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Nanocelluloses: A New Family of Nature-Based Materials

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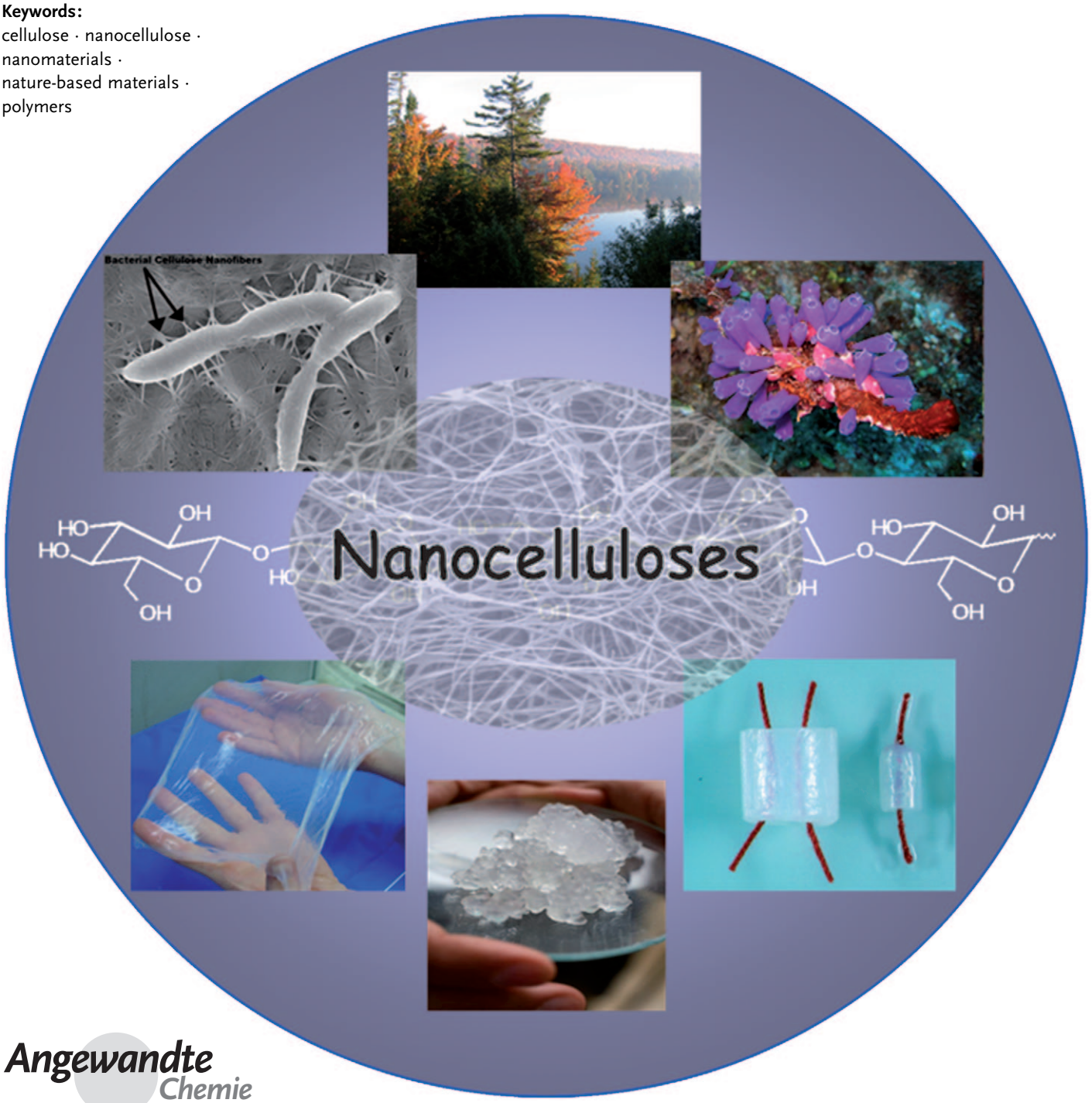

Cellulose fibrils with widths in the nanometer range are nature-based materials with unique and potentially useful features. Most importantly, these novel nanocelluloses open up the strongly expanding fields of sustainable materials and nanocomposites, as well as medical and life-science devices, to the natural polymer cellulose. The nanodimensions of the structural elements result in a high surface area and hence the powerful interaction of these celluloses with surrounding species, such as water, organic and polymeric compounds, nanoparticles, and living cells. This Review assembles the current knowledge on the isolation of microfibrillated cellulose from wood and its application in nanocomposites; the preparation of nanocrystalline cellulose and its use as a reinforcing agent; and the biofabrication of bacterial nanocellulose, as well as its evaluation as a biomaterial for medical implants.

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1. Introduction

Cellulose is one of the most important natural polymers, an almost inexhaustible raw material, and a key source of sustainable materials on an industrial scale. For millennia, cellulose has been used in the form of wood and plant fibers as an energy source, for building materials, and for clothing. Since the Egyptian papyri, cellulose products have played a central role in the recording and transmission of human culture. As a chemical raw material, cellulose has been used for about 150 years. Advancing insight into the structural features and reactivity of cellulose has driven the step-by-step creation of novel types of materials. Highlights were the development of cellulose esters and cellulose ethers as well as of cellulose regenerates and the discovery of the polymeric state of molecules. The reaction of cellulose with nitric acid to form cellulose nitrate was the basis of a process carried out by the Hyatt Manufacturing Company in 1870 to make celluloid, the very first thermoplastic polymer material. The chemical modification of cellulose on an industrial scale led to a broad range of products based on cellulose from wood. The first example was the fabrication of regenerated cellulose filaments by spinning a solution of cellulose in a mixture of copper hydroxide and aqueous ammonia. This development was followed by the particularly important large-scale viscose process for producing rayon fiber and filament. Novel materials for coatings, films, membranes, building materials, drilling techniques, pharmaceuticals, and foodstuffs were obtained by the large-scale production of cellulose esters and ethers.

The elucidation of the polymeric structure of cellulose can be traced back to 1920 and the pioneering work of Staudinger. These studies, along with Staudinger's research on other chain molecules, marked the discovery of the polymeric state of molecules and the origin of polymer science.

Currently, the isolation, characterization, and search for applications of novel forms of cellulose, variously termed crystallites, nanocrystals, whiskers, nanofibrils, and nanofibers, is generating much activity. Novel methods for their production range from top-down methods involving enzymatic/chemical/physical methodologies for their isolation from wood and forest/agricultural residues to the bottom-up production of cellulose nanofibrils from glucose by bacteria. Such isolated cellulosic materials with one dimension in the nanometer range are referred to generically as nanocelluloses. In a unique manner, these nanocelluloses combine important cellulose properties—such as hydrophilicity, broad chemical-modification capacity, and the formation of versatile semicrystalline fiber morphologies—with the specific features of nanoscale materials: features mainly caused by the very large surface area of these materials. On the basis of their dimensions, functions, and preparation methods, which in turn depend mainly on the cellulosic source and on the processing conditions, nanocelluloses may be classified in three main subcategories (Table 1). Typical structures of these cellulose types on the nanoscale can be seen in the electron micrographs in Figure 1.

As apparent from Table 1, the nomenclature of nanocelluloses has not been used in a completely uniform manner

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Table 1: The family of nanocellulose materials.

Type of nanocellulose	Selected references and synonyms	Typical sources	Formation and average size
microfibrillated cellulose (MFC)	microfibrillated cellulose,[1] 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,[2] whiskers,[3] rodlike cellulose microcrystals[4]	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,[5] microbial cellulose,[6] biocellulose[7]	low-molecular-weight sugars and alcohols	bacterial synthesis diameter: 20–100 nm; different types of nanofiber networks

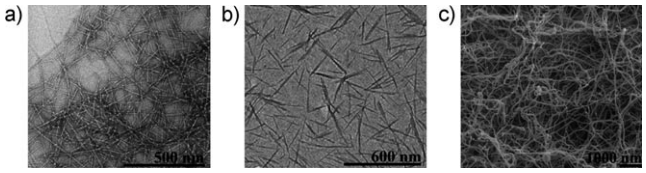

Figure 1. Transmission electron micrographs of a) MFC[1c] and b) NCC;[8] c) scanning electron micrograph of BNC.

in the past. Herein, we have used the terms MFC, NCC, and BNC. The name microfibrillated cellulose (MFC) was coined by the original investigators and is widely used in the scientific and commercial literature, whereas NCC and BNC seem simple and descriptive. Maybe, over time, the nomenclature "nanofibrillated cellulose" will prevail, and the nanocellulose terminology will become more consistent.

The manufacture of MFC was pioneered by Sandberg et al. at ITT Rayonnier, USA in the late 1970s and early 1980s.[1b,9] The forcing of suspensions of wood-based cellulose fibers through mechanical devices, such as high-pressure homogenizers, produces MFC. This mechanical treatment delaminates the fibers and liberates the microfibrils (around 20 nm wide, Figure 2a). The microfibrils have a high aspect ratio and exhibit gel-like characteristics in water (Figure 2b), with pseudoplastic and thixotropic properties.

The major impediment for commercial success has been the very high energy consumption amounting to over 25000 kWh per ton in the production of MFC as a result of the required multiple passes through the homogenizers. Extensive clogging of the homogenizer was also found to be a chronic problem. Later, it was discovered that it is easier to produce MFC from primary-wall materials (e.g., parenchyma

Dieter Klemm received his PhD for work on steroids. Following activities on synthetic polymers and in the pharmaceutical industry, he has been a professor of organic chemistry at the University of Jena since 1987. He is engaged in the research and development of carbohydrates as well as cellulose and nanocellulose biomaterials, and in the formation of Polymet Jena Association and Jenpolymer Materials Ltd. & Co. KG. His honors include the Anselme Payen Award of the American Chemical Society for the development of new cellulose-based materials.

Sebastian Moritz studied pharmacy at the Friedrich Schiller University of Jena and graduated in 2008 with a license to practice pharmacy. Since 2009, he has been a PhD student at Polymet Jena Association, where he is working in the field of biopolymers with his main focus on the structural design and characterization of bacterial nanocellulose for medical applications.

Friederike Kramer studied chemistry at the Friedrich Schiller University of Jena. She graduated in the group of Prof. D. Klemm in 2004 with a diploma thesis on interpenetrating polymer networks of bacterial nanocellulose and synthetic polymers. In 2008, she received her PhD from the University of Jena for research on nanocellulose and nanocellulose composites for the development of medical implants at Polymet Jena Association.

Tom Lindström holds the position of Director of the Biofibre Materials Research Centre (BiMaC Innovation) at the Royal Institute of Technology (KTH) and is also a Senior Research Scientist at Innventia AB in Stockholm. His interests span the physical and surface science of cellulosic fibers, including nanocelluloses and bio(nano)composite materials. He is a fellow of Tappi and the International Academy of Wood Science, a George Jayme medalist (ZellCheming), and an Ekman medalist (SPCI).

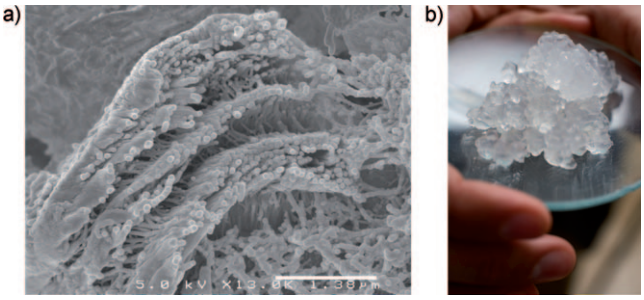

Figure 2. a) Electron microscopy (magnification: 13 000×; scale bar: 1.38 μm) of the cross-section of a spruce-fiber cell wall, showing fibril aggregates 20 nm in width (courtesy: Geoffrey Daniels, SLU, Sweden). b) Photograph of an MFC hydrogel (courtesy: Innventia AB, Sweden).

cells from sugar beet and citrus fruits) than secondary-wall materials,[10] as the stabilization of these suspensions by glucuronic and galacturonic acid residues made them easier to delaminate.[10d,11]

A lot of knowledge on cellulosic nanocomposites stems from research by French scientists at CERMAV-CNRS; Dufresne has covered these studies in excellent reviews.[12] Other reviews on the same topic are also available.[5b,13]

More recently, there has been a focus on energy-efficient production methods, whereby fibers are pretreated by various physical, chemical, and enzymatic methods before homogenization to decrease the energy consumption. The chemical literature also includes a fairly large number of patents on the subject of MFC manufacture and uses. The most relevant patents/applications are included herein to give the spirit of this emerging field. Anticipated applications of MFC range from food and emulsion/dispersion applications and medical, cosmetic, pharmaceutical, and hygiene/absorbent products to use in various nanocomposites and paper and board applications.

Nanocrystalline celluloses (NCCs), also known as whiskers, consist of rodlike cellulose crystals with widths and lengths of 5–70 nm and between 100 nm and several micrometers, respectively. They are generated by the removal of amorphous sections of a purified cellulose source by acid hydrolysis, often followed by ultrasonic treatment. Cellulose sources are variable, and their degree of crystallinity strongly influences the dimensions of the liberated crystals: cotton,[2e] wood, and Avicel yield a narrow distribution of highly crystalline (90% crystallinity) nanorods (width: 5–10 nm, length: 100–300 nm), whereas other sources, such as tunicin (extracted from the sea animals known as tunicates),[3a–c,14] bacteria,[2a,15] and algae, generate crystals with larger polydispersities and dimensions comparable to those of MFC (width: 5–60 nm, length: 100 nm to several micrometers).[2b,16] Although similar in size to MFC, they have very limited flexibility, as they do not contain amorphous regions but instead exhibit elongated crystalline rodlike shapes.

NCC crystals may also show different geometries, depending on their biological source; for example, algal cellulose membrane displays a rectangular structural arrangement, whereas both bacterial and tunicate cellulose chains have a twisted-ribbon geometry.[16,17] The surface functionalities of NCC depend on the mineral acid used in the hydrolysis: particles are weakly negatively charged if prepared with HCl, but more negatively charged if prepared with H_2SO_4, in which case approximately one tenth of the glucose units are functionalized with sulfate ester groups.[2d,18] Owing to their highly repulsive character, NCC suspensions prepared with sulfuric acid exhibit higher colloidal stabilities. The dimensions of crystals were also found to depend on the duration of the hydrolysis, whereby a longer reaction time produced shorter crystals.[2c,e,16]

In 1959, Marchessault et al. discovered that beyond a critical concentration, nanocrystal suspensions display birefringence.[19] Revol and co-workers demonstrated in the early 1990s[20] that NCCs generated by sulfuric acid hydrolysis in fact form a chiral nematic liquid-crystalline phase. Following this discovery, the optical and liquid-crystalline properties of cellulose suspensions were the focus of several studies and reviews.[2e,14a,21] The alignment of crystals exposed to an external magnetic field was first examined by Revol et al.[21a] and further investigated by Kimura et al.,[22] who reported the controlled alignment of the phase structure of NCC suspen-

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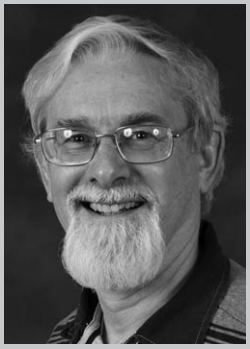

Born in Belfast, Northern Ireland, Derek Gray currently holds the Paprican/NSERC Industrial Research Chair in Cellulose Properties and Utilization in the Department of Chemistry, McGill University. Discoveries from his research group have included the first reported formation of liquid-crystalline cellulose derivatives, and the self-assembly of cellulose nanocrystals to give chiral nematic suspensions and ordered films. This work was recognized by the Anselme Payen Award of the American Chemical Society in 1994.

Annie Dorris was born in 1980 and received her BSc in chemistry from the Université de Montréal in 2003. She received her PhD from McGill University for studies on the preparation and characterization of polyelectrolyte-coated gold nanoparticles in the research group of Dr. Christopher Barrett. In March 2009, she joined Derek Gray's research group to pursue postdoctoral research on the viscosity of cellulose-nanocrystal alcogels.

sions in a rotating magnetic field to produce highly regular single domains. NCC incorporation into solid films and their orientation therein were also thoroughly investigated, as the liquid-crystalline order in cellulose suspensions was found to be preserved upon drying in a strong homogeneous magnetic field or by slow evaporation.[2c,23] Revol et al. also demonstrated that by varying the ionic content of NCC suspensions, films with unique optical properties can be prepared that are capable of reflecting colored light.[24] The commercialization of cellulose nanocrystals is still at an early stage, but appears very promising, as the strengthening effect and optical properties of NCC may find use in nanocomposites, paper making, coating additives, security papers, food packaging, and gas barriers.

Bacterial nanocellulose (BNC)—also called bacterial cellulose, microbial cellulose, or biocellulose—is formed by aerobic bacteria, such as acetic acid bacteria of the genus *Gluconacetobacter*, as a pure component of their biofilms. These bacteria are wide-spread in nature where the fermentation of sugars and plant carbohydrates takes place. In contrast to MFC and NCC materials isolated from cellulose sources, BNC is formed as a polymer and nanomaterial by biotechnological assembly processes from low-molecular-weight carbon sources, such as D-glucose. The bacteria are cultivated in common aqueous nutrient media, and the BNC is excreted as exopolysaccharide at the interface to the air. The resulting form-stable BNC hydrogel is composed of a nanofiber network (fiber diameter: 20–100 nm) enclosing up to 99% water. This BNC proved to be very pure cellulose with a high weight-average molecular weight (M_w), high crystallinity, and good mechanical stability. The biofabrication approach opens up the exciting option to produce cellulose by fermentation in the sense of white biotechnology and to control the shape of the formed cellulose bodies as well as the structure of the nanofiber network during biosynthesis. The resulting unique features of BNC lead to new properties, functionalities, and applications of cellulose materials.

This Review presents important developments and perspectives in the field of nanocelluloses. It is divided into three sections dealing with the three members of the nanocellulose family: MFC, NCC, and BNC. Although all nanocellulose types are based on cellulose fibrils with one dimension in the nanometer range, each has a distinctive preparation method and set of properties. From our point of view, it is essential to present these nanostructured types of cellulose not only in isolation but in a comprehensive review to accentuate their similarities and differences. This approach is important because of the strongly interdisciplinary character of the subject and should promote research, development, and application in the field of nanocelluloses.

2. Microfibrillated Cellulose (MFC) Retrieved from Wood-Based Fibers

2.1. MFC Manufacture from Wood-Based Raw Materials

MFC is normally produced from wood by the high-pressure homogenization of pulps (Figure 3a) according to

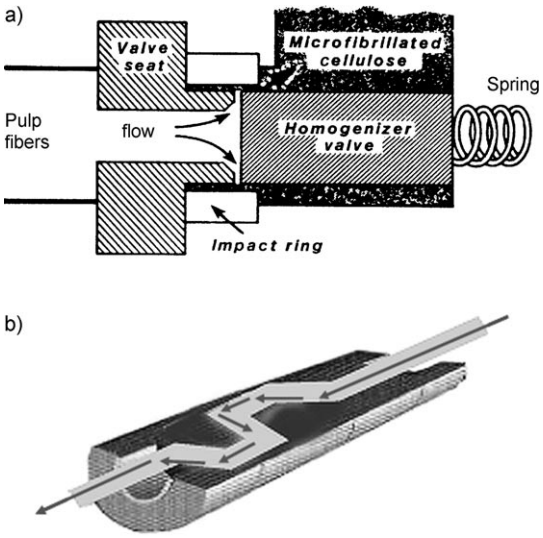

Figure 3. Some devices used for the delamination of fiber cell walls to make MFC. a) High-pressure homogenizer,[1a] in which fibers are pressed through a slit between the valve seat and the pressurized homogenizer valve.[1b] b) Interior view of a high-pressure microfluidizer, in which the fiber suspension is pumped through narrow slits under high pressure.

the procedures developed at ITT Rayonnier.[1b,9] Pulp is produced from wood by chemical treatment. By using a mixture of sodium hydroxide and sodium sulfide, so-called kraft pulp (almost pure cellulose fibers) is obtained. Pulping with salts of sulfurous acid leads to cellulose named sulfite pulp (which contains more by-products in the cellulose fibers). The delamination process was found to be assisted by the addition of hydrophilic polymers, such as carboxymethyl cellulose (CMC), methyl cellulose, hydroxypropyl cellulose (HPC), poly(acrylic acid), carrageenin, and guar gums.[25] These polymers decreased the clogging tendency and enabled higher pulp consistencies to be used during homogenization. Still, 5–10 passes through the homogenization equipment were usually necessary to provide MFC with gellike characteristics. Therefore, the specific-energy consumption was very high.

Sulfite pulps are easier to delaminate than kraft pulps, and a high hemicellulose content and/or charge density facilitates delamination.[26] Nevertheless, it was found early on that about 27000 kWh per ton of MFC was necessary to make a gellike MFC from a sulfite-pulp suspension with a high hemicellulose content.[27]

The introduction of charged groups into the pulp fibers has long been known to enhance delamination of the fiber walls, and through the introduction of carboxymethyl groups, a fully delaminated carboxymethylated MFC may be produced.[28] Such groups should be in the form of their sodium salts to cause as much swelling of the pulp as possible. Swollen pulps have lower cell-wall cohesion than less swollen pulps and should therefore be easier to delaminate. Hence, holocellulose pulps, which contain anionic polysaccharides, are very easy to delaminate.[29]

Table 2 illustrates the drastic decrease in energy consumption that is observed upon the introduction of charges by

Table 2: Approximate energy requirements for the production of MFC.

Pretreatment	Pulp type, bleached	Energy requirement [kWh t^{-1}]
none	kraft[31]	12000–70000
none	sulfite[32]	27000
carboxymethylation (DS = 0.1)[a]	kraft/ sulfite[28b,32]	500
enzymatic/refining	sulfite[1a,32]	1500

[a] DS = degree of substitution.

carboxymethylation. When the charge density of pulp fibers increases, charge repulsion leads to a drastic decrease in fiber–fiber friction and therefore less susceptibility to flocculation as well as a decrease in the clogging tendency.[30] Hence, the introduction of charged groups was a fairly obvious approach to the reduction of energy consumption; patent claims on both anionic and cationic MFC have been filed.[33] The use of oxidative transition-metal ions for the oxidization of fibers has also been the subject of patent claims, as well as persulfate-oxidized cellulose as a suitable substrate for MFC production.[33c,34]

A novel way of introducing charged carboxylate groups into cellulosic materials and making MFC is the TEMPO-mediated oxidation (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) of the primary hydroxy groups at C6 of the cellulose molecules: an approach primarily developed by Isogai and co-workers.[35]

There are also other ways to decrease energy consumption, as indicated in Table 2. A combination of refining and enzymatic treatment can open up a processing window for this purpose during homogenization.[1a,36] If the enzyme dosage is small enough, the degree of polymerization of cellulose is barely affected by such treatment.

Over the years, many different procedures for delamination have been developed, such as the use of microfluidizers (Figure 3b),[1a,36,37] supergrinding/refiner-type treatments,[38] combinations of beating, rubbing, and homogenization,[39] high-shear refining, and cryogenic crushing in various configurations.[40] Delamination with ball mills and ultrasonification have also been used to make nanofibers.[41] It is not possible to judge whether some types of treatment are better than others, as few groups studying MFC-production methods have determined the energy efficiency. Furthermore, the extent of delamination observed for a certain energy input can not be assessed in a quantitative way. Unless different kinds of pretreatment are carried out on the pulp prior to mechanical processing, both cellulose crystallinity and the M_w value of the MFC deteriorate owing to the high energy input. As a result, materials made from such MFC have inferior properties.[42]

The issue of the redispersion of MFC after drying is difficult, as irreversible aggregation of the fibrils occurs in a process known as "hornification", which results in a material with ivory-like properties that can neither be used in rheological applications nor dispersed for composite applications. The main strategy to prevent hornification has been the introduction of a steric barrier or electrostatic groups to block cooperative hydrogen bonding of the cellulose chains. Among the most useful additives are polyhydroxy-functionalized admixtures, particularly carbohydrates or carbohydrate-related compounds, such as glycosides, carbohydrate gums, cellulose derivatives (e.g., CMC), starches, oligosaccharides, seaweed extracts, and glycol compounds.[43] Unfortunately, large quantities of such substances seem to be necessary to prevent hornification (Figure 4).

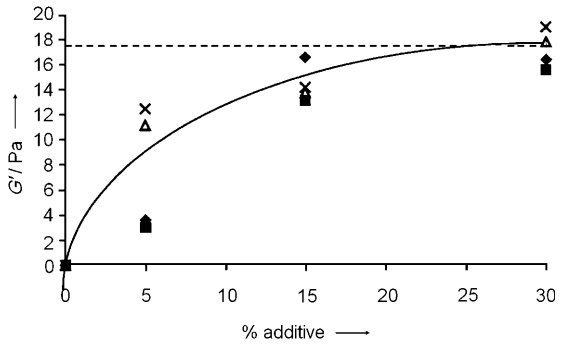

Figure 4. Graph showing the storage modulus of a redispersed MFC gel upon the addition of various amounts of CMC. The different symbols represent CMC with different degrees of substitution and molecular weights. The dashed line shows the modulus for the initial MFC dispersion (never-dried).[43e]

Another approach is to add functional groups to the cellulose, again to block cooperative hydrogen bonding.[44] Carboxymethylation is very effective. The introduction of carboxy groups (0.35 milliequiv (meq) per g) prevents the hornification of cellulose fibers and should be an equally effective method to prevent the hornification of MFC.[44]

2.2. Characterization of MFC

The most important characteristics of MFC are the dimensions and distribution of dimensions of the fibrillar material, and the rheology of the resulting dispersion.

2.2.1. Determination of Microfibril Widths

Atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM), often combined with image analysis, are used to characterize MFC. The size distribution is limited to the width distribution; owing to the high aspect ratio of the MFC fibrils, it is hard to obtain length-distribution values.

The fibrillar-aggregate width can be estimated by CP MAS NMR (cross-polarized magic angle spinning nuclear magnetic resonance)spectroscopy.[1a,45] The NMR spectroscopic method gave an average thickness of 17 nm, in good agreement with the results of TEM and SEM (scanning electron microscopy). Similar values (15 nm) were reported for other MFCs and for MFCs from carboxymethylated pulp.[1c,46]

Invariably, the presence of thinner fibrils can also be detected. For example, Lindström and co-workers reported fibrillar widths ranging from 5–15 nm for an MFC (Figure 5) with a negative charge density of around 0.5 meq g^{-1}.[1c] Isogai

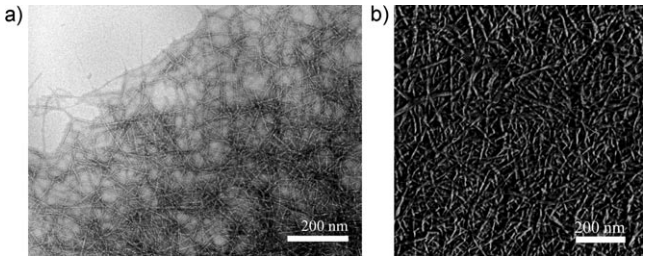

Figure 5. a) TEM image (image width: 1.1 μm),[1c] b) AFM image of carboxymethylated MFC (image width: 1.0 μm).[47]

and co-workers reported uniform microfibrils with widths of 3–5 nm for TEMPO-oxidized cellulose with a negative charge density of 1.5 meq g^{-1}.[35a,c] Thus, depending on the pretreatment, MFC appears to have two hierarchical levels—one in the range of 15–20 nm and another in the range of 3–5 nm. The latter corresponds to the elementary fibril, which results from extrusion from the cellulose-synthesizing complex (the so-called rosette complex) during biosynthesis. The former results from the aggregation of the microfibrils after biosynthesis. The aggregation phenomenon is well-known from ultrastructural studies of cellulose from wood cell walls by Bardage et al.[48]

The secondary cell wall of wood consists of different layers. The thin outer S1 layer and the dominant central S2 layer differ in terms of their cellulose content and the orientation of the cellulose fibrils. TEM studies on Norway spruce demonstrated a distinct aggregation with an aggregate width of approximately 18–20 nm (Figure 6), which is consistent with the aggregation of about four or five elementary fibrils. This result is also consistent with earlier observations that delamination under mild conditions tends to result in microfibrils of 15–20 nm in width, which corresponds to the aggregate size in the native cell walls of spruce. In contrast, harsher treatment, such as oxidation, enables delamination down to the size of elementary fibrils.

2.2.2. *Rheology*

MFC forms gels at very low concentrations in water. The dynamic rheological properties of MFC dispersions have been studied in detail.[1a] It was found that the storage modulus, G', and the loss modulus, G'', were independent of the angular frequency (ω) used in the experiments for all MFC concentrations (ϕ, solids content) between 0.125 and 5.9% (Figure 7). For classical viscous fluids, the storage and loss modulus have a characteristic frequency dependency, $G' \propto \omega^2$ and $G'' \propto \omega^1$, in which $G' \ll G''$. In contrast, an ideal gel behaves elastically, and $G' \propto \omega^0$; that is, the storage modulus is independent of frequency, and $G' \gg G''$. The value of the MFC storage modulus is considerably higher than the reported values for NCCs (see Section 3). A 3% dispersion of cellulose whiskers had a storage modulus of 10^2 Pa,[50] to be compared with the storage modulus of 10^4 Pa found in the investigation by Pääkkö et al.[1a]

The storage modulus is particularly strongly dependent on the MFC concentration. An increase in MFC concentration from 0.125 to 5.9% resulted in an increase in the storage modulus by five orders of magnitude (Figure 8a).

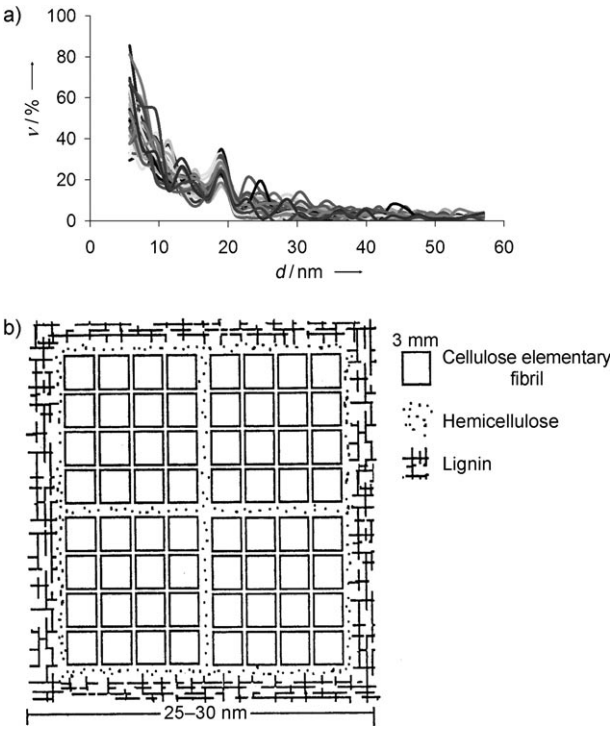

Figure 6. a) Frequency distribution of cellulose microfibrils within the S2 layer of Norway-spruce kraft-pulp fibers. The curves show the distribution of 300 measurement points per cell-wall layer for each pulp sample. Note the common peak in the range 18–20 nm.[48] b) Cross-sectional model of the ultrastructural organization of cell-wall components in wood, showing the two hierarchical structural levels.[49]

In many cases, there is a scaling law connecting the storage modulus to the solids content ($G' \propto \phi^n$). According to scaling theory,[51] the exponent, n, should be 2.25; however, at concentrations above 0.5%, n is around 3.0. On the basis of these data, Hill has suggested an alternative scaling-law formulation for MFC gels.[52]

The viscosity of MFC gels is decreased on shearing (Figure 8b). This shear-thinning behavior is of importance in industrial processing and particularly in coating applications.

2.2.3. *Polyelectrolyte Titration*

Polyelectrolyte titrations were initially developed to measure the charge density of polyelectrolytes and later applied to charge titrations on fiber materials.[53] The polyelectrolyte titration procedure is based on the fact that polyelectrolytes can form complexes with oppositely charged polyelectrolytes (direct titration) or surfaces (indirect titration). Generally, charge titrations are carried out at low ionic strengths, which enable the charge fields to overlap, so stoichiometry is attained. The technology can be used to determine the surface charge of (anionic) fibers if the (cationic) polyelectrolyte has a sufficiently high molecular weight that it does not penetrate the cell wall of fibers. In principle, this method may be used to titrate accessible surface charges and hence quantify the extent of cell-wall

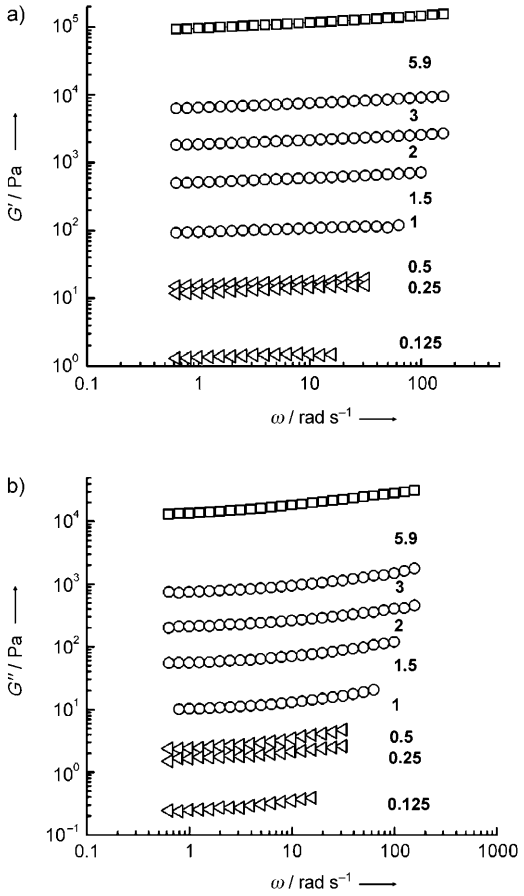

Figure 7. a) Storage modulus and b) loss modulus, both as a function of frequency (ω), for MFC suspensions of various concentrations (% w/w).[1a]

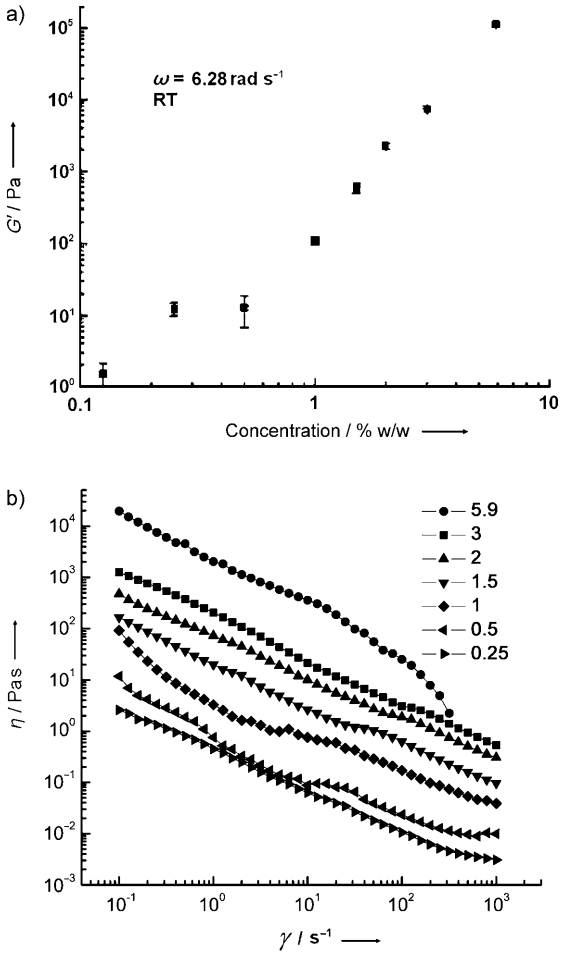

Figure 8. a) The storage modulus as a function of MFC concentration; b) influence of the shear rate (γ) on viscosity at different MFC concentrations (% w/w).

delamination; it has been used to characterize beating operations.[54] The technique was also used to determine the extent of delamination of carboxymethylated MFC,[28b] whereby full accessibility of all cell-wall charges was found and in principle full cell-wall delamination. However, the methodology has certain limitations when it is used on MFC.

The titration method is based on the fact that if the extension of the electrostatic surface field (Debye–Hückel shielding length, κ^{-1}) is larger than the distance between the charges, stoichiometry applies.[55] For this situation to occur, low ionic strengths are usually required. If the ionic strength is increased, there will be a deviation from stoichiometry (Figure 9a). The higher the charge density is, the higher the ionic strength can be without the loss of stoichiometry.

A second condition which must be fulfilled is that the value κ^{-1} must not be much larger than the thickness of the microfibrils, as all charges in larger fibril aggregates (defined by κ^{-1}) will otherwise be titrated. If, for example, the microfibrils are 30 nm thick, then an ionic strength of at least 10^{-4} M is required, and the necessary charge density for stoichiometry can then be deduced from Figure 9a. In Figure 9b, the Debye–Hückel shielding length has been plotted against the required charge density for stoichiometry to prevail.

So far, this is the only simple methodology available to determine the extent of cell-wall delamination.

2.3. MFC Films

The first data on the properties of MFC films were presented in 1998 by Taniguchi and Okamura, who concluded that the films were stronger than paper;[38c] however, no absolute values were given. Since then, many investigators have reported data on MFC films. Table 3 summarizes some recent studies (for the terms sulfite and kraft pulp, see Section 2.1).

Yano and Nakagaito,[56] found that the water-retention value (WRV) of the MFC suspension correlated with both the modulus of elasticity and the tensile strength. The higher the WRV is, the stronger the material is: a well-known correlation for papermakers.

By means of a vacuum-filtration method to dewater MFC, Berglund and co-workers formed cellulose nanopapers[1d] by using MFC from sulfite pulp with various DP values. The most important results are displayed in Figure 10. The stress–strain behavior is fairly linear up to the yield point at about 0.5%.

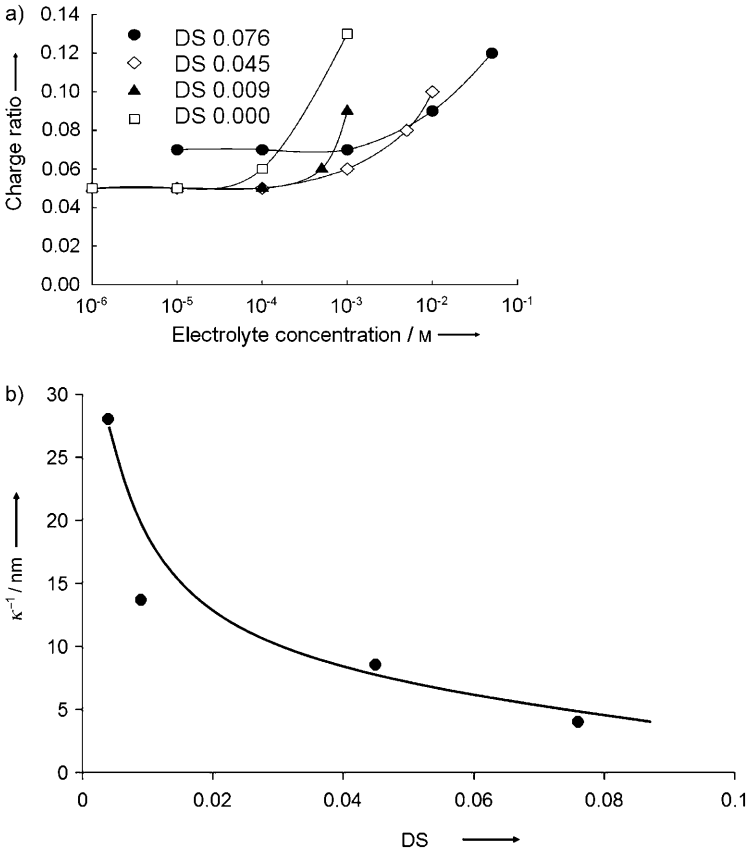

Figure 9. a) Charge ratio (surface/bulk charge) for carboxymethylated pulp as a function of the electrolyte concentration during adsorption. The lines drawn to connect the points show the critical electrolyte concentration for stoichiometry to be maintained (polyDADMAC, $M_w = 9.2 \times 10^{-5}$ Da).[55] b) Plot of the Debye–Hückel shielding length (κ^{-1}) against the degree of substitution (DS) that defines the necessary charge density for stoichiometry to be maintained.

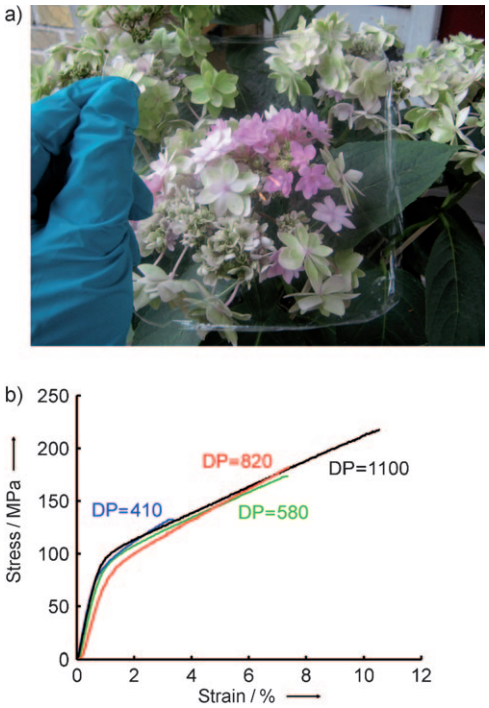

Figure 10. a) Transparent MFC film made from carboxymethylated MFC (courtesy: David Placket and Istvan Siro, Risø DTU, Roskilde). b) Typical stress–strain curves for MFC films prepared from pulps with various degrees of polzmerization.[1d]

After this point, a linear strain-hardening region was observed. The films were found to be very strong, particularly those with a high DP. The films are tough, as judged from the high strain to failure observed. The strength of the film under strain is very sensitive to the DP value of the MFC. The porosity of the films was between 20 and 28%. Films with higher porosities (40%) were also found to be strong (around 90 MPa).

Similar results from other research groups are shown in Table 3. Syverud and Stenius found that an increased basis weight of the film resulted in a strength and density increase.[57] It is not clear how manufacturing procedures (MFC choice, extent of delamination, formation procedure (e.g. vacuum filtration, casting, drying conditions)) affect these results. Whereas the MFC sheets made by Syverud and Stenius had densities between 0.8 and 1.07 g cm^{-3}, the highest values were reported by Nogi et al.,[59] who described a film with a density of 1.53 g cm^{-3}; the difference in density is strange considering the similarity in mechanical properties.

Film density is also an important variable in terms of the optical and barrier properties of MFC films.[57,58,60]

2.4. MFC Types Useful in Nanocomposite Materials

2.4.1. General Aspects of MFC Nanocomposite Materials

The production of cellulose nanocomposites can be subdivided into at least six broad categories:

- casting of aqueous MFC dispersions by using water-soluble matrix materials, such as starches (the simplest method)

Table 3: Results of representative studies on the properties of MFC films.

MFC type	Modulus [GPa]	Tensile strength [MPa]	Strain to failure [%]	Particularities
MFC from sulfite pulp[1d]	10.4–13.7	129–214	3.3–10.1	effect of DP and porosity
MFC from sulfite pulp[57]	17.5	146	8.6	effect of basis weight
MFC from kraft pulp blend[56a]	17	250	2–6	effect of WRV
TEMPO-oxidized SW[a]/HW[b] pulp[58]	6.2–6.9	222–233	7.0–7.6	optical/thermal properties
MFC from wood flour after extraction of lignin and/or hemicellulose[59]	13	223	–	optical properties

[a] SW = softwood. [b] HW = hardwood.

- casting of MFC dispersions to which a latex dispersion has been added (the latex enables the use of a hydrophobic matrix, and good dispersion may be attained)[61]
- dispersion of MFC and casting of films from a solvent in which the matrix material can be dissolved (this method usually requires surface modification of the MFC for good dispersion)
- dispersion of dried MFC (modified or not) into a hydrophobic matrix
- reinforcement of porous MFC films with an agent to improve their properties
- use of aqueous MFC dispersions to form composite materials with the matrix in the form of fibers by papermaking, pressing, and press molding

From a theoretical point of view, the studies based on the second (latex) method have been most important. Dufresne and co-workers have studied nanocomposite materials with various rubbery latex matrix materials.[12a,b,13b] They used cellulose nanowhiskers (for nanocrystalline celluloses, see Section 3), but from sources that gave nanocrystals whose length was comparable to that of MFC. Such sources included tunicin and parenchyma cell walls from agricultural residues, such as sugar beet and potato tubers. The matrix material was typically a poly(styrene-*co*-*n*-butyl acrylate) (PBA) latex with a low glass-transition temperature. Tunicin whiskers had an amazing reinforcing effect on the PBA latex (Figure 11); the reinforcing effect reached several orders of magnitude in the rubbery region of the polymer at low whisker concentrations.[62]

The data for whisker reinforcement are often interpreted by using a percolation model.[3a,63] Several arguments support the model:

- The rubbery region is unusually stable with respect to temperature.
- The glass-transition temperature is not affected by the whisker content.
- There is a disproportionate increase in the shear modulus above the percolation threshold.

Specifically, the series-parallel model of Takayanagi et al.[64] was used after modification to include a percolation approach. It was envisioned that above the percolation threshold, the cellulose nanoparticles connect with one another to form a three-dimensional continuous hydrogen-bonded pathway through the nanocomposite network of the film.

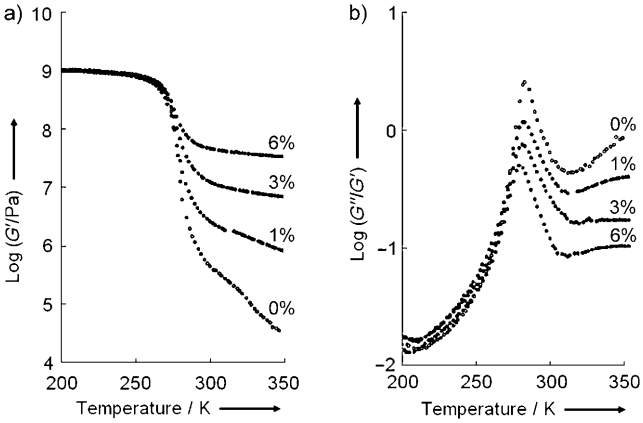

Figure 11. a) Evolution of the log of the shear modulus of an NCC-reinforced composite for several NCC concentrations. The NCC is hydrolyzed cellulose from tunicates; the matrix is PBA latex (35% styrene, 65% butyl acrylate units). b) Plot of log (G''/G') against the temperatures in Figure 11 a.[62]

In a recent review on nanocomposites by Schaefer and Justice, it was concluded that large-scale disorder is ubiquitous in nanocomposites, regardless of the level of dispersion,[61] and leads to a substantial deterioration of the mechanical properties relative to predictions based on an idealized filler morphology. To what extent this effect also applies to cellulose nanocomposites is not yet known.

2.4.2. *Specific Studies on MFC Composite Materials*

This section describes some specific studies on the use of MFC as reinforcement in composite materials. A list of representative studies is given in Tables 4 and 5. Again, the difference between MFC (nonhydrolyzed) and NCC (hydrolyzed, highly crystalline cellulose) should be recognized. Tables 3–5 do not contain studies on NCC composites, but Table 4 includes MFC from nonwood materials. Two of the studies in Table 4,[65] however, do include a direct comparison of the properties of MFC and NCC composites: Azizi Samir et al. investigated the effects of hydrolysis on a nanocellulose-reinforced PBA latex[65a] and concluded that the nonhydrolyzed nanocellulose (MFC) was superior in reinforcing the latex. In general, the reinforcement of latex by MFC and NCC has very strong effects on the shear modulus in the rubbery region, in line with the percolation theory referred to above. A study by Siqueira et al. in which they compared the reinforcement of polycaprolactone (PCL) by sisal MFC and NCC confirmed these results.[65b]

Table 4: Some representative studies of MFC composites made from nonwood materials.

MFC type and origin	Matrix material	Type of investigation
MFC from sugar-beet cellulose[65a]	PBA latex	DMA,[a] tensile strength, TEM
MFC from *opuntia ficus-indica*[69]	PBA latex	DMA,[a] tensile strength, TEM
MFC from potato-tuber cellulose[67,70]	potato starch, plasticized with glycerol	DMA,[a] SEM, tensile strength, moisture sorption
MFC from sweet root tissue[71]	PVOH, acrylic polymer, epoxy resin	SEM, tensile strength
MFC from sugar-beet cellulose[72]	phenol–formaldehyde resin, PVOH	SEM, tensile strength
bleached-sisal MFC[65b]	PCL	DMA,[a] tensile strength, TEM

[a] DMA = dynamic mechanical analysis.

Although these findings are interesting, there may be significant differences between NCC and MFC with regard to processing procedures. Such differences would affect the overall state of dispersion and residual stresses in the finished nanocomposite. In the study on PCL, it was necessary to modify the surface of the MFC by grafting with *N*-octadecyl isocyanate to enable dispersion of the MFC in dichloromethane, from which the films were solvent-casted. The direct grafting of PCL onto MFC to enhance compatibility has also been explored.[66]

The film casting of starches (with and without glycerol as a plasticizer) reinforced with MFC is straightforward, and strong reinforcement effects have been recorded with both nonwood and wood-based MFC (see references in Tables 4 and 5). Two typical examples are given in Figure 12.

Table 5 lists representative investigations of composites with wood-based MFC (for the terms sulfite and kraft pulp, see Section 2.1). Casting from aqueous solvents with starches, poly(vinyl alcohol) (PVOH), or HPC is straightforward and always yields strong reinforcement effects.

Different processing approaches have been examined with polylactide (PLA) matrix materials. Iwatake et al. dispersed MFC in excess acetone,[73] added dissolved PLA and evaporated the acetone, kneaded the residue in a twin-rotary-roll mixer, and finally compounded the residue at 140 °C. A good reinforcement effect was observed. Nakagaito et al. used PLA fibers and formed papers from a PLA-fiber suspension through the addition of MFC in a process like papermaking, followed by press molding at high temperatures.[74] Excellent reinforcement effects were observed (Figure 13). Mathew et al. used yet another approach,[84] whereby microfibers (produced by refining and cryogenic crushing) were added to a PLA melt in a corotating extruder. The processing was complicated by a steam-removal problem, which was eventually solved; however, the reinforcement effect was negative, a result attributed to poor dispersion of the microfibers.

It has been reported that MFC films impregnated with an epoxy resin give transparent composites with excellent thermal conductivity.[82] In another study,[83] MFC was modified with coupling agents (two silanes and a titanate agent). Solvent-exchanged MFC was dispersed in acetone and modified with the coupling agent. An epoxy resin was then dissolved in the dispersion, and the film was cast and finally cured. Better composite materials were obtained with treated MFC (hydrophobic) than with untreated MFC, which is difficult to disperse in acetone. Various other surface-modification technologies have also been investigated.[85]

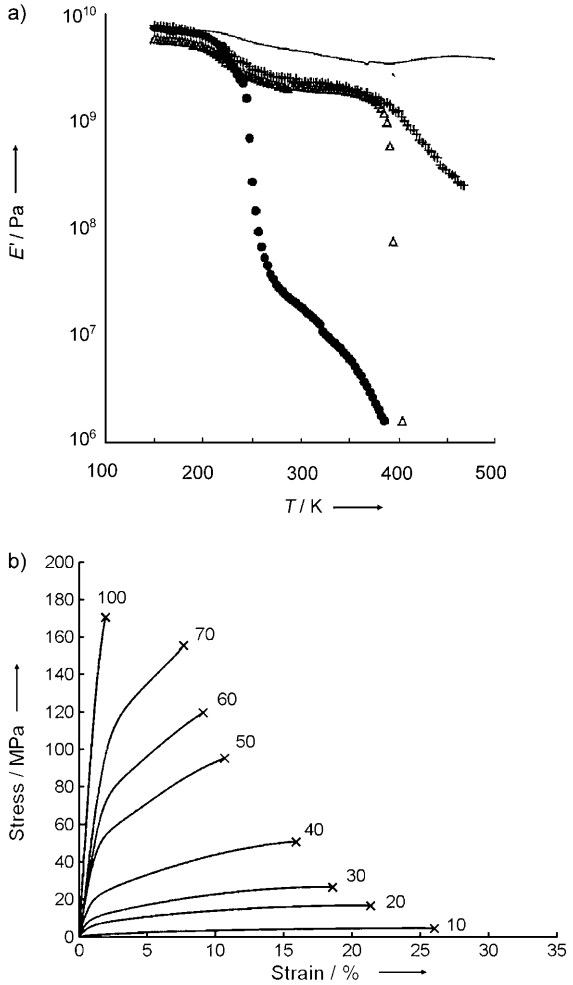

Figure 12. a) Plot of the storage tensile modulus (E') against temperature at 1 Hz for pure starch (——) and starch plasticized with 30 wt% glycerol and filled with 0 wt% (●), 5 wt% (△), and 10 wt% (+) potato-tuber MFC.[67] b) Stress–strain curves for a starch/glycerol (1/1) matrix reinforced with different amounts of wood-based MFC (the amounts of MFC added are indicated (wt%)).[68]

Table 5: Some representative studies of MFC composites made from wood-based materials.

MFC type and origin	Matrix material	Type of investigation
MFC from sulfite pulp[68,75]	amylopectin potato starch, plasticized with glycerol	SEM, tensile strength, moisture sorption
MFC from sulfite pulp[37]	PVOH, HPC	SEM, tensile strength
MFC from sulfite pulp[76]	chitosan	SEM, tensile strength
microfibers from kraft pulp[77]	PVOH	SEM, tensile strength
MFC from kraft pulp blend[78]	PVOH	SEM, tensile strength
MFC from kraft pulp blend[73]	PLA (press molding)	DMA, SEM, tensile strength
MFC from kraft pulp blend[74,79]	PLA fibers (press molding)	DMA, SEM, tensile strength
MFC from kraft pulp blend[60,79,80]	phenol–formaldehyde resin	SEM, tensile strength
MFC from kraft pulp blend[81]	polyurethane (PU)	DMA, SEM, tensile strength
MFC from kraft pulp blend[82]	epoxy resin	optical/thermal properties
MFC from kraft pulp blend[83]	epoxy resin	DMA, SEM, tensile strength, coupling agents
microfibers from kraft pulp[84]	PLA extrusion	SEM, tensile strength

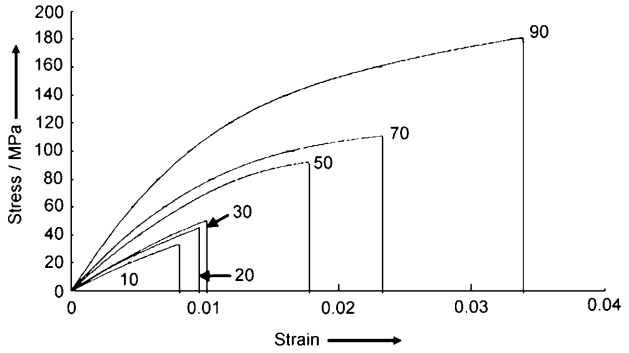

Figure 13. Stress–strain curves of MFC/PLA composites at different fiber contents. The percentage indicates the MFC-fiber content.[74]

In conclusion, MFC can have a reinforcing role in composites, but processing can be considered a key issue. Casting from aqueous solvents is straightforward; however, it is not clear which applications are the most promising. Papermaking applications are probably easier than composite applications, for which moisture resistance is often demanded. A major processing problem is that the low concentration of MFC dispersions makes it necessary to remove considerable quantities of water.

2.4.3. *Aerogels and MFC-Reinforced Foams*

Efforts are being made to use starch-based foams for packaging applications as a replacement for polystyrene-based foams; however, starch is brittle without a plasticizer, and its mechanical properties are sensitive to moisture. Svagan et al. have shown that through the use of a freeze-drying technique, MFC can reinforce starch foams.[75a,86] The advantage of using MFC instead of conventional wood-based pulp fibers is that the nanosized fibrils enable reinforcement of the thin cell walls in the starch foam; the larger dimensions of wood-based fibers make them much less suitable for structural reinforcement. Another benefit is that the MFC fibrils can be used to alter the viscosity of the melted polymer. This effect is of great importance in foaming. The foam structure of a starch/glycerol/MFC composite is shown in Figure 14a; Figure 14b shows typical stress–strain curves for MFC-reinforced amylopectin foams conditioned at 50% relative humidity.

By using various freeze-drying techniques, it is also possible to make pure MFC aerogels, which may be used as porous templates.[87]

2.4.4. *Sequential Assembly of MFC Nanocomposite Materials*

The formation of polyelectrolyte multilayers (PEMs) by the sequential addition of oppositely charged polyelectrolytes is a useful approach to the assembly of nanocomposite materials.[88] Recently, the technology has been applied to anionic NCC together with poly(diallyldimethylammonium chloride) (polyDADMAC) and poly(allylamine hydrochloride) (PAH) as cationic polyelectrolytes, and to a carboxymethylated MFC with poly(ethylenimine) (PEI), PAH, and polyDADMAC as polyelectrolytes.[1c,47,89]

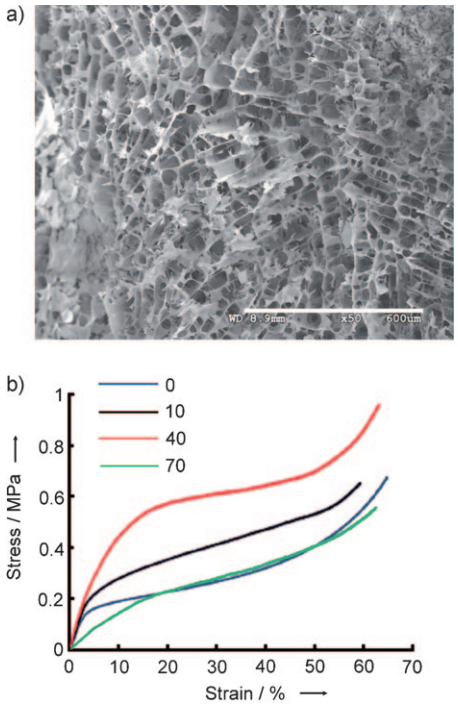

Figure 14. a) Cell structure of an amylopectin foam with 40 w% MFC (scale bar: 600 nm). b) Stress–strain curves for MFC-reinforced amylopectin foams conditioned in 50% relative humidity with different MFC contents (in w%).[86]

The typical way in which PEMs are built up is shown in Figure 15.[1c] The combination of PEI and carboxymethylated MFC in deionized water results in the formation of regular layers of MFC and PEI with alternating layer thicknesses of 20 and 3 nm, respectively, after the deposition of 10 layers. By changing the electrolyte concentration, it is possible to also change the thickness of the layers.

The PEMs had different colors depending on their total thickness (Figure 16), and simple estimates of the thickness of the PEMs from the colors, on the basis of the assumption of dense cellulose layers, showed surprisingly good agreement with data from ellipsometry measurements. This correlation indicates that the PEMs are basically compact films of cellulose with some of the cationic polyelectrolyte molecules intercalated between the MFC layers.

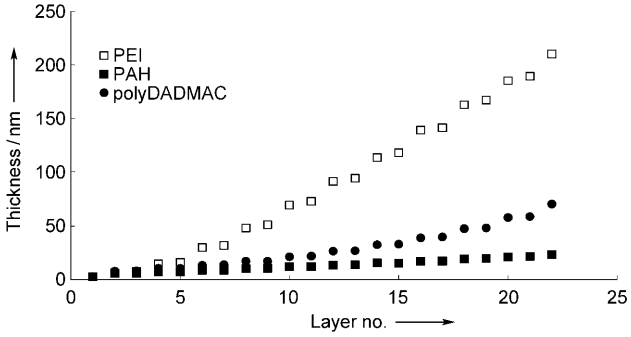

Figure 15. Thickness (as determined by ellipsometry) of PEM layers of carboxymethylated MFC with PEI, PAH, and polyDADMAC under electrolyte-free conditions at pH 7–8.[1c]

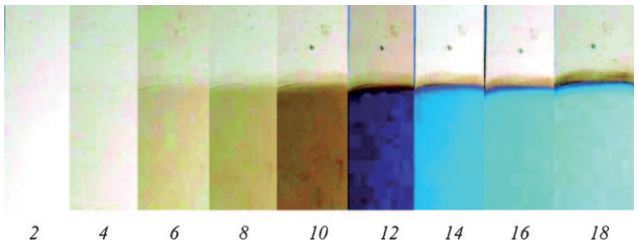

Figure 16. Interference colors of films of MFC and PEI as a function of the number of layers under electrolyte-free conditions at pH 7–8. For example, "12" in the figure refers to a combination of six layers of PEI and six layers of carboxymethylated MFC.[1c]

2.5. Potential Areas of Application for MFC

Although the colloidal and rheological properties of MFC have led to a wide range of patents, there are today very few, if any, large-scale commercial applications. However, the chemical and biochemical modifications described above of the original mechanical processes, along with a general renaissance of interest in renewable materials with nanometer-sized dimensions, have led to renewed interest in possible applications.

2.5.1. Paper and Paperboard Applications

The role of fiber fragments ("fines") in enhancing the bond strength between fibers in papermaking is well-known to papermakers.[26] MFC acts as a dry- and wet-strength agent and as a reinforcing agent to enhance the strength of pulps produced by thermomechanical processing.[31,90] Another potential application of MFC is as a barrier in greaseproof paper,[57,60] for which the film-forming properties of MFC are utilized. MFC has also been suggested to function as a reinforcing component in paper coatings.[39c,91]

2.5.2. Composite Applications

Some interesting applications of MFC in composites have been described by Yano and Nakahara, including high-strength materials made from cellulose microfibrils combined with a thermosetting resin,[92] and fiber-reinforced composite materials with good transparency.[93] MFC from tunicin was patented as a component of paints when combined with latex particles, and after surface modification as a reinforcing agent for cellulose acetate.[94] Rubber latex can be blended with MFC, followed by vulcanization and drying, to make natural rubber products with improved hardness and resistance to cuts and abrasion.[95]

2.5.3. Miscellaneous Applications

The nontoxic, hydrophilic, and rheological properties of MFC have led to a wide range of proposed applications. Most numerous are claimed applications as a low-calorie thickener and suspension stabilizer in food applications.[41b,96] MFC is also of interest in cosmetics and pharmaceutical applications.[97] The absorptive and strength properties of finely divided cellulose lead to applications in sanitary products,[98] wound dressings,[98i,99] and coating agents.[100] The grafting of quaternary ammonium groups to MFC gives antimicrobial films.[101]

Many proposed applications involve the stabilization of emulsions and dispersions by MFC and modified MFC.[102] Potential high-volume applications include the use of MFC as a component of suspending fluids for drilling and for oil recovery.[97,103] Applications in the solid state include its use as a component of drug tablets[104] and regenerated-cellulose products,[105] and as a battery separator.[106]

3. Nanocrystalline Cellulose (NCC): A Sustainable Reinforcing Agent

In this section, the preparation and properties of NCC are summarized, with emphasis on the incorporation of NCC in composite materials.

3.1. NCC Preparation

Nanocrystalline cellulose is the term often used for the cellulose nanocrystals prepared from natural cellulose by acid hydrolysis. The nanocrystals formed from wood pulp are shorter and thinner than the MFC described in Section 2. The reduction of cellulose fibers to particles of nanometer dimensions was described many years ago by Rånby,[18a] and a renaissance of interest stemmed from the unexpected observation that suspensions of nanocrystals formed a stable chiral nematic liquid-crystalline phase.[20,107] In the biphasic concentration range, the isotropic and chiral nematic phases are in equilibrium (Figure 17). As the concentration of NCC is further increased, the suspension becomes completely liquid-crystalline.[108]

As previously mentioned, NCC has been isolated from a wide variety of cellulosic sources, including plants,[2e,14a,109] microcrystalline cellulose,[2d] animals,[3c,62] bacteria, and algae.[2a,b,15,110] Tunicin whiskers have been a favored source because of their length and high crystallinity,[3c,62] although their widespread usage may be restricted by the high cost of harvesting and limited availability. Wood, owing to its natural abundance, is a key source of cellulose, as is cotton because of its widespread availability, high cellulose content (94%),[111] and uniformity. Filter paper and related products were the preferred substrate for initial basic research on cellulose nanocrystals, because of their purity and ready availability in laboratories.

Cellulose nanocrystals are generated by the liberation of crystalline regions of the semicrystalline cellulosic fibers by hydrolysis with mineral acids. This chemical process starts with the removal of polysaccharides bound at the fibril surface and is followed by the cleavage and destruction of the more readily accessible amorphous regions to liberate rodlike crystalline cellulose sections. When the appropriate level of glucose-chain depolymerization has been reached, the acidic mixture is diluted, and the residual acids and impurities are fully removed by repeated centrifugation and extensive

dialysis. The hydrolysis is followed by a mechanical process, typically sonication, which disperses the nanocrystals as a uniform stable suspension. The structure, properties, and phase-separation behavior of cellulose-nanocrystal suspensions are strongly dependent on the type of mineral acid used and its concentration, the hydrolysis temperature and time, and the intensity of the ultrasonic irradiation.[2c,e,19a,109b,112]

The type of mineral acid employed in the hydrolysis step has a major influence on the surface properties of the nanocrystals; crystals generated with HCl exhibit poor colloidal stability,[2d,14a,21b] whereas those hydrolyzed with sulfuric acid also undergo some surface sulfation and are thus stabilized by strong electrostatic repulsion between the anionic sulfate ester groups at the surface.[18a,21a] The morphology and dimensions of the nanocrystals depend on the cellulose source: the highly crystalline tunicate and algal cellulose liberate nanocrystals of several microns in length, whereas the less crystalline wood fibers (53–80 % crystallinity) yield shorter nanocrystals.[2b,3c,62,110,113]

3.2. NCC Stabilization and Surface Modification

Hydroxy groups present in the native cellulose and sulfate ester units introduced during hydrolysis with sulfuric acid both contribute to the hydrophilic character of the cellulose nanocrystals. The almost neutral nanocrystals obtained by HCl hydrolysis show limited dispersibility in water, whereas those obtained by sulfuric acid hydrolysis are more stable over a wide range of pH values, since the pK_a value of sulfate groups is around 1.9. Owing to the electrostatic character of NCC, increasing the ionic strength can induce flocculation.[19a] Not only the surface properties, but also the dimensions of the dispersed particles influence the stability of NCC suspensions. Typically, smaller nanoparticles with a low aspect ratio are dispersed more homogeneously in solution.

Cellulose nanocrystals show some dispersibility in aqueous-based mixtures and in organic solvents with high dielectric constants, such as dimethyl sulfoxide (DMSO) and ethylene glycol,[114] but tend to aggregate in highly hydrophobic solutions. Azizi Samir et al. freeze-dried NCC samples and redispersed them by sonication in *N*,*N*-dimethylformamide (DMF).[115] However, the addition of a small amount of water to DMF is necessary to resuspend the crystals homogeneously.[116] Several surface modifications have been applied to cellulose nanocrystals to improve their stability in organic media or to make them compatible with hydrophobic thermoplastic matrices. Those methods include surface hydrophobization by silylation or acylation,[15,117] carboxylation,[118] esterification,[119] FITC labeling (FITC = fluorescein-5′-isothiocyanate),[120] polymer grafting (PCL, poly(ethylene glycol) (PEG), poly(styrene)), and cationic surface functionalization.[118a,121]

The main challenge with chemical modification is to choose a reagent and reaction medium that enable modification of the nanocrystal surface without the nanocrystal dissolving in the reaction medium and without undesired bulk changes. An alternative to chemical surface modification is the adsorption of surfactants at the colloid surface to improve nanoparticle stability in organic solvents. This type of stabilization has been used to stabilize cellulose nanocrystals with a surfactant (a phosphoric ester of polyoxyethylene(9) nonylphenyl ether) in toluene and cyclohexane.[114,122]

A potential drawback to surface functionalization is the possibility that the distinctive properties of the NCC may be lost upon modification. For example, mechanical properties could be compromised by surface chemical modification of the NCC as a result of disruption of the 3D crystal network, as reported for nanofibrils of the polysaccharide chitin.[123]

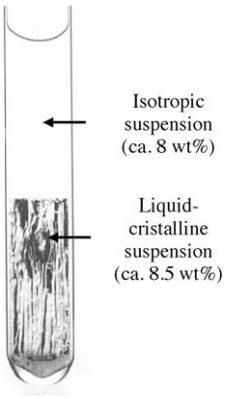

Figure 17. Photograph (taken between crossed polars) of a biphasic suspension of cellulose nanocrystals in water. The sample is in a flat glass microslide (width: 10 mm, depth: 1 mm).

3.3. NCC in Composite Films

Factors that influence the mechanical properties of plastics include cross-linking processes (largely used in thermosetting plastics), polymer molecular weight, and the degree of matrix crystallinity. For most plastics, semicrystallinity is highly desired, as it allies the strength of the crystalline regions resulting from the secondary bonding that occurs between the closely packed and parallel molecular chains with the flexibility of the amorphous sections of the matrix. The introduction of a small amount of a filler into an amorphous polymer matrix is a common approach to increase material strength and endurance. Fillers are also used to reduce cost, minimize curing time and shrinkage, and improve mechanical, electrical, and chemical properties.[124]

Owing to their high aspect ratio and high degree of crystallinity, cellulosic fibers have been extensively incorporated into plastics to improve strength and decrease cost. Their potential in automotive applications and construction materials has been exploited.[125] The major problem with these fibers is that it is difficult to avoid aggregation during their dispersion in the matrix because of their length, which leads to entanglement. Moreover, their hydrophilic nature prevents their use as reinforcing agents in most hydrophobic thermoplastics. Nonhomogeneous filler dispersion usually results and in turn leads to poor composite properties and an inefficient strengthening effect. The tendency of cellulosic fibers to absorb moisture is also problematic, as it causes the fiber to swell and fiber–matrix adhesion to decrease. The low degradation temperature of the fibers, about 230 °C, is also a major inconvenience, as it restricts composite processing to temperatures below 200 °C.

The replacement of long cellulosic fibers by cellulosic material of smaller axial ratios is an interesting option for composite preparation. With their better dispersibility and their lower susceptibility to bulk moisture absorption, a theoretical elastic modulus of 138 GPa (comparable to that of

steel),[126] and a large surface area of several hundreds of square meters per gram,[15] cellulose nanocrystals are more efficient filler candidates. As mentioned in Section 2, Favier et al. were the first to demonstrate the reinforcing properties of cellulose nanocrystals; they prepared a PBA latex composite which showed a significant improvement in the matrix modulus in the rubbery state.[62] Following this advance, the incorporation of cellulose nanocrystals from different sources into composite materials with enhanced properties has been investigated thoroughly and summarized in several review articles.[4,12b,121a,127]

In the following Sections, we emphasize the reinforcing properties of NCC generated by the hydrolysis with acid of wood, cotton, and other sources of cellulose and consisting of true nanoparticles (in all dimensions) with high crystallinity and high suspension stability.

3.3.1. Incorporation Methods

The properties of composites depend on the nature of the matrix and the cellulose crystals, and on the strength and extent of their interfacial interactions. Processing techniques will also have an impact on the resulting composite performance. Several composite matrices were explored among natural and synthetic polymers and latexes, including cellulose acetate butyrate (CAB),[15,128] starch,[109a,129] PLA,[3b,130] poly(hydroxyalkanoate) (PHA),[131] soy protein,[132] chitosan,[133] regenerated cellulose, and silk fibroin as natural matrices, and PBA,[3a,62,134] poly(oxyethylene),[55,123,124] PCL-based water-borne polyurethane (WPU),[135] polypropylene (PP),[136] poly(vinyl chloride) (PVC),[137] and PVOH[138] as synthetic polymers.

The first step of the polymer nanocomposite preparation is to select the appropriate matrix for the anticipated application. Owing to the inherent hydrophilic nature of NCC, it seems most useful in combination with water-soluble polymer matrices. If an organic matrix is considered, surface modification of NCC is required to improve biocompatibility with the medium and to enable acceptable dispersion; however, surface modification may result in the loss of mechanical properties. Typical experiments involve the preparation of films with NCC loadings that normally range between 0 and 10%. The key step of the composite preparation is the mixing process used to disperse NCC and polymers, as homogeneity significantly affects composite performance.

Polymers are usually mixed with NCC in aqueous media by simple stirring at room temperature, and sometimes under vacuum to prevent the presence of air bubbles in the final film.[135] Films can be formed from these mixtures either by film casting, whereby the solvent is evaporated at moderate temperatures, or by classical processes, such as hot pressing and extrusion (usually preceded by solvent casting or freeze drying). The type of container used for casting should be carefully chosen to enable ready removal of the film without damaging it. Typical containers are made from Teflon, PP, or glass. Thermal, chemical, or photo-cross-linking agents are sometimes used to make NCC/polymer and/or polymer/polymer interactions stronger.[115,138a,139]

Cellulose crystals have been incorporated not only in thin films, but also in other types of matrices, such as light-weight aerogels prepared by freeze drying of a simple dispersion of clay and cellulose whiskers.[140] Incorporation methods applied to a wide variety of polymer matrices are summarized in Table 6.

3.3.2. Experimental Variables That Influence Reinforcing Properties

Characteristic features of heterogeneous materials depend on the behavior and properties of each phase, the volume fractions of the phases, their spatial arrangement or morphology, and their interfacial properties.[141] The extent and strength of the filler–filler interactions also have a significant impact on the resulting mechanical behavior of the composite.[127a] Parameters that affect the mechanical performance of polymer–NCC composite films are described below.

Cellulose Aspect Ratio

In theory, the performance of reinforced materials relies on the efficiency with which mechanical stress is transferred from an external energy source to the reinforcing phase through the matrix. The efficiency of transfer is a function of the amount and quality of the interfacial area between the reinforcing agent and the matrix. In principle, high-aspect-ratio fibers have a better ability to sustain mechanical stress uniformly over the matrix than short fibers. Although high-aspect-ratio fibers provide more efficient strengthening, they are harder to disperse owing to their tendency to entangle, which limits the improvement of mechanical properties. The effectiveness of reinforcement is often addressed by percolation theory (see also Section 2), which can predict long-range connectivity in the matrix during film formation. This extended network is presumably generated through hydrogen-bond formation between the cellulose nanocrystals, whose packing structure depends on the distribution and orientation of the rods as well as their aspect ratios l/d (l = length, d = diameter).[62,142] In principle, the higher the aspect ratio, the lower the percolation threshold, which defines the critical value at which continuous connectivity between fillers first arises.

Some studies compared the strengthening efficiency of cellulose nanomaterials of various lengths and demonstrated that size and shape influence the properties of the resulting composites; a superior reinforcing effect was observed with MFC.[143] The crystallinity of a PCL matrix was also found to be influenced by the cellulose component: shorter nanocrystals resulted in enhanced matrix crystallinity, whereas long MFC had no effect on the PCL matrix.[143b] A comparative study of reinforcement by three cellulosic species demonstrated that improved physical properties of polyacrylic films were most significant with cellulose whiskers.[144]

Processing and Surface Functionalization

The effect of processing techniques on the mechanical properties of composites made from latex has been inves-

Table 6: Ways to incorporate NCC into composites.

Process	Matrix	Applications
compression molding or extrusion[132, 134c,d, 137a, 154]	thermoplastics: PLA, soy protein suspensions and latexes: PVC, PBA, $LiClO_4$-doped ethylene oxide–epichlorohydrin copolymer[a]	nanocomposites, ion-conducting solid polymer electrolytes
solution casting[3a,b, 15, 62, 109a, 117a, 121b,c, 128–131, 133–136, 138b, 143b, 144, 146, 155]	thermoplastics: starch, PLA, PP biopolymers: chitosan, regenerated cellulose synthetic polymers: PCL-based WPU, PCL, polyaniline, and poly(phenyl ethylene), derivatives latexes and copolymers: poly(hydroxyoctanoate) (PHO), PBA, CAB, acrylic latex (UCAR), poly(vinyl alcohol-*co*-vinyl acetate)	biodegradable plastics, coatings, adhesives, foams, biothermoplastic elastomers, synthetic metals, organic semiconductors, field-effect transistors, photovoltaic cells, sensors
solution casting followed by cross-linking (photo- or thermal) or polymerization[115, 138a, 139, 156]	synthetic polymers: poly(ethylene oxide)–LiTFSI,[b] poly(methyl vinyl ether-*co*-maleic acid)–PEG monomers and prepolymers: acrylate/methacrylate, PU (polyols and polyisocyanate), PVOH and PAH, water-based epoxy emulsion	ion-conducting solid polymer electrolytes, hydrogels, elastomers, membranes in food and medical packaging
in situ polymerization[157]	furfuryl alcohol	nanocomposites
template approach with an organogel[14b, 158]	copolymer of ethylene oxide and epichlorohydrin	nanocomposites
self-assembly (spin coating and dip coating)[89b, 159]	polyelectrolytes: PAH, cellulose I	optical films, drug-delivery systems

[a] Solution casting is first required. [b] TFSI = bis(trifluoromethanesulfonyl)imide.

tigated by several groups. Hajji et al. classified processing methods according to their reinforcement efficiency, whereby evaporation was the most efficient technique, followed by hot pressing and extrusion.[134c] Poor results obtained by freeze drying followed by hot pressing arise from rough dispersion of the fillers, which creates film irregularities,[134d] whereas extrusion causes the gradual breakage of whiskers, which decreases their aspect ratio and their efficiency.[134c] On the other hand, when the dispersion medium is evaporated from a film, whiskers have enough time to interact to form a three-dimensional hydrogen-bonded network; in this way, the matrix is strengthened.

The reaction of the surface hydroxy groups of cellulose whiskers with nonpolar substituents often leads to improvements in the performance of organic polymeric matrices. A recent study showed an enhanced tensile modulus for a PCL matrix reinforced with alkylated whiskers in comparison to the use of native cellulose whiskers.[143b] Improvements in the physical properties of composites were also reported by Roman and Winter, who incorporated silylated crystals into a CAB matrix.[117a] Despite their lower reinforcement ability relative to that of native crystals, such modified fillers exhibited higher compatibility with the matrix, which resulted in an increase in the melting point and a decrease in damping of the CAB matrix. Habibi et al. also demonstrated improved load transfer and interfacial properties of their PCL-grafted NCC incorporated into a PLC matrix, as reflected by an increase in the overall crystallinity of the composite and higher mechanical performance.[121c]

Other Factors That Influence Composite Strength

The optimal enhancement of mechanical properties usually occurs at the limit of the percolation threshold, at which just enough reinforcing agent has been added to establish connectivity. This percolation threshold was evaluated theoretically to be 1 % (v/v) for cellulose whiskers with an aspect ratio of 100.[145] A plateau in stiffness is often observed as more filler is added. On the other hand, if the filler content is too high, the matrix modulus may decrease as a consequence of poor whisker dispersibility and aggregate formation. This effect is observed particularly with fillers that have a weak affinity for the matrix.[121c]

Matrix crystallinity is also affected by the cellulose component, as pointed out by Mathew and Dufresne, who reported an increase in the crystallinity of their plasticized starch matrix as the whisker content was increased.[146] The water resistance of the film is strongly influenced by the composite microstructure and was also found to be affected by the whisker content; a high whisker loading (30 %) decreased water uptake by a soy-protein thermoplastic film by 10 %.[132]

Moisture might be expected to strongly influence cellulose-containing composites in two distinct ways. First, during formation of the composites, cellulose–matrix adhesion, especially with hydrophobic matrices, would be expected to be diminished by a weak boundary layer of hard-to-remove water on the cellulose surface. Second, mechanical properties of the composite may be sensitive to relative humidity and exposure to liquid water. In the case of the incorporation of cellulose whiskers in plasticized starch, water content also induces starch crystallization and plasticizer distribution.[129a]

Transcrystallization is the phenomenon whereby a highly oriented layer of a semicrystalline polymer forms at the matrix/filler interface.[147] Such layers only develop under specific conditions and affect the quality of interactions between the matrix components. The formation of a spherulitic transcrystalline layer at the edge of an NCC film embedded in a PP melt has been reported.[148] Dufresne et al. invoked transcrystallization of a PHA latex by cellulose-whisker surfaces to explain the enhanced performance of the composite.[131a]

3.4. NCC Self-Ordering Properties

Although most studies on cellulose nanocrystals have centered on their potential application in reinforcing composites, perhaps their most interesting property centers on the observation that suspensions of nanocrystalline cellulose self-order to give a liquid-crystalline chiral nematic phase.[20] Chiral nematic (cholesteric) phases have long been known for concentrated solutions of cellulose derivatives,[149] but the discovery that the rodlike cellulose nanocrystals showed a chiral (helicoidal) ordering at concentrations of a few weight percent in water was unexpected. Furthermore, although the molecularly dispersed cellulose derivatives showed both right- and left-handed chiral nematic phases, depending on their substitution pattern, the solvent, and the temperature,[150] only left-handed helicoidal structures have been reported for cellulose nanocrystal suspensions.

The liquid-crystalline properties of cellulose nanocrystals are most readily observed for low-ionic-strength suspensions of the relatively short nanocrystals isolated by acid hydrolysis. Suspensions of longer nanocrystals tend to gel before attaining the equilibrium liquid-crystalline structure. The axial ratio of the nanocrystals is the key variable in the determination of the critical concentration for phase separation, but factors such as the ionic strength,[2e] the nature of the counterion,[108] the reaction conditions, and the added polymer are also important.[2c,151] A distinct glassy phase is also observed under appropriate conditions with respect to the surface charge and axial ratio.[21b] The cooperative nature of the liquid-crystalline phase enhances the response to applied fields. For example, cellulose-nanocrystal suspensions are readily oriented by applied magnetic fields;[21a,152] this behavior suggests potential applications in NMR spectroscopy.[8]

The essential features of the chiral nematic arrangement are maintained when water is allowed to evaporate from the suspensions. The decrease in chiral nematic pitch that accompanies increasing nanocrystal concentration and increasing ionic strength results in iridescent films that reflect circularly polarized light in the visible range.[24b] In contrast to the composite films mentioned above, these films are essentially pure cellulose, but with a small quantity of sulfate ester groups on the surface of the nanocrystals. The films are thus redispersible in water. Mild heating causes partial desulfation and renders the films stable in water. The films are useful as smooth model films of cellulose I, the crystalline form of cellulose found in nature.[18b] Dyes may be incorporated into the films. The chiral film structure orients the dye molecules, which results in induced circular dichroism.[153] Proposed applications of the films include their use as optical taggants for security papers.[24b]

Films containing cellulose nanocrystals can also be prepared by polyelectrolyte multilayering (see also the PEM of MFC, Section 2), whereby the interaction between the anionically charged nanocrystals and cationic polyelectrolytes is exploited.[89a,b] These films are also iridescent, but as a result of normal thin-film interference rather than chiral reflection.[89b] PEM films formed with the longer fibers of MFC also display interference colors (see Figure 16, Section 2.4.4).

4. Biofabrication of Bacterial Nanocellulose (BNC): Potential and Perspectives

4.1. White Biotechnology of Cellulose

Acetic acid bacteria of the genus *Gluconacetobacter* have the ability to form not only acids but also, and in high yield, the natural polymer cellulose—an ability normally associated with plants. The *Acetobacteraceae* are Gram-negative, aerobic, rodlike microorganisms of unusual acid tolerance (growing well below pH 5.0), active motility, and high ubiquity. They are found wherever the fermentation of sugars and plant carbohydrates takes place, for example, on damaged fruits, on flowers, and in unpasteurized or unsterilized juice, beer, and wine. Pure *Gluconacetobacter* strains can be bought from international collections of microorganisms.

Surprisingly, *Gluconacetobacter xylinus* cultures form biofilms composed of pure cellulose on most nontoxic surfaces. In larger volumes of aqueous media, the bacteria synthesize the polymer at the interface between liquid and air.[5a,160] The type of *Gluconacetobacter* strain, the material of the support and its surface structure, the components of the culture medium (including additives), and the temperature determine the effectiveness of cellulose production; most importantly, a continuous supply of oxygen (air) and a carbon source (such as D-glucose) is required. It is an exciting benefit of fermentative cellulose fabrication that the shape of the cellulose bodies formed and their supramolecular network structure, which determines the properties, can be designed by changing these parameters. As is well-known in the context of other bacterial biofilms, the cellulose-forming bacteria use the produced cellulose fleece as a designed architecture for living in different environments and protection against drying out, enemies, irradiation, and lack of oxygen and food.[5f,161]

The bacterial cellulose biosynthesis from low-molecular-weight sugars or other carbon sources via uridine diphosphate glucose has been elucidated in detail.[5e,161d,162] The formed cellulose chains were excreted into the aqueous culture medium as fibers with diameters in the nanometer range (Figure 18, black arrows).[2a,161b,c,162e] The cellulose fibrils released by the bacteria combined to form ribbons (Figure 18) and finally a 3D nanofiber network (Figure 19).[162e] The electron microscope images in Figure 19 also show the dramatic difference in the fiber diameters of common plant cellulose and bacterial cellulose.

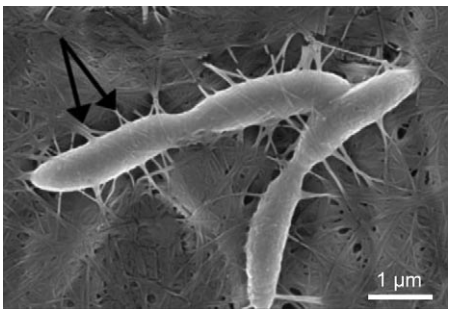

Figure 18. *Gluconacetobacter* bacteria forming cellulose nanofibers and ribbons.[163]

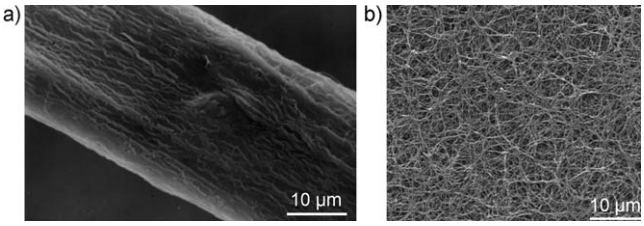

Figure 19. Electron micrographs of fibers of a) common pulp from plant cellulose[164] and b) bacterial cellulose.

BNC formed as described has the same molecular formula as plant cellulose but is fundamentally different because of its nanofiber architecture.[5a,c] After simple purification, BNC contains no impurities and no functional groups other than hydroxy groups.[5a] Owing to its nanoscale fiber structure, the properties of BNC are quite different from those of common plant celluloses.[5d–f,162b,e] Therefore, BNC opens up novel fields of application for cellulose materials.

BNC is formed in yields up to 40% (in relation to the D-glucose substrate): a high efficiency for a biotechnological process.[5d] Because of the important features of BNC, the biofabrication of cellulose materials in the sense of white biotechnology is a challenge for the future. Moreover, the practical use of a bacterial biofilm is one aim of intensive efforts in that field.

For commercial application, cost-efficient processes for the mass production of BNC are required. During the last few years, a broad range of new concepts were investigated. Often, they were based on a combination of static and agitated cultivation. Typical examples of procedures for agitated cultivation have been reported since 1997.[165]

Further approaches included the continuous harvesting of cellulosic filaments, pulps, and fibers.[166] Other examples are the linear conveyor reactor and the rotary disk reactor, developed by Bungay and Serafica.[167] These approaches lead to rather nonuniform BNC material owing to the bundling and aggregation of thin layers or filaments. Frankenfeld et al. developed a process for the production of specifically molded shapes or layers.[168] Levy et al. and Farah et al. suggested the production of sheets and membranes of BNC.[169] The sheets are collected from the surface of the culture medium and are then submitted to processes of purification. When these types of reactors are used, the homogeneity of the material can be retained, but the widths and lengths of the cultured sheets are still restricted by the dimensions of the culture vessel.

By manufacturing with a novel horizontal lift reactor (HoLiR), an efficient process could be developed for the (semi-)continuous cultivation of planar BNC fleeces and films of freely selectable length and adjustable height. Comprehensive investigations demonstrated the comparability of the BNC harvested with that gained from static cultivation under batch conditions.[170]

The main remarkable features of BNC that set it apart from common plant celluloses and other polymers are:

- the synthesis of these cellulose materials from simple low-molecular-weight substrates under laboratory and pilot-plant conditions,
- the introduction of unique product features by combining important properties of cellulose with exciting features of nanoscale materials, and
- the direct control of the cellulose synthesis, including shape, structure, and composite formation of the products, during biosynthesis (in situ).

The field of BNC has been the focus of an ever-increasing number of original-research articles, reviews, and meeting lectures, particularly in the last three years. Reviews have mainly dealt with BNC biofabrication,[171] the status and prospects of the new nanobiomaterial,[172] nano/microfiber development,[173] adhesion and surface characteristics of cellulose nanofibers that have an impact on their properties and application in nanomaterials,[174] the physicochemical properties of BNC,[175] and the potential of BNC for medical[176] and technical applications,[177] as well as uses in cosmetics and veterinary medicine.[129]

4.2. Unique Material Properties of BNC

The nanometer dimension of the BNC fibers causes a large fiber surface and for this reason strong interactions with the surroundings like water, other low-molecular-weight and polymer compounds with functional groups active in hydrogen-bond formation (such as carbohydrates, polysaccharides, and proteins), and different types of nanoparticles, including particles of various metals. The nanofibers of BNC are immobilized in a stable network: an important aspect with respect to the ongoing discussion on the health risk of distributed and mobile nanoparticles.

During the biosynthesis of BNC, well-defined cellulose network structures are formed. Large amounts of water—in some cases more than 99%—are incorporated, and form-stable hydrogels are produced. This direct formation of cellulose bodies is quite different from plant-cellulose processing. Such bodies are of high transparency and form pore systems, in most cases with pore diameters below 10 μm. The incorporated water plays an important role as a spacer element and—as a hydrogen-bond-forming partner of cellulose—as a stabilizing agent with respect to the network and pore structure. The original structure can be destroyed by drying but can also be modified in a controlled manner (see Section 4.4).

Moreover, BNC is characterized by a high DP in the range of 4000–10000 anhydroglucose units, a high crystallinity of 80–90%, and high stability of the single cellulose fibers similar to that of steel or Kevlar.[5b,162a,c,d,178] After isolation of the never-dried BNC, bacteria and residues from the culture medium can be removed, for example, by heating in 0.1M aqueous sodium hydroxide under reflux for 10–120 min, depending on the thickness of the cellulose body. Under these conditions, no detectable damage to the polymer occurs.

4.3. In Situ Modification of BNC

A particular benefit of BNC is the already highlighted in situ control of cellulose formation. The shape and supramolecular structure of the cellulose and the generation of composites can be regulated directly during biosynthesis, mainly according to the *Gluconacetobacter* strain used, the composition and shape of the reactor, and the constituents of the culture medium (including additives). A temperature in the range of 25–29 °C is generally used to meet the needs of these bacteria.

Of course, the large number of control elements also provides problems in terms of the reproducibility of the method and comparability of the products. However, reliable control of these specific factors enables access to novel materials for applications in medicine, the life sciences, and technology.

4.3.1. Shaping

The shape of the BNC hydrogels can be designed effectively by choosing the appropriate reactor form and function (static or agitated cultivation). In this manner, fleeces of several centimeters height, films/patches, spheres, and bodies, including hollow bodies, such as tubes, could be produced (Figure 20). Moreover, the surface at the region of BNC deposition can distinctly influence cellulose formation. The use of nematically ordered liquid-crystalline cellulose patterns as templates led to the deposit of BNC along tracks defined by the template.[179] Honeycomb-shaped BNC types could be produced on a template formed as a corresponding structural negative with peaks and troughs.[180]

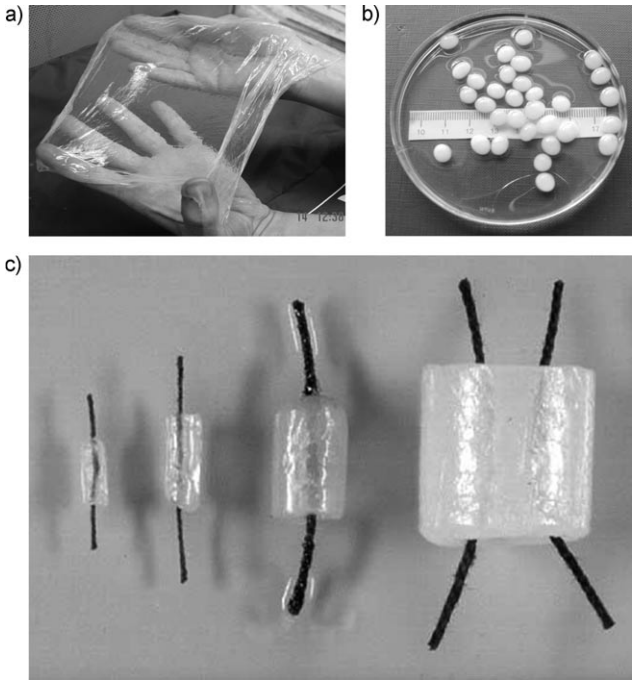

Figure 20. BNC hydrogels formed in situ. a) Film prepared in a PP container under static conditions; dimensions: 25 × 25 cm^2, thickness: 200 μm.[181] b) Spheres formed by agitated cultivation with a shaking rate of 80–100 rpm; diameter: 2–3 mm, smooth surface.[181] c) Tubes created by a matrix technology as blood-vessel implants; inner diameter: 0.6–6 mm.[182]

4.3.2. Structure Control

The first point of consideration for the selective construction of the fiber-network structure of BNC materials is the selection of the bacterial culture. Figure 21 shows pictures of BNC fleeces formed by different *Gluconacetobacter* strains and their network structure. The differences in the stability of the hydrogels and in the network architecture are evident.

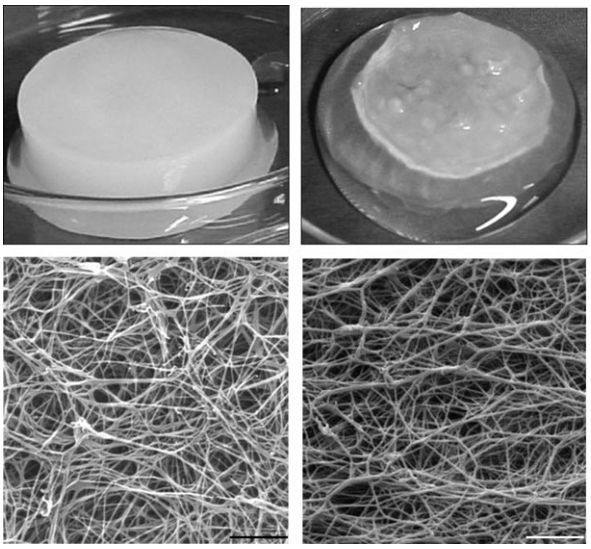

Figure 21. Fleeces of bacterial nanocellulose produced by two different *Gluconacetobacter* strains (left: DSM 14666; right: ATCC 23769; DSM = Deutsche Sammlung für Mikroorganismen und Zellkulturen, Braunschweig, Germany; ATCC = American Type Culture Collection, Manassas, VA, USA) and the corresponding electron micrographs (scale bars: 2 μm).

Water-soluble additives in the culture medium have a remarkable influence on the network structure. Low-molecular-weight compounds, such as glycerol and β-cyclodextrin, as well as PEG 400, can modify the network organization and be extracted from the BNC during the purification step. Thus, these additives act as structure-forming auxiliaries. Some polysaccharides, such as CMC and types of cationic starch, modify the supramolecular structure and remain partially incorporated in the O–H hydrogen-bond system within the BNC architecture.[183]

Oriented BNC fibril structures controlled by the viscoelasticity of the culture interface (e.g., silicone oil) were prepared recently by Gong and co-workers.[184] An increase in the viscosity of the oil interface caused an increase in the degree of orientation, fibril width, swelling degree, and tensile modulus.

4.3.3. Composite Formation

The preparation of BNC composites leads to a great variety of products. Composites can be formed by in situ modification of BNC, that is, by the addition of the composite

partners to the culture medium, or by postprocessing of BNC synthesized conventionally. Typical composite partners are organic compounds, such as bioactive agents and polymerizable monomers, polymers, such as polyacrylates, resins, polysaccharides, and proteins, as well as inorganic substances, such as metals and metal oxides.[156a,162d,164,178a,185]

Characteristic examples of the in situ modification and postprocessing of BNC with metal oxides and metals are the ready formation of BNC composites with silica, titania, and silver nanoparticles. The addition of nanosilica to the culture medium led to BNC–nanosilica composites.[186] The treatment of BNC fleeces with titanium tetraisopropoxide ($Ti(OiPr)_4$), followed by its hydrolysis, resulted in titania-coated BNC fibers. Upon removal of the BNC by heating up to 500 °C, TiO_2 nanotubes were obtained. In this case, the BNC nanofibers acted as a support for titania and as a precursor.[185f] The activity of the BNC nanofibers as nanotemplates for the formation and fixation of different types of nanoparticles is of fundamental significance.

The treatment of BNC fleeces with aqueous silver nitrate and subsequent reduction with $NaBH_4$ dissolved in water resulted in the precipitation of silver as nanoparticles on the BNC fibers. The freeze-dried silver-nanoparticle-impregnated bacterial cellulose exhibited strong antimicrobial activity against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive).[187] The templated synthesis of silver nanoparticles with BNC fibers oxidized by TEMPO was described as an example of the use of chemically modified BNC as a nanosupport.[188]

Blends/grafts showing a controlled increase in strength and a remarkable WRV are formed by inserting acrylate monomers and cross-linkers into never-dried BNC bodies by solvent exchange and subsequent photopolymerization. The shape of the BNC bodies remains unchanged during this postprocessing. Such products are of interest as biomaterials, for example, if they have cartilage-like properties.[156a] "All-cellulose" nanocomposites were produced by the surface-selective dissolution of BNC.[189]

The preparation, characterization, and application of BNC composites (as well as composites of MFC and NCC) with a variety of plastic materials were reviewed recently[127c] in a summary report describing the considerable progress that has been made in the effective liberation/formation of the cellulosic nanofibrillar structures, ways to improve the compatibility of the celluloses with a variety of synthetic polymers as composite partners, and the resulting innovation potential for the use of cellulosic nanocomponents in a wide range of high-tech applications.

4.3.4. BNC Coating

The depositing of BNC onto natural fibers to create hierarchical fiber-reinforced nanocomposites has also been described. The coating of sisal fibers with BNC during fermentation (Figure 22) leads to better adhesion properties without affecting the strength and biodegradability of the composite materials and enables the extended application of natural fibers in renewable composites.[190,191] The production of 3D functionalized cellulose materials through the use of template surfaces has already been mentioned in Section 4.3.1.

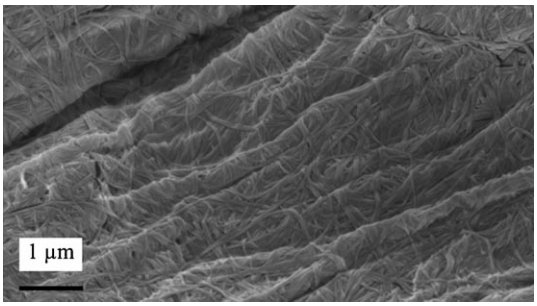

Figure 22. BNC coating of sisal fibers during fermentation.[191]

4.4. BNC Postprocessing (Drying)

As described in Section 4.3.3, postprocessing steps are important options for the development of novel types of BNC composites. Further possibilities are the incorporation of bioactive agents for controlled-release technologies and the partial or complete removal of product-specific water from shaped BNC hydrogels. The water is part of different types of hydrogen bonds between the BNC crystallites.[5b,192] For medical applications in soft-tissue repair, for example, as wound dressings, patches on variable lesions, and blood-vessel substitutes, the high-water-content hydrogel biomaterial is a good choice. However, from the viewpoint of material storage and supply, and for broader application in the fields of the life sciences and technology, partial or complete dewatering can be important. In principle, the water can be removed from BNC by storage of the fleeces in air (intense wrinkling occurs as a result of strong shrinkage), the use of water-absorbing materials under pressure and if necessary with additional heating (complete water removal leads to planar layers/films, the thickness of which is about 1 % of the original thickness, hornification), stepwise solvent exchange (e.g., in the order ethanol, acetone, hexane), drying over the gas phase (critical-point drying), and the sublimation of frozen water (freeze drying).

To prevent an irreversible collapse of the natural supramolecular structure as result of dewatering, the two last-mentioned gentle methods have to be used. With effective procedures, largely reswellable aerogels with the dimensions of the starting fleeces can be obtained. Both methods are also of importance in the preparation of BNC samples for electron microscopy. Thin and flat BNC layers formed by partial or complete dewatering are mechanically stable materials with a more or less compressed nanofiber network structure and reduced water uptake. They are of interest for wound dressings and implants and of growing importance for technical applications as membranes, barrier layers, and films.

4.5. Cellulose Hydrogels Designed for Medical Applications

Hydrogels were the first biomaterials to be rationally designed for use in humans. They have moved forward to now

mimic basic living processes and are of growing importance as bioactive implants in the sense of "in vivo" scaffolds. Biodesigned BNC hydrogel materials are exponents of this process. Because of their hydrogel nature, the certification of these biomaterials according to common methods and standards for approval is limited. Specific characterization methods are now being developed by ASTM International, Subcommittee F04.42 and published as a "Guide for Characterization of Hydrogels Used in Regenerative Medicine" (ASTM WK 21927).

Because of the specific structure and properties of BNC (its especially stable nanofiber network, high water content, shapability during biosynthesis, and biocompatibility), this biofabricated polymer type opens up the important and strongly expanding fields of personal care, medicine, and life sciences for the polysaccharide cellulose.[5b]

The nanostructured network and morphological similarities with collagen make BNC very attractive for cell immobilization, cell migration, and the production of extracellular matrices. In vitro and in vivo evaluation showed that the BNC implants did not elicit any foreign-body reaction. Fibrosis, capsule formation, or giant cells were not detected around the implants, and connective tissue was very nicely integrated with the BNC structures.[193]

Although BNC had been shown not to be cytotoxic or genotoxic, the properties of isolated BNC nanofibers on cells and tissues had never been analyzed. In a recent study, nanofibers were produced from bacterial cellulose by a combination of acid and ultrasonic treatment. The tests demonstrated that isolated BNC nanofibers are also not genotoxic. This result is of importance, because such isolated BNC fibers could be formed under strong shear stress.[194] Intensive efforts are now being made world-wide in the research, development, and application of never-dried and partially dewatered BNC materials in medicine. The main fields are wound care and novel types of bioactive implants. In the case of wound dressings, the first products are on the market.[195] The development of medical implants ranges from the design of materials for bone and cartilage repair to the development of tubular prototypes as grafts for vascular surgery. In all cases, BNC is active as a 3D template for in vitro and in vivo tissue growth.[5b,6,162d,196]

Regarding wound care, the potential of BNC to be operative in the healing of chronic wounds by reducing proteolytic enzymes, cytokines, and reactive oxygen species is of growing interest. BNC–collagen composites formed in situ reduce selected proteases and interleukins and show distinct antioxidant capacity.[197] Silver chloride containing BNC films were produced as antibacterial dressings from the never-dried material by postprocessing immersion steps. The products contained silver chloride nanoparticles on the BNC fiber in quantities up to 21 % w/w.[198]

Silver nanoparticles were prepared in situ by the hydrolytic decomposition of silver–triethanolamine complexes. SEM images and X-ray diffraction patterns both showed that the spherical metallic silver particles with a mean diameter of 8 nm were well-adsorbed on the BNC fibrils.[199]

Generally, the recent development of BNC implants has been characterized by a broad patenting of BNC materials. However, these patent claims are frequently based on insufficient background investigations to determine the manufacture-dependent structure of the material and its function and stability in the body. The same is true for BNC scaffolds for tissue engineering. In particular, the ingrowth of living cells requires further investigation and a deeper understanding. In this context, the fabrication of BNC scaffolds and implants with a porosity and pore size relevant to the particular application is of importance. Examples of approaches that have been used to create pores of different sizes are the use of porogenes, the use of different cultivation times and inoculation volumes, and posttreatment with different alkaline solutions and by freeze drying.[200] Moreover, results on the behavior of freezable water in BNC and thermoporosity investigations have been reported.[201] In the case of the formation of pores by porogenes and leaching of the porogenes, additional information on the purity and integrity of the implants and their essential structure is desirable. Further insight is required with respect to the pore parameters in the never-dried state and after different drying methods.

As cardiovascular diseases are together the number one illness world-wide, the development of blood-vessel implants with an inner diameter of 6 mm and lower stands at the center of activities in terms of the fabrication of BNC scaffolds and implants. Every year in the USA, 250000 patients have heart by-pass surgery. In Germany, there are 73000 by-pass operations per year. Because of the lack of thin artificial substitutes for this purpose until now, vessels are usually drawn from the legs or thorax of patients in an operation in advance.

Several research groups have developed prototypes of BNC tubes in the required diameter range and with a length of 5–25 cm or more. The material properties depend on the preparation conditions. The wall of the tubes is formed by the typical transparent BNC hydrogel and is also characterized by a stable inner lumen, good stability of sutures, essential mechanical strength, and the important feature of being permeable to water, other liquids, ions, and small molecules. Moreover, the tubes show very good surgical handling and can be sterilized in standard ways.[5d] A typical example is shown in Figure 23.

In animal experiments with rats and later pigs and sheep (implantation in the carotid artery, Figure 24), good biocompatibility and incorporation into the body were demonstrated. Inspections after 1 week, 1 month, and 1 year (for rats) showed that these tubular implants were integrated by endothelization of the inner surface (directed toward the bloodstream), colonized on the outside by connecting tissue, and characterized by the ingrowth of vital collagen-forming fibroblasts.[5b,d,202] Confocal laser scanning microscopy showed that the inner surface of the BNC tubes was smooth and not structured from its preparation (Figure 25). It is assumed that the low surface roughness causes good endothelization and a low risk of thrombosis and aneurysms.[203]

Commonly used artificial vascular grafts formed from synthetic polymers, such as poly(tetrafluoroethylene) or polyesters, are prone to thrombosis when used as small-diameter vessels, which are essential for heart by-passes. A

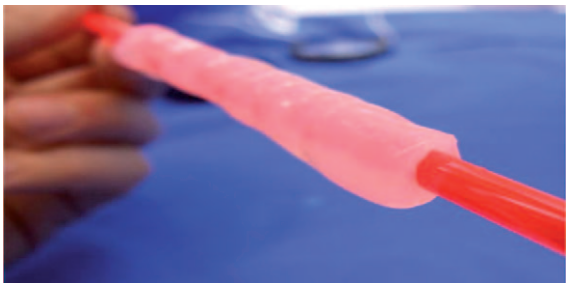

Figure 23. Tube of bacterial nanocellulose designed by a matrix technology and presented on a red glass rod, which symbolizes the blood flow when the tube is used as a blood-vessel substitute; inner diameter: 6 mm, length: 15 cm.[182]

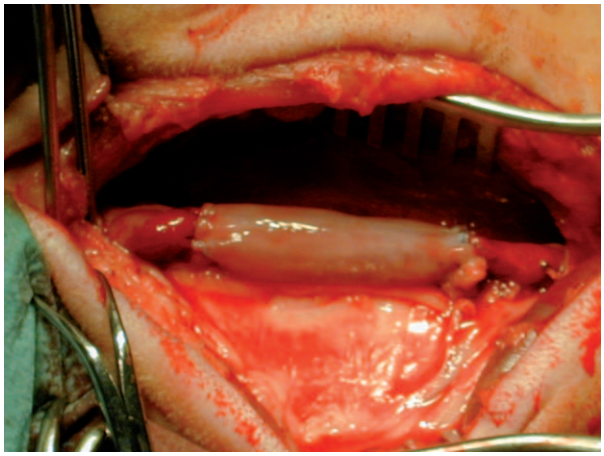

Figure 24. BNC tube used as a long-segment vascular graft (5 cm) for the right carotid artery of a sheep (courtesy: Priv.-Doz. Dr. J. Wippermann, Department of Cardiothoracic Surgery, University Hospital Cologne, Germany).

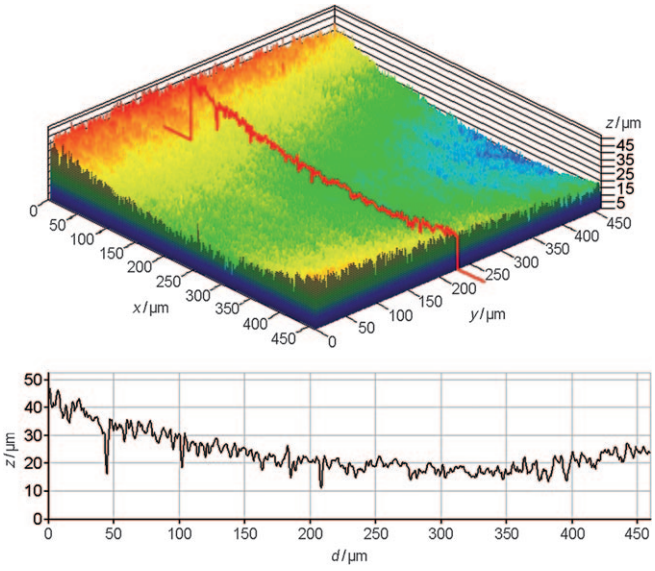

Figure 25. Surface parameters of a tubular bacterial nanocellulose implant as determined by confocal laser scanning microscopy (Ar laser, 400 nm).

study in which BNC tubes were compared with synthetic grafts over a period of 2 weeks also demonstrated the good biocompatibility of BNC and its incorporation in the body. When the efficacy and safety of stents (endoluminal vascular prostheses) covered with BNC were evaluated in a rabbit iliac-artery model, evidence was found that the implantation was safe and there was no acute or late vessel occlusion caused by stent thrombosis.[204]

BNC hydrogels with a uniaxially oriented fibril structure and excellent mechanical properties could be prepared by the cultivation of *Gluconacetobacter xylinus* strains on ridged oxygen-permeable silicon substrates. Cultivation inside silicone tubes led to BNC tubes with the uniaxially oriented fibrils along the longitudinal axis of the silicon template.[205]

A limitation to the use of BNC for tissue substitution can be its inability to degrade in vivo. It could be shown that limited periodate oxidation of BNC leads to a modified BNC (containing 2,3-dialdehyde cellulose structural units) that can break down at physiological pH values. The BNC retains its hydrogel structure, crystallinity, and, for example, the ability to form biomimetically calcium-deficient hydroxyapatite nanocrystallites within the oxidized matrix.[206] The resorbable BNC hydrogel has a great capacity for tissue repair.[207]

4.6. Potential of BNC for Technical Applications

The in situ deposition of platinum nanoparticles on BNC fleeces leads to membranes suitable for fuel cells. TEM images and XRD patterns both showed spherical metallic Pt particles with mean diameters of 3–4 nm well-impregnated in the BNC fibrils. The membranes have high electrocatalytic activity for the hydrogen-oxidation reaction.[208]

When BNC fleeces were submerged in a dispersion of multiwalled carbon nanotubes (MWCNTs) for several hours, individual MWCNTs adhered strongly to the surface and inside of the BNC fleeces. Conductivity measurements demonstrated that the incorporation of carbon nanotubes is a suitable way to prepare electrically conductive BNC membranes.[209]

Transparent and electrically conducting films were also fabricated by the adsorption of single-walled carbon nanotubes on bacterial cellulose membranes embedded in a transparent polymer resin. In this way, films with a wide range of transmittance and surface-resistance properties could be obtained by controlling the immersion time and carbon-nanotube concentration. A transparent conducting film with a transmittance and surface resistance of 77.1 % at 550 nm and 2.8 $k\Omega\,sq^{-1}$, respectively, was fabricated from a 0.01 wt % carbon-nanotube dispersion during an immersion time of 3 h. The transparent conducting films were quite flexible and maintained their properties even after crumpling.[210]

BNC layers have also been investigated as loudspeaker vibration films. It was demonstrated that these films have the advantages of simple manufacturing by bacterial biofabrication, good mechanical properties and thermal stability, good fundamental characteristics of a sound-vibration film, high specific elasticity and loss factor, long service life, and environmental friendliness.[211]

By a phase-inversion method with BNC as the polymer and lithium chloride/dimethylacetamide as the solvent, BNC membranes were also prepared from solution with BNC regeneration. The mechanical properties of the membrane improved as the bacterial-cellulose concentration was increased, the coagulation-bath temperature was decreased, and the coagulation-bath concentration was increased.[212]

5. Summary and Outlook

Over the last decade, and particularly in the last five years, a growing number of research groups worldwide have reported the formation and utilization of celluloses with widths of the fibrils or crystals in the nanometer range. It has been shown that the cellulose microfibrils present in wood can be liberated by high-pressure homogenizer procedures. The product, microfibrillated cellulose (MFC), exhibits gel-like characteristics. A second type of nanocellulose, nanocrystalline cellulose (NCC), is generated by the removal of amorphous sections of partially crystalline cellulose by acid hydrolysis. NCC suspensions have liquid-crystalline properties. In contrast to MFC and NCC, which are prepared from already biosynthesized cellulose sources, a third nanocellulose variant, bacterial nanocellulose (BNC), is prepared from low-molecular-weight resources, such as sugars, by using acetic acid bacteria of the genus *Gluconacetobacter*. The in situ biofabrication of BNC opens up unique possibilities for the control of shape, the structure of the nanofiber network, and composite formation. Thus, this form of cellulose can be designed to have useful properties.

The rapidly advancing state of knowledge of all three categories of the nanocellulose family motivated this overview of the preparation, structural analysis, important specific properties, and innovative functionalities of these novel types of cellulose. It is our intention to broaden knowledge in this subject area and to stimulate the development of practical uses of nanocelluloses. Science and technology continue to move towards the use of renewable raw materials and more environmentally friendly and sustainable resources and processes. The development of nanocelluloses is an important component of this vital movement. Their potential application areas vary from additives in food, reinforcing agents in nanocomposites and paper, biodegradable films and barriers for packaging, texturing agents in cosmetics, and stabilizing components in dispersions across technical films and membranes, to medical devices, such as wound dressings and novel types of bioartificial and bioactive implants, including cardiovascular grafts.

The high-end applications of MFC are fairly straightforward, but any nanoscale material used in these branches will be subject to careful scrutiny with respect to its interactions with living tissue. Low-end, large-scale applications are evident; however, the upscaling of manufacturing may be an issue for consideration. When it comes to films and composite materials, the situation will be more complex, as a number of issues have to be solved, such as the hornification of MFC during drying, the mixing of materials, and finally the drying (energy requirements) of coatings/films with a low solid content.

In the field of NCC, the potential backed by research and development is very high. For industrial use, scaled-up production and the standardization of NCC types (dimensions and surface properties) are necessary.

In the case of BNC, the comparability of the described bacterially produced celluloses has to be established. Different bacterial strains, culture and workup procedures, and post-processing steps lead to quite different materials. Therefore, these parameters have to be included as part of standardized procedures. In particular, it is essential that bacterial strains be classified in a competent microorganism collection. Many patent claims have been filed for BNC products with potential medical uses. However, in most cases, prototypes were not presented, and the corresponding proofs of concept are missing. In view of technical applications of BNC, the high water content of the fleeces and of fibers and fiber aggregates should be kept in mind, for example, for composite formation and papermaking. Moreover, the large-scale industrial production of BNC is still in a state of development.

Nevertheless, all signs seem to indicate that the impressive rate of development in the field of nanocelluloses will increase further. The establishment of research and development groups, new pilot processes, and production plants, and the developmental effort on larger-scale technical products and medical devices are distinct evidence of this trend.

Abbreviations

ASTM	American Society for Testing and Materials
BNC	bacterial nanocellulose
CAB	cellulose acetate butyrate
CMC	carboxymethylcellulose
DP	degree of polymerization
DS	degree of substitution
DMA	dynamic mechanical analysis
G'	storage modulus
G''	loss modulus
HPC	hydroxypropyl cellulose
$meq\,g^{-1}$	milliequivalents per gram
MFC	microfibrillated cellulose
NCC	nanocrystalline cellulose
PAH	poly(allylamine hydrochloride)
PBA	poly(styrene-*co*-*n*-butyl acrylate)
PCL	polycaprolactone
PEG	poly(ethylene glycol)
PEI	poly(ethylenimine)
PEM	polyelectrolyte multilayer
PHA	poly(hydroxyalkanoate)
PLA	polylactide
polyDADMAC	poly(diallyldimethylammonium chloride)
PP	polypropylene
PU	polyurethane
PVC	poly(vinyl chloride)
PVOH	poly(vinyl alcohol)
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
WRV	water-retention value

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