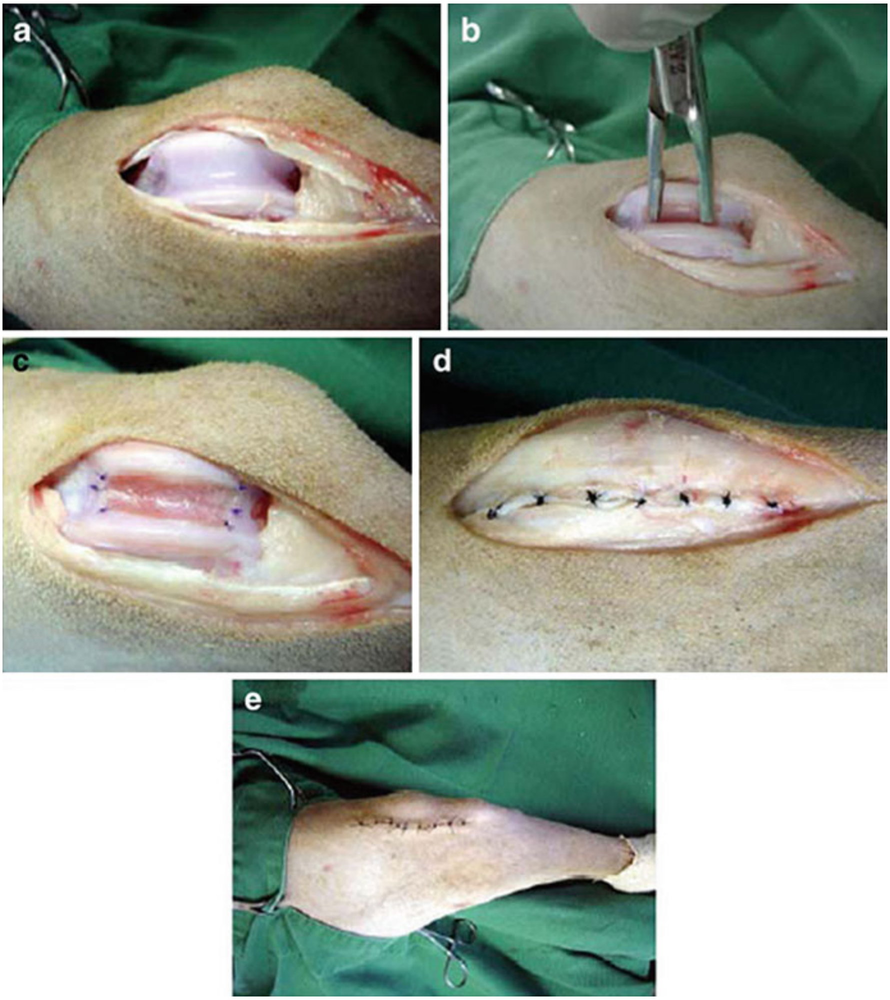


**Fig. 25.10** (**a**) Dislocation of the patella to expose the trochlear groove, (**b**) deepening of the groove trochlear with the aid of gouge forceps, (**c**) fixing the biosynthesized cellulose membrane with 6-0 synthetic absorbable sutures, (**d**) suturing the joint capsule and retinaculum in type of points of suture, with 3-0 monofilament nylon thread, and (**e**) suture the skin with simple stitches apart

with Prolene® and continuous suture, anchored at the four angles of the rectangle. Then the skin was closed with thread of Mononylon® through an interrupted suture.

## 7.4 Dental

Nanocellulose was tested in dental tissue regeneration. Microbial cellulose produced by the Gluconacetobacter xylinus strain can be used to regenerate dental

**Fig. 25.11** Nanocellulose used in dental tissue regeneration in a 39-year-old female patient

tissues in humans (Fig. 25.11). Nanocellulose products Gengiflex® and Gore-Tex® have intended applications within the dental industry. It was developed to aid periodontal tissue recovery [144]. A description was given of a complete restoration of an osseous defect around an IMZ implant in association with a Gengiflex® therapy. The benefits included the reestablishment of aesthetics and function of the mouth and that a reduced number of surgical steps were required.

The bandage, called Gengiflex®, consists of two layers: the inner layer is composed of microbial cellulose, which offers rigidity to the membrane, and the outer alkali-cellulose layer is chemically modified [145]. Salata et al. [146] compared the biological performance of Gengiflex® and Gore-Tex® membranes using the in vivo nonhealing bone defect model proposed by Dahlin et al. [147].

The study showed that Gore-Tex® membranes (a composite with polytetrafluoroethylene, urethane, and nylon) were associated with significantly less inflammation, and both membranes promoted the same amount of bone formation during the same period of time. A greater amount of bone formation was present in bone defects protected by either Gore-Tex® or microbial cellulose membrane, when compared to the control sites. Gore-Tex® is better tolerated by the tissues than Gengiflex®. Recently, in a similar vein, Macedo et al. [148] also compared bacterial cellulose and polytetrafluoroethylene (PTFE) as physical barriers used to treat bone defects in guided tissue regeneration.

In this study, two osseous defects (8 mm in diameter) were performed in each hindfoot of four adult rabbits, using surgical burs with constant sterile saline solution irrigation. The effects obtained on the right hindfeet were protected with PTFE barriers, while Gengiflex® membranes were used over wounds created in the left hindfeet. After 3 months, the histological evaluation of the treatments revealed that the defects covered with PTFE barriers were completely repaired with bone tissue, whereas incomplete lamellar bone formation was detected in defects treated with Gengiflex® membranes, resulting in voids and lack of continuity of bone deposition [160].

Nanocellulose with its characteristics, like nanofiber size and distribution, mechanical properties, compatibility, and ability to mold, creates a unique biomaterial indispensable in health area. The nanocellulose composite scaffolds are biocompatible with less rejection with cellular contact and blood contact cells interaction, to be a promissory biomaterial and may be suitable for cell adhesion/attachment, suggesting that these scaffolds can be used for wound dressing or tissue-engineering scaffolds [161].

## 8 Conclusions

The potential applicability of cellulose-based biocomposites and nanocomposites are widely extended. Due to a great number of properties, applications of nanocellulose-based materials are mainly considered to be in a wide range of biomaterial applications such as medical products, pharmacy, cosmetics, dental, and veterinary applications are also being considered. The mechanical properties such as high strength and stiffness, the surface reactivity (with numerous hydroxyl groups), and the specific organization as well as the small dimensions of nanocellulose may well impart useful properties to nanocomposite materials reinforced with these fibers.

The aim of this article was to demonstrate the current state of research and development in the field of nanocellulose – a biofabricated sustainable type of polymer material. The extraordinary supramolecular nanofiber network structure and the resulting valuable properties have led to real opportunities and extensive activity in the field of biomedical applications. The intention of this work is to broaden the knowledge in this subject area and to stimulate the practical application of nanocellulose. In the biomedical field, bacterial nanocellulose implants have opened up new uses for bioartificial medical devices.

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## References

1. Nakagaito AN, Yano H (2005) Novel high-strength biocomposites based on microfibrillated cellulose having nano-order-unit web-like network structure. Appl. Phys. A: Mater. Sci. Process 80:155–159
2. Nakagaito AN, Yano H (2004) The effect of morphological changes from pulp fibre towards nano- scale fibrillated cellulose on the mechanical properties of high-strength plant fibre based composites. Appl Phys A: Mater Sci Process 78:547
3. Bledzki AK, Reihmane S, Gassan J (1996) Properties and modification methods for vegetable fibers for natural fiber composites. J Appl Polym Sci 5:1329
4. Hornsby PR, Hinrichsen E, Tarverdi K (1997) Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibers. J Mater Sci 32:1009
5. Oksman K, Wallstrom L, Berglund LA, Filho RDT (2002) Morphology and mechanical properties of unidirectional sisal-epoxy composites. J Appl Polym Sci 84:2358
6. Nabi Saheb D, Jog JP (1999) Natural fiber polymer composites: a review. Adv Polym Technol 18:351
7. Georgopoulos ST, Tarantili PA, Avgerinos E, Andreopoulos AG, Koukios EG (2005) Thermoplastic polymers reinforced with fibrous agricultural residue. Polym Degrad Stab 90:303

8. Crawford RL (1981) Lignin biodegradation and transformation. Wiley, New York
9. Jawaid M, Abdul Khalil HPS (2011) Cellulosic/synthetic fibre reinforced polymer hybrid composites: A Review. Carbohydr Polym 86:1
10. Dorée C (1947) The methods of cellulose chemistry. Chapman & Hall, London
11. Visakh PM, Thomas S (2010) Preparation of bionanomaterials and their polymer. nanocomposites from waste and biomass. Valorization 1:121
12. Bhat AH, Khalil Abdul HPS (2011) Oil palm biomass: fibre cultivation, production and its varied applications under book publication title: oil palm: cultivation, production and dietary components. Nova Publishers, Hauppauge, New York. ISBN: 978-1-61761-934-2
13. Williams GI, Wool RP (2000) Composites from natural fibers and soy oil resins. Appl Compos Mater 7:421
14. Torres FG, Diaz RM (2004) Morphological characterisation of natural fibre reinforced thermoplastics (NFRTP) processed by extrusion, compression and rotational moulding. Polym Polym Compos 12:705
15. Abdul Khalil HPS, Hanida S, Kang SCW, Nik Fuaad NA (2007) Agro-hybrid composite:the effects on mechanical and physical properties of oil palm fiber (EFB)/glasshybrid reinforced polyester composites. J Reinf Plast Compos 26:203
16. Abdul Khalil HPS, Ismail H, Ahmad MN, Ariffin A, Hassan K (2001) The effect of various anhydride modifications on mechanical and water absorption properties of oil palm empty fruit bunches. Polym Int 50:1
17. Kalia S, Kaith BS, Kaur I (2009) Polym Eng Sci 49:1253
18. Rong MZ, Zhang MQ, Liu Y, Yang GC, Zeng HM (2001) The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. Compos Sci Technol 61:1437
19. Abdul Khalil HPS, Kumar RN, Asri SM, Nik Fuaad NA, Ahmad MN (2007) Hybrid thermoplastic pre-preg oil palm frond fibers (OPF) reinforced in polyester composites. Polym-Plast Technol Eng 46:43
20. Van de Velde K, Kiekens P (2001) Thermoplastic pultrusion of natural fibre reinforced composites. Compos Struct 54:355
21. Boss HL, van den Oever MJA, Peters OCJJ (2002) Tensile and compressive properties of flax fibres for natural fibre reinforced composites. J Mater Sci 37:1683
22. Baley C (2000) Influence of kink bands on the tensile strength of flax fibers. Compos Part A 33:939
23. Lamy B, Baley C (2000) J Mater Sci Lett 19:979
24. Jähn A, Schröder MW, Füting M, Schenzel K, Diepenbrock W (2002) Characterization of alkali-treated flax fibres by means of FT Raman spectroscopy and environmental scanning electron microscopy. Spectrochim Acta A Mol Biomol Spectrosc 58:2271
25. Gassan J, Bledzki AK (1996) Einfluss von haftvermittlern auf das feuchteverhalten naturfaserverstärkter Kunststoffe. Die Angew Makromaol Chem 236:129
26. Michell AJ (1989) Compos Asia Pacific, Adelaid 89:19
27. Moloney TM (1995) In: Lee SM, Rowell RM (eds) International encyclopedia of composites. VCH Publishers, New York, p 656
28. Mieck KP, Nechwatal A, Knobeldorf C (1994) Melliand Texilberichte 11:892
29. Mukherjee PS, Satyanarayana KG (1986) An empirical evaluation of structureproperty relationships in natural fibres and their fracture behaviour. J Mater Sci 21:51
30. Zimmermann T, Bordeanu N, Strub E (2010) Properties of nanofibrillated cellulose from different raw materials and its reinforcement potential. Carbohydr Polym 79:1086
31. Wang B, Sain M (2007) Isolation of nanofibers from soybean source and their reinforcing capability on synthetic polymers. Polym Int 56:538
32. Kaushik A, Singh M, Verma G (2010) Green nanocomposites based on thermoplastic starch and steam exploded cellulose nanofibrils from wheat straw. Carbohydr Polym 82:337
33. Teixeira EM, Corrêa AC, de Oliveira CR (2010) Cellulose nanofibers from white and naturally colored cotton fibers. Cellulose 17:595

34. Stelte W, Sanadi AR (2009) Indust Eng Chem Res 48:11211
35. Habibi Y, Goffin AL, Schiltz N, Duquesne E, Dubois P, Dufresne A (2008) J Mater Chem 18:5002
36. Grunert M, Winter WT (2002) J Polym Environ 10:27
37. Garcia de Rodriguez NL, Thielemans W, Dufresne A (2006) Cellulose 13:261
38. Kvien I, Tanem BS, Oksman K (2005) Biomacromolecules 6:3160
39. Anglés MN, Dufresne A (2000) Macromolecules 33:8344
40. Helbert W, Cavaillé JY, Dufresne A (1996) Polym Compos 17:604
41. Fleming K, Gray D, Prasannan S, Matthews S (2000) J Am Chem Soc 122:5224
42. Revol JF (1982) Carbohydr Polym 2:123
43. Hanley SJ, Giasson J, Revol JF, Gray DG (1992) Polymer 33:4639
44. Pu Y, Zhang J, Elder T, Deng Y, Gatenholm P, Ragauskas AJ (2007) Compos Part B 38:360
45. Elmabrouk AB, Wim T, Dufresne A, Boufi S (2009) J Appl Polym Sci 114:2946
46. Dufresne A (2006) J Nanosci Nanotechnol 6:322
47. Dufresne A (2008) Can J Chem 86:484
48. Hubbe MA, Rojas OJ, Lucia LA, Sain M (2008) BioResources 3:929
49. Sturcova A, Davies GR, Eichhorn SJ (2005) Biomacromolecules 6:1055
50. Herrick FW, Casebier RL, Hamilton JK, Sandberg KR (1982) J Appl Polym Sci 37:797
51. Wagberg L (2005) Wood material science. Finnish-Swedish Research Programme, Stockholm 2007
52. Payen A (1838) Compt Rend 7:1052, 1125
53. Tanahashi M (1990) Wood Res 77:49
54. Kokta BV (1991) Steam explosion pulping. In: Focher B, Marzetti A, Crescenzi V (eds) Steam explosion techniques: fundamentals and industrial applications. Gordon and Breach Science, Philadelphia, pp 163–206
55. Excoffier G, Toussaint B, Vignon MR (1991) Biotechnol Bioeng 38:1308
56. Vignon MR, Garcia-Jaldon C, Dupeyre D (1995) Biomacromolecules 17:395
57. Cristobal C, Encarnacion R, Ignacio B, Maria JN, Eulogio C (2006) Process Biochem 41:423
58. Cristobal C, Encarnacion R, Mercedes B, Paloma M, Jose MN, Eulogio C (2008) Fuel 87:692
59. Marchessault RH (1991) Steam explosion: a refining process for lignocellulosics. In: Focher B, Marzetti V, Crescenci V (eds) Steam explosion techniques: fundamentals and industrial applications. Gordon and Breach Science, Philadelphia, pp 1–19
60. Abdul Khalil HPS, Bhat AH, Ireana Yusra AF (2012) Carbohydr Polym 87:963
61. Abe K, Yano H (2009) Comparison of the characteristics of cellulose microfibril aggregates of wood, rice straw and potato tuber. Cellulose,16 (6), 1017–1023
62. Abe K, Yano H (2010) Cellulose 17:271
63. Lo¨nnberg H, Zhou Q, Brumer H, Teeri TT, Malmstro¨m E, Hult A, Lo¨nnberg H, Zhou Q, Brumer H, Teeri TT, Malmstro¨m E, Hult A (2006) Biomacromolecules 7:2178
64. Bochek A, Petropavlovsky G, Kallistov O (1993) Cellulose Chem Technol 27:137
65. Cui W, Li X, Zhou S, Weng J (2007) J Appl Polym Sci 103:3105
66. Iguchi M, Yamanaka S, Budhiono A (2000) J Mater Sci 35:261
67. Orts WJ, Shey J, Imam SH, Glenn GM, Guttman ME, Revol JF (2005) J Polym Environ 13:301
68. Wang Y, Cao X, Zhang L (2006) Macromol Biosci 6:524
69. Eichhorn SJ, Dufresne A, Aranguren M, Marcovich NE, Capadona JR, Rowan SJ, Weder C, Thielemans W, Roman M, Renneckar S, Gindle W, Veigel S, Keckes J, Yano H, Abe K, Nogi M, Nakagaito AN, Mangalam A, Simonsen J, Benight AS, Bismarck A, Berglund LA, Peijs T (2010) J Mater Sci 45:1–33
70. Svensson A, Nicklasson E, Haraah T, Panilaitis B, Kaplan DL, Brittberg M, Gatenholm P (2005) Bacterial cellulose as a potential scaffold for tissue engineering of cartilage. Biomaterials 26:419–431
71. Helenius G, Backdahl H, Bodin A, Nannmark U, Gatenholm P, Reisberg B (2006) J Biomed Res 76A:431

72. Yamanaka S, Watanabe K, Kitamura N (1989) The structure and mechanical properties of sheets prepared from bacterial cellulose. Journal of Material Science 24:3141–3145
73. Grunet M, Winter T (2002) J Polym Environ 10:27
74. Geyer U, Heinze T, Stein A, Klemm D, Marsch S, Schumann D, Schrnauder HP (1994) Int J Biol Macromol 16:343
75. Yamanaka S, Ishihara M, Sugiyama J (2000) Cellulose 7:213
76. Masaoka S, Ohe T, Sakota N (1993) J Ferment Bioeng 75:18
77. Wulf PD, Joris K, Vandamme EJ (1996) J Technol Biotechnol 62:1290
78. Sokollek SJ, Hertel C, Hammes WP (1998) J Biotechnol 60:195
79. Watanabe K, Tabuchi M, Ishikawa A, Takemura H, Tsuchida T, Morinaga Y, Yoshinaga F (1998) Biosci Biotechnol Biochem 62:1290
80. Nakai T, Tonouchi N, Konishi T, Kojima Y, Tsuchida T, Yoshinaga F, Sakai F, Hayashi T (1999) Appl Biol Sci 96:14
81. Kawano S, Tajima K, Uemori Y, Yamashita H, Erata T, Munekata M, Takai M (2002) DNA Res 9:149
82. Bae SO, Sugano Y, Ohi K, Shoda M (2004) Appl Microbiol Biotechnol 65:315
83. Anglés MN, Dufresne A (2001) Macromolecules 34:2921
84. Mathew AP, Dufresne A (2002) Biomacromolecules 3:609
85. Mathew AP, Thielemans W, Dufresne A (2008) J Appl Polym Sci 109:4065
86. Dagang L, Zhong Tuhua R, Chang P, Kaifu L, Qinglin W (2010) Bioresour Technol 101:2529
87. Noishiki Y, Nishiyama Y, Wada M, Kuga S, Magoshi J (2002) J Appl Polym Sci 86:3425
88. Samir MASA, Alloin F, Paillet M, Dufresne A (2004) Macromolecules 37:4313
89. Samir MASA, Alloin F, Sanchez JY, Dufresne A (2004) Polymer 45:4149
90. Samir MASA, Alloin F, Gorecki WJ, Sanchez Y, Dufresne A (2004) J Phys Chem B 108:10845
91. Samir MASA, Alloin F, Dufresne A (2006) High performance nanocomposite polymer electrolytes. Compos Interfaces 13:545
92. Zimmermann T, P¨ohler E, Geiger T (2004) Cellulose fibrils for polymer reinforcement. Adv Eng Mater 6:754
93. Zimmermann T, P¨ohler E, Schwaller P (2005) Mechanical and morphological properties of cellulose fibril reinforced nanocomposites. Adv Eng Mater 7:1156
94. Lu J, Wang T, Drzal LT (2008) Compos Part A 39:738
95. Paralikar SA, Simonsen J, Lombardi J (2008) J Membr Sci 320:248
96. Roohani M, Habibi Y, Belgacem NM, Ebrahim G, Karimi AN, Dufresne A (2008) Eur Polym J 44:2489
97. Choi Y, Simonsen J (2006) Cellulose nanocrystal-filled carboxymethyl cellulose nanocomposites. J Nanosci Nanotechnol 6:633
98. Favier V, Canova GR, Cavaillé JY, Chanzy H, Dufresne A, Gauthier C (1995) Nanocomposites materials from latex and cellulose whiskers. Polym Adv Technol 6:351
99. Dufresne A, Cavaillé JY, Helbert W (1997) Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part II: effect of processing and modeling. Polym Compos 18:198
100. Dufresne A, Kellerhals MB, Witholt B (1999) Transcrystallization in mcl-PHAs/ cellulose whiskers composites. Macromolecules 32:7396
101. Dubief D, Samain E, Dufresne A (1999) Polysaccharide microcrystals reinforced amorphous poly(β-hydroxyoctanoate) nanocomposite materials. Macromolecules 32:5765
102. Dufresne A (2000) Dynamic mechanical analysis of the interphase in bacterial polyester/ cellulose whiskers natural composites. Compos Interfaces 7:53
103. Chazeau L, Paillet M, Cavaillé JY (1999) Plasticized PVC reinforced with cellulose whiskers: 1- linear viscoelastic behavior analyzed through the quasi point defect theory. J Polym Sci Part B 37:2151

104. Chazeau L, Cavaillé JY, Terech P (1999) Mechanical behaviour above Tg of a plasticized PVC reinforced with cellulose whiskers, a SANS structural study. Polymer 40:5333
105. Chazeau L, Cavaillé JY, Canova G, Dendievel R, Boutherin B (1999) Viscoelastic properties of plasticized PVC reinforced with cellulose whiskers. J Appl Polym Sci 71:1797
106. Chazeau L, Cavaillé JY, Perez J (2000) Plasticized PVC reinforced with cellulose whiskers. II. Plastic behavior. J Polym Sci B 38:383
107. Ruiz MM, Cavaillé JY, Dufresne A, Graillat C, Gérard JF (2001) Macromol Symposia 169:211
108. Bendahou A, Habibi Y, Kaddami H, Dufresne A (2009) Physico-chemical characterization of palm from phoenix dactylifera – L, preparation of cellulose whiskers and natural rubber–based nanocomposites. J Biobased Mater Bioenerg 3:81
109. Rosa MF, Medeiros ES, Malmonge JA (2009) Proceedings of the 11th international conference on advanced materials (ICAM'09), Rio de Janeiro, September 2009
110. Bendahou A, Kaddami H, Dufresne A (2010) Investigation on the effect of cellulosic nanoparticles' morphology on the properties of natural rubber based nanocomposites. Eur Polym J 46:609
111. Oksman K, Mathew AP, Bondeson D, Kvien I (2006) Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. Compos Sci Technol 66:2776
112. Bondeson D, Oksman K (2007) Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol. Compos Part A 38:2486
113. de Menezes AJ, Siqueira G, Curvelo AAS, Dufresne A (2009) Polymer 50:4552
114. Goffin AL, Raquez JM, Duquesne E, Habibi Y, Dufresne A, Dubois P (2011) Polymer 52:1532
115. Lemahieu L, Bras J, Tiquet P, Augier S, Dufresne A (2011) Macromol Mater Eng J 296
116. Lu Y, Weng L, Cao X (2005) Biocomposites of plasticized starch reinforced with cellulose crystallites from cottonseed linter. Macromol Biosci 5:1101
117. Chauve G, Heux L, Arouini R, Mazeau K (2005) Biomacromolecules 6:2025
118. Njuguna J, Wambua P, Pielichowski K, Kayvantash K (2011) Natural fiber-reinforced polymer composites and nanocomposites for automotive applications. In: Kalia S, Kaith BS, Kaur I (eds) Cellulose fibers: bio- and nano-polymer composites. Springer, Heidelberg
119. Mishra S, Mohanty AK, Drzal LT, Misra M, Hinrichsen G (2004) Macromol Mater Eng 289:955
120. Millon LE, Wan WK (2006) The polyvinyl alcohol-bacterial cellulose system as a new nanocomposite for biomedical applications. J Biomed Mater Res Part B 79:245
121. Alderman DAA (1984) Int J Pharm Tech Prod Manuf 5:1
122. Heller J (1987) Use of polymers in controlled release of active agents in controlled drug delivery. In: Robinson JR, Lee VHL (eds) Fundamentals and applications, 2nd edn. Marcel Dekker, New York, pp 210–180
123. Longer MA, Robinson JR (1990) Sustained-release drug delivery systems. In: Remington JP (ed) Remington's pharmaceutical sciences, 18th edn. Mack Publishing, Easton, pp 1676–1693
124. Watanabe Y, Mukai B, Kawamura KI (2002) Yakugaku Zasshi 122:157
125. Baumann MD, Kang CE, Stanwick JC (2009) J Control Release 138:205
126. Shaikh S, Birdi A, Qutubuddin S, Lakatosh E, Baskaran H (2007) Ann Biomed Eng 35:2130
127. Lönnberg H, Fogelstr¨om L, Samir MASA, Berglund L, Malmstr¨om E, Hult A (2008) Eur Polym J 44:2991
128. Fontana JD, de Souza AM, Fontana CK (1990) Appl Biochem Biotech 24–25:253
129. Mello LR, Feltrin Y, Selbach R, Macedo G Jr, Spautz C, Haas LJ (2001) Arq Neuropsiquiatr 59:372
130. Klemm D, Schumann D, Udhardt U, Marsch S (2001) Prog Polym Sci 26:1561
131. Negrão SW, Bueno RRL, Guérios EE (2006) Rev Bras de Cardiologia Invasiva 14:10
132. Czaja WK, Young DJ, Kawecki M, Brown RM Jr (2007) Biomacromolecules 8:1
133. Croce MA, Silvestri C, Guerra D (2004) J Biomater Appl 18:209
134. Madihally SV, Matthew HWT (1999) Biomaterials 20:1133
135. Nehrer S, Breinan HA, Ramappa A (1997) J Biomed Mater Res 38:95

136. Kumari TV, Vasudev U, Kumar A, Menon B (2001) Trends in Biomater Artif Organs 15:37
137. Ikada Y (2006) J R Soc Interface 3:589
138. Chen GQ, Wu Q (2005) Polyhydroxyalkanoates as tissue engineering materials. Biomaterials 26:6565
139. Anselme K (2000) Osteoblast adhesion on biomaterials. Biomaterials 21:667
140. Barud HS (2009) São Paulo Research Foundation – FAPESP, Brazil
141. Czaja W, Krystynowicz A, Bielecki S, Brown RM Jr (2006) Biomaterials 27:145
142. Iamaguti LS, Branda˜o CVS, Minto BW (2008) Vet e Zootec 15:160
143. Falcão SC, Neto JE, Coelho ARB (2008) Acta Cir Bras 23:78
144. Novaes AB Jr, Vidigal GM Jr, Novaes AB, Grisi MFM, Polloni S, Rosa A (1998) Immediate implants placed into infected sites: A histomorphometric study in dogs. Int J oral Maxillofac Implants 13:422–7
145. Novaes AB Jr, Novaes AB (1995) Immediate implants placed into infected sites: a clinical report. Int J oral Maxillofac Implants 10:609–13
146. Salata LA, Craig GT, Brook IM (1995) J Dental Res 74:825
147. Dah Dahlin C, Linde A, Gottlow J, Nyman S (1988) Plast Reconstr Surg 81:672
148. Macedo NL, Matuda FS, Macedo LGS, Monteiro ASF, Valera MC, Carvalho YR (2004) Braz J Oral Sci 3:395
149. Fink H-P, Weigel P, Purz H (2001) Prog Polym Sci 26:1473
150. Mis'kiewicz M, Biele S (2002) J Ind Microbiol Biotechnol 29:189
151. Samir MASA, Mateos AM, Alloin F, Sanchez JY, Dufresne A (2004) Plasticized nanocomposite polymer electrolytes based on poly(oxyethylene) and cellulose whiskers. Electrochim Acta 49:4667
152. Berglund L (2005) Cellulose-based nanocomposites. In: Mohanty A, Misra M, Drzal L (eds) Natural fibers, biopolymers and biocomposites. CRC Press, Boca Raton
153. Samir MASA, Chazeau L, Alloin F, Dufresne A, Sanchez JY (2005) Review of recent research into cellulose whiskers, their properties and their application in nanocomposite field. Biomacromolecules 6:612
154. Saxena IM, Brown RM Jr (2005) Cellulose biosynthesis: Current views and evolving concepts. Ann Bot 96:9–21
155. Ljungberg N, Bonini C, Bortolussi F, Boisson C, Heux L, Cavaillé JY (2005) New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: Effect of surface and dispersion characteristics. Biomacromolecules 6:2732
156. Samir MASA, Alloin F, Dufresne A (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. Biomacromolecules 6:612
157. Wan YZ, Hong L, Jia SR, Huang Y, Zhu Y, Wang YL, Jiang HJ (2006) Synthesis and characterization of hydroxyapatite–bacterial cellulose nanocomposites cellulose. Compos Sci Technol 66:1825
158. Alemdar A, Sain M (2008) Biocomposites from wheat straw nanofibres: Morphology, thermal and mechanical properties. Compos Sci Technol 68:557
159. Alemdar A, Sain M (2008) Isolation and characterization of nanofibres from agricultural residues - wheat straw and soy hulls. Bioresour Technol 99:1664
160. Svagan AJ, Hedenqvist MS, Berglund L (2009) Reduced water vapour sorption in cellulose nanocomposites with starch matrix. Compos Sci Tech 69(3–4):500–506
161. Berglund LA, Peijs T (2010) Cellulose biocomposites-from bulk moldings. J Mater Sci 45:1
162. Siro I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: A review. Cellulose 17:459
163. Kalia S, Dufresne A, Cherian BM, Kaith BS, Avérous L, Njuguna J, Nassiopoulos E (2011) Cellulose-Based Bio- and nanocomposites: a review. International Journal of Polymer Science 35:837–875

164. Kalia S, Vashistha S, Kaith BS (2011) Cellulose Nanofibers reinforced bioplastics and their applications. In: Pilla S (ed) Handbook of bioplastics and biocomposites engineering applications. Wiley-Scrivener, New York (Chap 16)
165. Kalia V, Sarkar S, Subramaniam S, Haining WN, Smith KA, Ahmed R (2010) Prolonged interleukin-2Ralpha expression on virus-specific CD8+ T cells favors terminal-effector differentiation in vivo. Immunity 32:91–103
166. Joseph G, Rowe GE, Margaritis A, Wan W (2003) Effects of polyacrylamide-co-acrylic acid on cellulose production by Acetobacter xylinum. J Chem Technol Biotechnol 78:964–970
167. Krystynowicz A, Czaja W, Wiktorowska-Jezierska AM, Turkiewicz M, Gonçalves-Miśkiewicz M, Biele S (2002) Factors affecting the yield and properties of bacterial cellulose. J Indust Microbiol Biotechnol 29:189–195
168. Ljungberg N, Wesslen B (2005) Preparation and Properties of Plasticized Poly(Lactic acid) Films. Biomacromolecules 6:1789–1796