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Chapter 7

Nanocellulose-Based Composites

Kelley Spence, Youssef Habibi, and Alain Dufresne

Abstract When subjected to acid hydrolysis or mechanical shearing, lignocellulosic fibers yield defect-free, rod-like, or elongated fibrillar nanoparticles. These nanoparticles have particularly received great attention as reinforcing fillers in nanocomposite materials due to their low cost, availability, renewability, light weight, nanoscale dimension, and unique morphology. Preparation, morphological features, and physical properties of nanocelluloses are discussed in this chapter. Their incorporation in nanocomposite materials including processing methods and ensuing properties such as microstructure, thermal properties, mechanical performances, swelling behavior, and barrier properties are also presented.

Keywords Cellulose-based composites · Composite properties · Microfibrillated cellulose · Nanofibrillated cellulose · Production methods

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7.1 Introduction

Over the last two decades, a significant amount of research has been dedicated to the use of lignocellulosic fibers as reinforcing elements in polymeric matrices, and for the potential of replacing conventional fibers, such as glass, by natural fibers in reinforced composites. However, one of the main drawbacks of lignocellulosic fibers is the significant variation of properties inherent to any natural product. Indeed, fiber properties are related to climatic conditions, maturity, and soil type. Disturbances during plant growth also affect the plant structure and are responsible for the enormous variation of mechanical plant fiber properties.

One of the basic ideas to further improve fiber and composite properties is to eliminate the macroscopic flaws by disintegrating the naturally grown fibers, and separating the almost defect-free, highly crystalline fibrils; this can be achieved by exploiting the hierarchical structure of the natural fibers. Aqueous suspensions of cellulose nanoparticles can be prepared by a mechanical treatment or acid hydrolysis of cellulosic biomass. The objective of the latter treatment is to dissolve regions of low lateral order, so that the water-insoluble, highly crystalline residue may be converted into a stable suspension by subsequent vigorous mechanical shearing action. The resulting nanocrystals occur as rod-like particles, known as whiskers, in which the dimensions depend on the nature of the substrate, but range in the nanometer scale. Because these whiskers contain only a small number of defects, their axial Young's modulus is close to the value derived from theoretical chemistry, potentially making them stronger than steel and similar to Kevlar. These highly stiff nanoparticles are, therefore, suitable for the processing of green nanocomposite materials.

Cellulosic nanoparticles, generally known as nanocellulose, have garnered interest from the scientific community because of their biodegradability, strength, and other characteristics. Sustainability and green issues continue as top priorities for many businesses and individuals, stimulating the search for nonpetroleum-based structural materials like bionanocomposites that are biodegradable, high performing, and lightweight.

7.2 Hierarchical Structure of Cellulose Fibers

Cellulose, discovered and isolated by Payen (1838), is considered to be the most abundant polymer on Earth. It is certainly one of the most important structural elements in plants, serving to maintain cell structure. Cellulose is also important to other living species such as bacteria, fungi, algae, amoebas, and even animals. It is a ubiquitous structural polymer that confers its mechanical properties to higher plant cells.

Cellulose is a high-molecular weight homopolysaccharide composed of β -1,4-anhydro-D-glucopyranose units. These units do not lie exactly in plane with the structure, rather they assume a chair conformation with successive glucose residues rotated through an angle of 180° about the molecular axis and hydroxyl groups in an equatorial position. This repeated segment is frequently taken to be the cellobiose dimer (Klemm et al. 2005).

In nature, cellulose chains have a degree of polymerization (DP) of approximately 10,000 glucopyranose units in wood cellulose and 15,000 in native cotton cellulose (Sjöström 1981). One of the most specific characteristics of cellulose is that each of its monomer bears three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing crystalline packing and in governing important physical properties of these highly cohesive materials.

In plant cell walls, cellulose fiber biosynthesis results from the combined action of biopolymerization spinning and crystallization. These events are orchestrated by specific enzymatic terminal complexes (TCs) that act as biological spinnerets resulting in the linear association of cellulose chains to form cellulose microfibrils. Depending on the origin, the microfibril diameters range from approximately 2 to 20 nm with lengths that can reach several tens of microns. The cellulose obtained from nature is referred to as cellulose I, or native cellulose. In this type of cellulose, the chains within the unit cell are in a parallel conformation (Woodcock and Sarko 1980), making it an unstable form. Special treatments of native cellulose result in other forms of cellulose, namely cellulose II, III, and IV (Marchessault and Sundararajan 1983). This conversion also allows for the possibility of conversion from one form to another (O'Sullivan 1997).

The cellulose microfibril constitutes the basic structural unit of the plant cell wall; each microfibril can be considered as a string of cellulose crystallites, linked along the chain axis by amorphous domains (Fig. 7.1). Their structure consists of a predominantly crystalline cellulosic core which is covered with a sheath of paracrystalline polyglucosan material surrounded by hemicelluloses (Whistler and Richards 1970). These microfibrils are conjoined by other polymers like lignin and hemicelluloses and aggregate further to form lignocellulosic fibers. As they are almost defect free, the modulus of these sub-entities is close to the theoretical limit for cellulose.

The expectation placed on cellulose-based composites lies in the Young's modulus of the cellulose crystallite. This was first experimentally studied in 1962 from the crystal deformation of cellulose I using highly oriented fibers of bleached

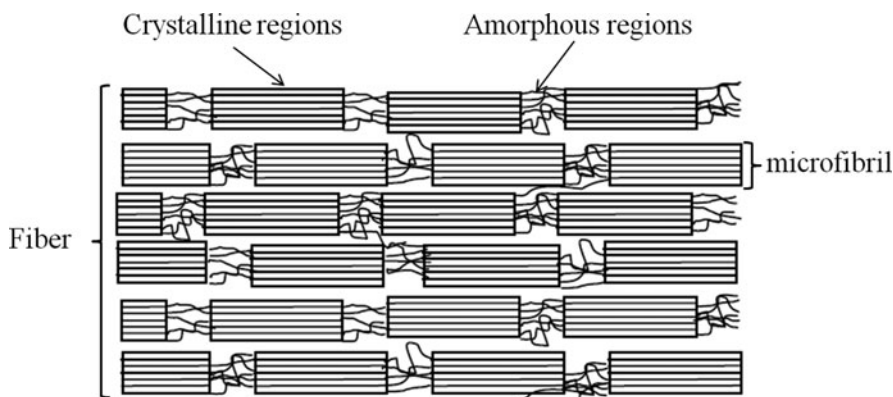


Fig. 7.1 Schematic diagram of the physical structure of a semicrystalline cellulose fiber

ramie (Sakurada et al. 1962); a value of 137 GPa was reported. This value differs from the theoretical estimate of 167.5 GPa reported by Tashiro and Kobayashi (1991). More recently, the Raman spectroscopy technique has been used to measure the elastic modulus of native cellulose crystals (Štuncová et al. 2005), with a reported value of approximately 143 GPa. The elastic modulus of a single microfibril from tunicate was measured by atomic force microscopy (AFM) using a three-point bending test (Iwamoto et al. 2009). Values of 145 and 150 GPa were reported for the single microfibrils prepared by 2,2,6,6-tetramethylpiperidinel-oxyl radical (TEMPO)-oxidation and sulfuric acid hydrolysis, respectively.

These impressive mechanical properties make nanocellulose substrates ideal candidates for reinforcing polymer-based composites. Incorporating these nanoparticles in a synthetic or natural polymeric matrix consists in mimicking nature.

7.3 Top-to-Down Fiber Processing

The major drawback of natural fibers for composite applications is the large variation in properties inherent to natural products. The properties could be impacted by climatic conditions, maturity, and soil type. Disturbances during plant growth also affect the plant structure and are responsible for the enormous variation of mechanical plant fiber properties. For instance, the number of knobby swellings and growth-induced lateral displacement present in plant fibers influence the tensile strength and elongation at break of the fibers obtained. One of the basic ideas to avoid this problem consists of decreasing the size of the natural particles from the micro to the nanoscale. Conceptually, nanoparticles refer to particles with at least one dimension less 100 nm.

When reducing the fibers into microfibrils, the hierarchical structure of natural fibers is exploited and important consequences occur. The first one is obviously an increase in the specific area of the particles, from values of approximately a few

square meter per gram to few hundred square meter per gram, resulting in an increase in the interfacial area with the polymeric matrix. There is also a decrease in the average inter-particle distance in the matrix as the particle size decreases. Thus, some particle–particle interactions can be expected. The homogeneous dispersion of nanoparticles in a continuous medium is generally difficult because the surface energy increases when decreasing the particle dimensions.

Another important feature of nanoparticles is the possibility to improve properties of the material for low filler content without detrimental effect on impact resistance and plastic deformation. A reduction of gas diffusion (a barrier effect) is also likely to occur. Moreover, cellulosic nanoparticles are distinguished by their liquid crystal behavior when suspended in water, presenting birefringence phenomena under polarized light.

Native cellulose fibers are formed by smaller and mechanically stronger entities, the cellulose fibrils. Fibrils contain both crystalline nanoparticles and noncrystalline domains; the latter being located at the surface and along the main axis. Noncrystalline domains form weak spots along the fibrils.

Different descriptors have been used in the literature to designate the crystalline rod-like nanoparticles. These particles are mainly referred to as whiskers, nanowhiskers, cellulose nanocrystals, NCC (nanocrystalline cellulose), monocrystals, microcrystals, or microcrystallites, despite their nanoscale dimensions. The terms microfibrils, microfibrillated cellulose (MFC), and nanofibrillated cellulose (NFC) are used to designate cellulosic nanoparticles obtained by a simple mechanical shearing disintegration process (Fig. 7.2) as described in the next section.

7.4 Preparation of Nanocellulose Substrates

7.4.1 *Preparation of Nanofibrillated Cellulose*

The process for isolating NFC consists of the disintegration of cellulose fibers along their long axis. They include simple mechanical methods or a combination of enzymatic or chemical pretreatments with mechanical processing. Two main technologies, e.g., Manton Gaulin Homogenizer and Microfluidizer, are commonly used for the mechanical treatment.

Homogenization, utilized most popularly in the food processing industry, particularly to homogenize milk, is estimated to consume approximately 4,000 kJ of energy per pass per kilogram of NFC (Spence et al. 2010). Materials are defibrillated utilizing rapid pressure drops and high shear and impact forces against a valve and an impact ring.

In comparison, microfluidization, utilized most commonly in the cosmetic and pharmaceutical industries, consumes approximately 200, 390, and 630 kJ/kg per pass at processing pressures of 10, 20, and 30 kpsi, respectively. Materials are defibrillated during processing using a large pressure drop and an interaction chamber that imposes shear and impact forces on the fibers.

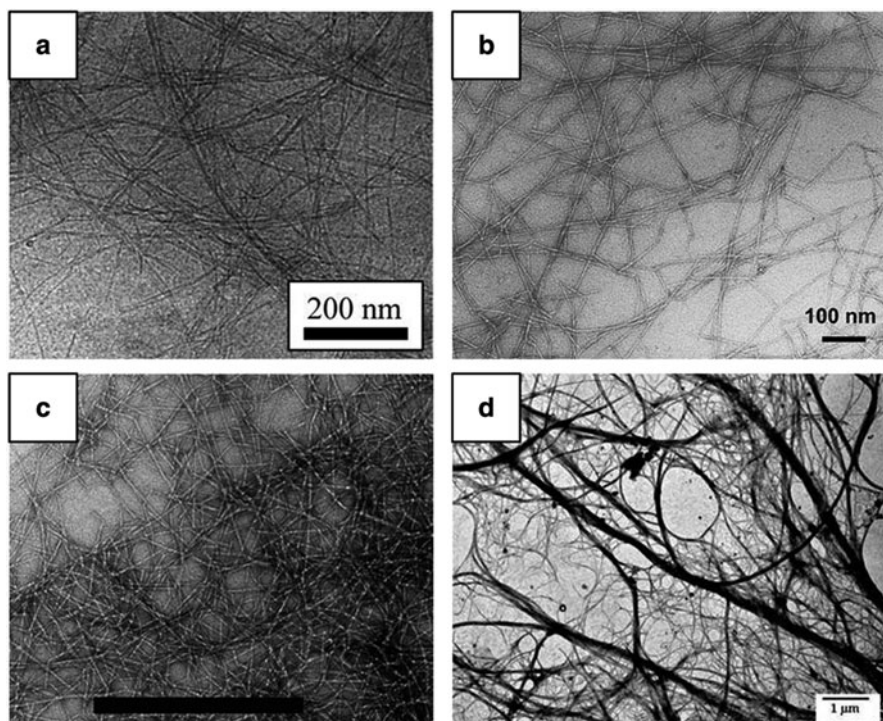


Fig. 7.2 Transmission electron micrographs from a dilute suspension of NFC obtained from wood fibers by mechanical processing combined to (a) enzymatic (Pääkkö et al. 2007), (b) TEMPO-mediated oxidation (Saito et al. 2007), (c) carboxymethylation pretreatment (Wågberg et al. 2008), (d) extracted from *Opuntia ficus-indica* (Malainine et al. 2005). (a, b, c) Reprinted with permission from copyright (2007) (2008) American Chemical Society (d) Reproduced by permission of Elsevier

The main issue with these processing methods is that the wood fibers tend to tangle during processing, causing equipment pluggage. Pretreatments are required for these methods to decrease the initial fiber length and to reduce energy consumption.

Another method, micro-grinding, is typically used in food processing. It is estimated to consume approximately 620 kJ/kg per pass to generate NFC. This method forces wood pulp through a gap between a rotary and a stator disks (Nakagaito and Yano 2004). These disks have patented bursts and grooves that contact the fibers.

NFC were first developed in by Turbak et al. (1983) using, as starting materials, purified cellulose fibers from wood pulp after high pressure mechanical homogenization. Cellulosic fibers were disintegrated into their substructural fibrils and microfibrils having lengths in the micron scale and widths ranging from ten to few hundred nanometers depending on the nature of the plant cell walls. The resulting aqueous suspensions exhibit gel-like characteristics in water with pseudoplastic and thixotropic properties even at low solid content.

The major obstacle for industrial production has been related to the very high-energy consumption involved in processing pure cellulosic fibers. Thus, chemical and/or enzymatic pretreatments were introduced in order to facilitate the fibrillation and mechanical shearing. NFC were produced by an environmentally friendly method by combining enzymatic hydrolysis and mechanical shearing of wood pulp (Henriksson et al. 2007; Lindström et al. 2007; Pääkkö et al. 2007). A cost-effective chemical pretreatment was also attempted prior to the mechanical shearing, by oxidizing cellulose fibers, using TEMPO-mediated oxidation, creating carboxyl groups on the fiber and microfibril surfaces. The TEMPO-oxidized cellulose fibers can be converted, utilizing mechanical shearing, to transparent and highly viscous dispersions in water, consisting of highly crystalline individual nanofibers (Saito et al. 2006, 2007; Fukuzumi et al. 2008). At pH 10 optimal conditions were reached, giving cellulose nanofibers with 3–4 nm in width and a few microns in length. Carboxymethylation was also successfully used to chemically pretreat cellulose fibers before the mechanical processing in order to generate NFC (Aulin et al. 2008; Wågberg et al. 2008). The processing of cellulosic materials extracted from primary cells such as parenchyma cells from sugar beet pulps (Dinand et al. 1996, 1999) or cactus cladodes (Malainine et al. 2005) and fruits (Habibi et al. 2009) were shown to be easier to mechanically process without any enzymatic or chemical pretreatment.

7.4.2 *Preparation of Cellulose Nanocrystals*

The extraction or isolation of crystalline cellulosic regions, in the form of rod-like nanocrystals, is a simple process based on acid hydrolysis that cleaves the cellulose fibers transversely.

The biomass is first subjected to purification and bleaching processes and, after the removal of noncellulosic constituents such as lignin and hemicelluloses, the bleached material is submitted to a hydrolysis treatment with acid under controlled conditions. The amorphous regions of cellulose act as structural defects and are responsible for the transverse cleavage of the cellulose fibers into short nanocrystals under acid hydrolysis. This transformation consists of the disruption of the amorphous regions surrounding the microfibrils, as well as those embedded between them while leaving the crystalline segments intact; this is ascribed to the faster hydrolysis kinetics of amorphous domains compared to crystalline ones. The hydronium ions penetrate the cellulosic material in the amorphous domains, promoting the hydrolytic cleavage of the glycosidic bonds and releasing individual crystallites. The resulting suspension is subsequently diluted with water and washed by successive centrifugations. Dialysis against distilled water is then performed to remove the free acid in the dispersion. Disintegration of aggregates and complete dispersion of the whiskers is obtained by a sonication step. These suspensions are generally more diluted because of the formation of a gel for low nanoparticle contents. The exact determination of the whisker content can be done by gravimetric methods before and after drying

suspension aliquots. The dispersions are stored in the refrigerator after filtration to remove residual aggregates. This general procedure has to be adapted depending on the nature of the substrate.

Dong et al. (1998) were among the first researchers to study the effect of hydrolysis conditions on the properties of the resulting cellulose nanocrystals. They proved that longer hydrolysis time leads to shorter monocystals and to an increase in surface charge. The acid concentration was also found to affect the morphology of whiskers prepared from sugar beet pulp as reported by Azizi Samir et al. (2004b). Beck-Candanedo et al. (2005) reported the properties of cellulose nanocrystals obtained by hydrolysis of softwood and hardwood pulp and investigated the influence of hydrolysis time and acid-to-pulp ratio. It was found that the reaction time is one of the most important parameters to consider in the acid hydrolysis of wood pulp. Moreover, it was observed that a too long reaction time will completely digest the cellulose to yield its component sugar molecules. On the contrary, lower reaction time will only yield large undispersable fibers and aggregates. It was reported that an increase in the hydrolysis time of pea hull fibers resulted in a decrease of both length and diameter, while the aspect ratio first increases and then decreases (Chen et al. 2009). The effect of the reaction conditions on cellulose nanocrystal surface charge and sulfur content was not significant and it was supposed to be controlled by factors other than hydrolysis conditions. However, chiral nematic pitch decreases when increasing the cellulose concentration and decreasing nanocrystals' length. An attempt to find optimized conditions to prepare cellulose nanocrystals from microcrystalline cellulose (MCC) derived from Norway spruce (*Picea abies*) was also reported (Bondeson et al. 2006). The processing parameters have been optimized by using a response surface methodology.

It was also shown that the hydrolysis of amorphous cellulosic chains can be performed simultaneously with the esterification of accessible hydroxyl groups to produce surface functionalized whiskers in a single step (Braun and Dorgan 2009). The reaction was carried out in an acid mixture composed of hydrochloric and an organic acid (acetic and butyric). Resulting nanocrystals are of similar dimensions compared to those obtained by hydrochloric acid hydrolysis alone. Narrower diameter polydispersity indices indicate that surface groups aid in the individualization of the nanowhiskers. The resulting surface-modified cellulose whiskers are dispersible in ethyl acetate and toluene, indicating increased hydrophobicity and presumably higher compatibility with hydrophobic polymers.

Cellulose nanoparticles are obtained as aqueous suspensions; the stability depends on the dimensions of the dispersed species, size polydispersity, and surface charge. The use of sulfuric acid to prepare cellulose nanocrystals leads to a more stable aqueous suspension than that prepared using hydrochloric acid (Araki et al. 1998). It was shown that the H_2SO_4 -prepared nanoparticles present a negatively charged surface while the HCl -prepared nanoparticles are not charged. During acid hydrolysis utilizing sulfuric acid, acidic sulfate ester groups are likely formed on the nanoparticle surface. This creates electric double-layer repulsion between the nanoparticles in suspension, which plays an important role in their interaction with a polymer matrix and with each other. The density of charges on the cellulose

nanocrystal surface depends on the hydrolysis conditions and can be determined by elementary analysis or conductimetric titration to exactly determine the sulfur content. The sulfate group content increases with acid concentration, acid-to-polysaccharide ratio, and hydrolysis time. Based on the density and size of the cellulose whiskers, Araki et al. (1998, 1999) estimated the charge density to be 0.155 e/nm^2 , where e is the elementary charge, for a nanocrystal with dimensions of $7 \times 7 \times 115 \text{ nm}^3$. With the following conditions: cellulose concentration of 10 wt% in 60% sulfuric acid at 46°C for 75 min, the charge coverage was estimated at 0.2 negative ester groups per nanometer (Revol et al. 1992). Other typical values of the sulfur content of cellulose whiskers prepared by sulfuric acid hydrolysis were reported (Marchessault et al. 1961; Revol et al. 1994). It was shown that even at low levels, the sulfate groups caused a significant decrease in degradation temperature and increase in char fraction confirming that the sulfate groups act as flame retardants (Roman and Winter 2004).

If the cellulose nanocrystals are prepared by hydrochloric acid hydrolysis, the resulting dispersability is limited and their aqueous suspensions tend to flocculate. Habibi et al. (2006) performed TEMPO-mediated oxidation of cellulose whiskers that were obtained from HCl hydrolysis of cellulose nanoparticles from tunicin to introduce negative charges on their surface. They showed that after hydrolysis and TEMPO-mediated oxidation, the nanoparticles kept their initial morphological integrity and native crystallinity, but at their surface, the hydroxymethyl groups were selectively converted to carboxylic groups, thus imparting a negative surface charge to the whiskers. When dispersed in water these oxidized cellulose nanocrystals did not flocculate, and their suspensions appeared birefringent.

7.5 Morphological Properties of Cellulose Nanoparticles

The origin of the cellulose fibers, mainly the nature of the plant cell wall, e.g., primary or secondary, determines the morphology of the generated NFC. They are elongated nanoparticles with widths ranging from 3 to 20 nm and lengths of few microns. NFC from primary cell walls, such as sugar beet pulps or *Opuntia ficus indica*, are generally thinner and longer and were much easier to produce compared to those extracted from secondary walls, such as wood. Figure 7.2 shows example of NFC extracted from primary or secondary cell walls.

Cellulose nanocrystals can be prepared from any botanical source containing cellulose. In the literature, different cellulosic sources have been used as shown in Fig. 7.3. Regardless of the source, cellulose nanocrystals occur as elongated nanoparticles. The persistence of the spot diffractogram when the electron probe is scanned along the rod during transmission electron microscopy (TEM) observation is evidence of the monocrystalline nature of the cellulosic fragment (Favier et al. 1995a); therefore, each fragment can be considered as a cellulosic crystal with no apparent defect. Their dimensions depend on several factors, including the source of the cellulose, the exact hydrolysis conditions, and ionic strength.

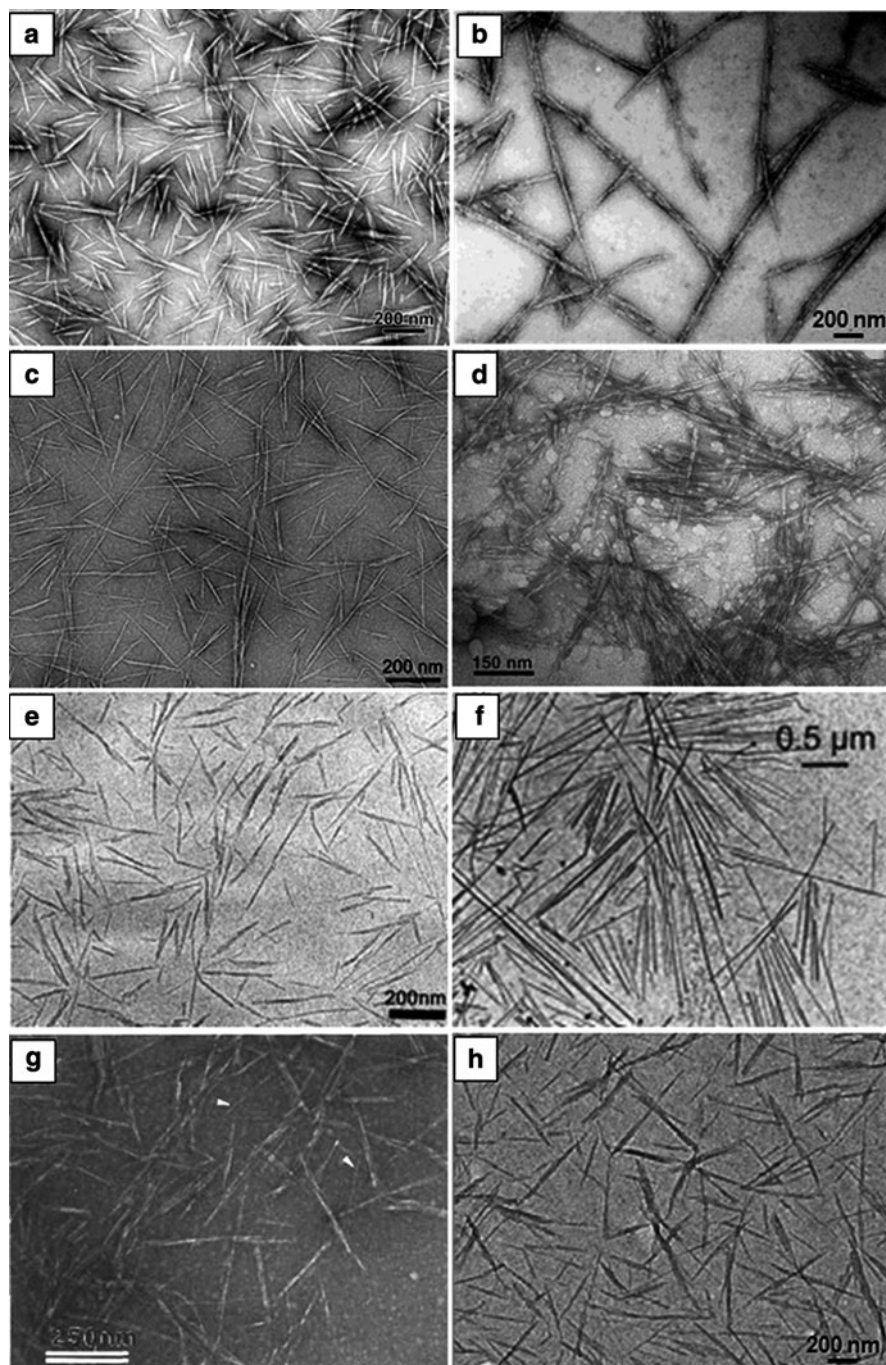


Fig. 7.3 Transmission electron micrographs from dilute suspension of cellulose nanocrystals from: (a) ramie (Habibi et al. 2008), (b) bacterial (Grunnert and Winter 2002), (c) sisal (Garcia de Rodriguez et al. 2006), (d) microcrystalline cellulose (Kvien et al. 2005), (e) sugar beet pulp

Table 7.1 Geometrical characteristics of cellulose nanocrystals from various sources: length (*L*) and cross section (*D*)

Source	<i>L</i> (nm)	<i>D</i> (nm)	Ref.
Alfa	200	10	Ben Elmabrouk et al. (2009)
Algal (Valonia)	>1,000	10–20	Revol (1982), Hanley et al. (1992)
Bacterial	100–several 1,000	5–10 × 30–50	Tokoh et al. (1998), Grunnert and Winter (2002), Roman and Winter (2004)
Cladophora	–	20 × 20	Kim et al. (2000)
Cotton	100–300	5–10	Fengel and Wegener (1983), Dong et al. (1998), Ebeling et al. (1999), Araki et al. (2000), Podsiadlo et al. (2005)
Cottonseed linter	170–490	40–60	Lu et al. (2005)
Flax	100–500	10–30	Cao et al. (2007)
Hemp	Several 1,000	30–100	Wang et al. (2007)
Luffa Cylindrica	242	5.2	Siqueira et al. (2010c)
MCC	150–300	3–7	Kvien et al. (2005)
Ramie	200–300	10–15	Habibi et al. (2007, 2008)
Sisal	100–500	3–5	Garcia de Rodriguez et al. (2006)
Sugar beet pulp	210	5	Azizi Samir et al. (2004b)
Tunicin	100–several 1,000	10–20	Favier et al. (1995a)
Wheat straw	150–300	5	Helbert et al. (1996b)
Wood	100–300	3–5	Fengel and Wegener (1983), Araki et al. (1998, 1999), Beck-Candanedo et al. (2005)

The typical geometrical characteristics for nanocrystals derived from different species and reported in the literature are collected in Table 7.1. Although, if often composed of few laterally bound elementary crystallites that are not separated by conventional acid hydrolysis and sonication process (Elazzouzi-Hafraoui et al. 2008), the length and width of hydrolyzed cellulose nanocrystals is generally in the order of few hundred nanometers and few nanometers, respectively. It was observed that the length polydispersity has a constant value, whereas the diameter polydispersity depends on the acid used for isolation (Braun et al. 2008). A smaller diameter polydispersity was obtained when using sulfuric acid instead of hydrochloric acid, because of electrostatic charges resulting from the introduction of sulfate ester groups when using the former.

Fig. 7.3 (continued) (Azizi Samir et al. 2004b), (f) tunicin (Anglès and Dufresne 2000), (g) wheat straw (Helbert et al. 1996a), and (h) cotton (Fleming et al. 2000). (a) Reproduced by permission of the Royal Society of Chemistry, (b, c) Reproduced by permission of Elsevier, (d, e, f, h). Reprinted with permission from copyright (2008) American Chemical Society and (g) Reproduced by permission of John Wiley & Sons Inc

An important parameter for cellulosic whiskers is the aspect ratio, defined as the ratio of the length to the width (Table 7.1). It determined the anisotropic phase formation and reinforcing properties. The average length ranges between 1 μm for nanocrystals prepared, for instance, from tunicate, and around 200 nm for cotton. The cellulose extracted from tunicate, a sea animal, is referred as tunicin. The diameter ranges between 15 nm for tunicin and 4–5 nm for sisal or wood. The high value reported for cottonseed linter corresponds to aggregates. The aspect ratio varies between 10 for cotton and 67 for tunicin. Relatively large and highly regular tunicin whiskers are ideal for modeling rheological and reinforcement behaviors and were extensively used in the literature. The shape and dimensions of cellulose whiskers can be accessed from microscopic observations or scattering techniques. The cross-sections of microfibrils observed by TEM are square, whereas their AFM topography shows a rounded profile due to convolution with the shape of the AFM tip (Hanley et al. 1992). AFM images of the surface of highly crystalline cellulose microfibrils showed periodicities along the microfibril axis of 1.07 and 0.53 nm that were supposed to correspond to the fiber and glucose unit repeat distances, respectively. Scattering techniques include small-angle light (de Souza Lima et al. 2003) and neutron (Orts et al. 1998) scattering.

7.6 Processing of Cellulose Nanocomposites

The main challenge with nanoparticles is related to their homogeneous dispersion within a polymeric matrix. The presence of sulfate groups resulting from the acid hydrolysis treatment when using sulfuric acid to prepare cellulose whiskers or nanocrystals induces the stability of the ensuing aqueous suspension. Water is therefore initially the preferred processing medium. A high level of dispersion of the filler within the host matrix in the resulting composite film is expected when processing nanocomposites in aqueous medium.

7.6.1 Polymer Latexes

The first publication reporting the preparation of cellulose nanocrystal reinforced polymer nanocomposites was carried out using a latex obtained by the copolymerization of styrene and butyl acrylate (poly(S-*co*-BuA)) and tunicin whiskers (Favier et al. 1995a). The same copolymer was used in association with wheat straw (Helbert et al. 1996a) or sugar beet (Azizi Samir et al. 2004b) cellulose nanocrystals. Other latexes such as poly (β -hydroxyoctanoate) (PHO) (Dubief et al. 1999; Dufresne et al. 1999, 2000), polyvinylchloride (PVC) (Chazeau et al. 1999a, b, c, 2000) waterborne epoxy (Matos Ruiz et al. 2001), natural rubber (NR) (Bendahou et al. 2009, 2010; Siqueira et al. 2010a), and polyvinyl acetate (PVAc) (Garcia de Rodriguez et al. 2006) were also used as a matrix. Recently,

stable aqueous nanocomposite dispersions containing cellulose whiskers and a poly (styrene-*co*-hexyl-acrylate) matrix were prepared via miniemulsion polymerization (Ben Elmabrouk et al. 2009). Addition of a reactive silane was used to stabilize the dispersion. Solid nanocomposite films can be obtained by mixing and casting the two aqueous suspensions followed by water evaporation. Alternative methods consist in freeze drying and hot pressing or freeze drying, extruding and hot pressing the mixture.

7.6.2 *Hydrosoluble or Hydrodispersible Polymers*

The preparation of cellulosic particle reinforced starch (Anglès and Dufresne 2000; Mathew and Dufresne 2002; Orts et al. 2005; Kvien et al. 2007; Mathew et al. 2008); (Svagan et al. 2009), silk fibroin (Noishiki et al. 2002), poly(oxyethylene) (POE) (Azizi Samir et al. 2004a, c, f, 2005b, 2006), polyvinyl alcohol (PVA) (Zimmerman et al. 2004a, 2005; Lu et al. 2008; Paralikar et al. 2008; Roohani et al. 2008a), hydroxypropyl cellulose (HPC) (Zimmerman et al. 2004a, 2005), carboxymethyl cellulose (CMC) (Choi and Simonsen 2006a), or soy protein isolate (SPI) (Wang et al. 2006) has been reported in the literature. The hydrosoluble or hydrodispersible polymer is first dissolved in water and this solution is mixed with the aqueous suspension of cellulose nanocrystals. The ensuing mixture is generally evaporated to obtain a solid nanocomposite film. It can also be freeze dried and hot pressed.

7.6.3 *Nonaqueous Systems*

Excluding the use of an aqueous polymer dispersion, or latex, an alternative way to process nonpolar polymer nanocomposites reinforced with cellulose nanocrystals consists of their dispersion in an adequate (with regard to matrix) organic medium. Coating with a surfactant or a surface chemical modification of the nanoparticles can be considered. The global objective is to reduce their surface energy in order to improve their dispersibility/compatibility with nonpolar media.

Coating of cotton and tunicin whiskers by a surfactant such as a phosphoric ester of polyoxyethylene (9) nonyl phenyl ether was found to lead to stable suspensions in toluene and cyclohexane (Heux et al. 2000) or chloroform (Kvien et al. 2005). Coated tunicin whisker reinforced atactic polypropylene (aPP) (Ljungberg et al. 2005), isotactic polypropylene (iPP) (Ljungberg et al. 2006), or poly(ethylene-*co*-vinyl acetate) (EVA) (Chauve et al. 2005) were obtained by solvent casting using toluene. The same procedure was used to disperse cellulosic nanoparticles in chloroform and process composites with poly lactic acid (PLA) (Kvien et al. 2005; Petersson and Oksman 2006). Nanocomposite materials were also prepared by dispersing cellulose acetate butyrate (CAB) in a dispersion of topochemically

trimethylsilylated bacterial cellulose nanocrystals in acetone and subsequent solution casting (Grunnert and Winter 2002).

Surface chemical modification of cellulosic nanoparticles is another way to decrease their surface energy and disperse them in organic liquids of low polarity. It generally involves reactive hydroxyl groups from the surface. Experimental conditions should avoid swelling media and the peeling effect of surface-grafted chains inducing their dissolution in the reaction medium. The chemical grafting has to be mild in order to preserve the integrity of the nanoparticle. Goussé et al. (2002) stabilized tunicin microcrystals in tetrahydrofuran (THF) by a partial silylation of their surface. Grunnert and Winter (2002) reported the preparation of bacterial cellulose nanocrystals topochemically trimethylsilylated. Resulting nanoparticles were dispersed in acetone to process nanocomposites with a cellulose acetatebutyrate matrix. Araki et al. (2001) prepared original sterically stabilized aqueous rod-like cellulose microcrystals suspensions by the combination of HCl hydrolysis, oxidative carboxylation, and grafting of poly(ethylene glycol) (PEG) having a terminal amino group on one end using water-soluble carbodiimide. The PEG-grafted microcrystals demonstrated drastically enhanced dispersion stability shown through resistance to the addition of 2 M sodium chloride. They also demonstrated ability to redisperse into either water or chloroform from the freeze-dried state. Alkenyl succinic anhydride (ASA) can be used for acylating the surface of cellulose nanocrystals. Surface chemical modification of tunicin whiskers with ASA was reported by Yuan et al. (2006). The acylated whiskers were found to disperse in medium- to low-polarity solvents. It was shown that by controlling the heating time, whiskers with different dispersibility could be obtained. Nogi et al. (2006a) and Ifuku et al. (2007) were among the first to use acetylated cellulosic nanofibers in the preparation of reinforced clear plastic.

Preparation of stable cellulose whisker suspensions in dimethylformamide (DMF) (Azizi Samir et al. 2004e; Marcovich et al. 2006) and dimethyl sulfoxide (DMSO) or *N*-methyl pyrrolidine (NMP) (van den Berg et al. 2007) without either addition of a surfactant or any chemical modification was also reported. From DMF, tunicin whiskers reinforced POE plasticized with tetraethylene glycol dimethyl ether (TEGDME) were prepared by casting and evaporation of DMF (Azizi Samir et al. 2004f). Cross-linked nanocomposites were also prepared by dispersing cellulose nanocrystals in a solution of an unsaturated linear polycondensate, addition of a photo-initiator, casting, evaporating the solvent, and UV curing (Azizi Samir et al. 2004d).

7.6.4 Long Chains Grafting

Long chain surface chemical modification of cellulosic nanoparticles consisting of grafting agents bearing a reactive end group and a long “compatibilizing” tail was also reported in the literature. The general objective is, of course, to increase the apolar character of the nanoparticle. In addition, it can yield some extraordinary

possibilities. The surface modifications can act as binding sites for active agents in drug delivery systems or for toxins in purifying and treatment systems. These surface modifications may also be able to interdiffuse, upon heating, to form the polymer matrix phase. The covalent linkage between reinforcement and matrix will result in near-perfect stress transfer at the interface with exceptional mechanical properties of the composite as a result.

Nanocomposite materials were processed from polycaprolactone (PCL)-grafted cellulose whiskers using the grafting “onto” (Habibi and Dufresne 2008) and grafting “from” (Habibi et al. 2008) approaches. The ensuing nanoparticles were used to process nanocomposites using PCL as a matrix and a casting/evaporation technique from dichloromethane. A co-continuous crystalline phase around the nanoparticles was observed. Cellulose whiskers were also surface grafted with PCL via microwave-assisted ring-opening polymerization yielding filaceous cellulose whisker-graft-PCL nanocrystals which were incorporated into PLA as matrix (Lin et al. 2009). Epoxy functionality was introduced onto the surface of cellulosic nanoparticles by oxidation by cerium (IV) followed by grafting of glycidyl methacrylate (Stenstad et al. 2008). The length of the polymeric chain was varied by regulating the amount of glycidyl methacrylate. The surface of cellulose whiskers was also chemically modified by grafting organic acid chlorides presenting different lengths of the aliphatic chain by an esterification reaction (de Menezes et al. 2009). These functionalized nanoparticles were extruded with low density polyethylene (LDPE) to prepare nanocomposite materials. Cellulose whisker reinforced water-borne polyurethane nanocomposites were synthesized via in situ polymerization using a casting/evaporation technique (Cao et al. 2009). The grafted chains were able to form a crystalline structure on the surface of the nanoparticles and induce the crystallization of the matrix. Cellulose nanoparticles were modified with *n*-octadecyl isocyanate ($C_{18}H_{37}NCO$) using two different methods with one consisting of an in situ solvent exchange procedure (Siqueira et al. 2010b). Phenol was also enzymatically polymerized in the presence of TEMPO-oxidized cellulosic nanoparticles to prepare nanocomposites under ambient conditions (Li et al. 2010).

7.6.5 *Extrusion and Impregnation*

Very few studies have been reported concerning the processing of cellulose nanocrystal reinforced nanocomposites by extrusion methods. The hydrophilic nature of cellulose causes irreversible agglomeration during drying and aggregation in non-polar matrices because of the formation of additional hydrogen bonds between amorphous parts of the cellulose nanoparticles. Therefore, the preparation of cellulose whisker reinforced PLA nanocomposites by melt extrusion was carried out by pumping the suspension of nanocrystals into the polymer melt during the extrusion process (Oksman et al. 2006). An attempt to use PVA as a compatibilizer to promote the dispersion of cellulose whiskers within the PLA matrix was reported (Bondeson and Oksman 2007). Organic acid chlorides-grafted cellulose whiskers



Fig. 7.4 Photographs of the neat LDPE film and extruded nanocomposite films reinforced with 10 wt% of unmodified and C18 acid chloride-grafted cellulose whiskers (de Menezes et al. 2009). Reproduced by permission of Elsevier

were extruded with LDPE (de Menezes et al. 2009). The homogeneity of the ensuing nanocomposite was found to increase with the length of the grafted chains (Fig. 7.4).

Another possible processing technique of nanocomposites using cellulosic nanoparticles in the dry state consists in the filtration of the aqueous suspension to obtain a film or dried mat of particles followed by immersion in a polymer solution. The impregnation of the dried mat is performed under vacuum. Composites were processed by filling the cavities with transparent thermosetting resins such as phenol formaldehyde (Nakagaito et al. 2004; Nakagaito and Yano 2004, 2008), epoxy (Shimazaki et al. 2007), acrylic (Yano et al. 2005; Nogi et al. 2005; Iwamoto et al. 2008), and melamine formaldehyde (Henriksson and Berglund 2007). Nonwoven mats of cellulose microfibrils were also used to prepare polyurethane composite materials using film stacking method (Seydibeyoğlu and Oksman 2008).

Water-redispersible NFC in powder form was recently prepared from refined bleached beech pulp by carboxymethylation and mechanical disintegration (Eyholzer et al. 2010). However, the carboxymethylated sample displayed a loss of crystallinity and strong decrease in thermal stability limiting its use for nanocomposite processing.

7.6.6 *Electrospinning*

Electrostatic fiber spinning, also known as electrospinning, is a versatile method to prepare continuous fibers with diameters ranging from several microns down to 100 nm through the action of electrostatic forces (Huang et al. 2003; Greiner and Wendorff 2007). Basically, the electrospinning process consists in the uniaxial

stretching of a viscoelastic solution by means of electrostatic forces. The desired polymer solution is held in a syringe, which is connected to a positive electrode from a power supply, by its surface tension. The other electrode is connected to a collector which can be static (plate) or dynamic (rotating drum). When the intensity of the electrical field increases, the resulting electrostatic forces overcome the surface tension of the polymer solution inducing a stretching of the solution and series of jets are ejected. As the solvent in the jet evaporates, it hits the collector which is no longer a solution but a collection of solvent-free fiber mats. Electrospinning has received great attention in the fabrication of polymer nanofibers and composites (Huang et al. 2003). It has recently been reported as an alternative processing method for nanocellulose-based polymer composites. However, the dispersion of cellulose nanoparticles discussed before can be challenging.

Bacterial cellulose whiskers were incorporated into POE nanofibers with a diameter of less than 1 μm by the electrospinning process to enhance the mechanical properties of the electrospun fibers (Park et al. 2007). The whiskers were found to be globally well embedded and aligned inside the fibers, even though they were partially aggregated. Likewise, electrospun PVA fiber mats loaded with cellulose nanocrystals (Fig. 7.5), with diameter in the nanoscale range and enhanced mechanical properties, were successfully produced (Medeiros et al. 2008; Peresin et al. 2010). “Core-in-shell” electrospinning approach in which cellulose nanoparticles constitute the discrete “core” component surrounded by a cellulose “shell” was reported (Magalhaes et al. 2009).

Electrospun polystyrene (PS) (Rojas et al. 2009) and PCL (Zoppe et al. 2009) micro or nanofibers reinforced with cellulose nanocrystals were obtained by electrospinning. Nonionic surfactant sorbitan monostearate was used to improve the dispersion of the particles in the hydrophobic PS matrix while surface grafting of long chains was used in the case of PCL.

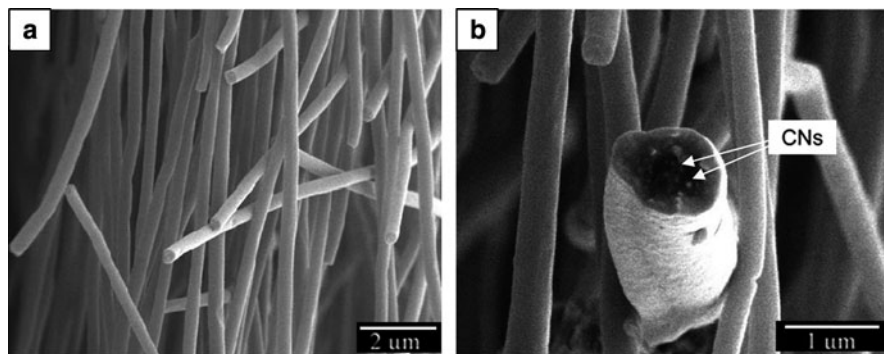


Fig. 7.5 Cryo-scanning electron microscopy micrographs of electrospun polyvinylalcohol loaded with 15% of cellulose nanocrystals (CNs) (Peresin et al. 2010) (copyright (2000) American Chemical Society)

7.6.7 Multilayer Films

The use of layer-by-layer (LBL) technique is expected to maximize the interaction between cellulose whiskers and a polar polymeric matrix, such as chitosan (de Mesquita et al. 2010). It also allows the incorporation of high amounts of cellulose whiskers, presenting a dense and homogeneous distribution in each layer.

Podsiadlo et al. (2005) reported the preparation of cellulose whisker multilayer composites with a polycation, poly-(dimethyldiallylammonium chloride) (PDDA), using LBL technique. The authors concluded that the multilayer films presented high uniformity and dense packing of nanocrystals. Orientated self-assembled films were also prepared using a strong magnetic film (Cranston and Gray 2006a) or spin coating technique (Cranston and Gray 2006b). The preparation of thin films composed of alternating layers of orientated rigid cellulose whiskers and flexible polycation chains was reported (Jean et al. 2008). Alignment of the rod-like nanocrystals was achieved using anisotropic suspensions of cellulose whiskers. Green composites based on cellulose nanocrystals/xyloglucan multilayers have been prepared using the nonelectrostatic cellulose–hemicellulose interaction (Jean et al. 2009). The thin films were characterized using neutron reflectivity experiments and AFM observations. More recently, biodegradable nanocomposites were obtained from the LBL technique using highly deacetylated chitosan and cellulose whiskers (de Mesquita et al. 2010). Hydrogen bonds and electrostatic interactions between the negatively charged sulfate groups on the nanoparticle surface and the ammonium groups of chitosan were the driving forces for the growth of the multilayered films. A high density and homogeneous distribution of cellulose nanocrystals adsorbed on each chitosan layer, each bilayer being around 7 nm thick, were reported. Self-organized films were also obtained using only charge-stabilized dispersions of cellulose nanoparticles with opposite charges (Aulin et al. 2010) from the LBL technique.

7.7 Properties of Nanocellulose-Based Composites

7.7.1 Microstructure

A visual examination is the simplest way to assess the dispersion of cellulosic nanoparticles within the host polymeric matrix. Because of the nanoscale dimensions of the reinforcing phase, the transparency of the nanocomposite film should remain if initially observed for the unfilled matrix. Opacity suggests the presence of aggregates of micrometric sizes (Ljungberg et al. 2005). Optical properties of UV-cured acrylic resin impregnated bacterial cellulose nanofibers were studied by Nogi et al. (2006b). Polarized optical microscopy was used by Azizi Samir et al. (2004c) to observe and follow the growth of POE spherulites in tunicin whisker reinforced films. For the unfilled POE matrix, birefringent spherulites were clearly

identified through the characteristic Maltese cross pattern indicating a spherical symmetry. For a 10 wt% tunicin whisker reinforced material, the supermolecular structure was found to be quite different. It was observed that the spherulites exhibited a less birefringent character, most probably due to a weakly organized structure. It was supposed that the cellulosic filler most probably interfered with the spherulite growth and that during growth, the whiskers are ejected and then occluded in interspherulitic regions. The high viscosity of the filled medium most likely restricts this phenomenon and limits the size of the spherulites.

Scanning electron microscopy (SEM) is generally employed for the more extensive morphological inspection of cellulose nanocrystals reinforced polymers. It consists of the observation of cryofractured surfaces. By comparing the micrographs showing the surface of fracture of the unfilled matrix and composites, the nanoparticles can be easily identified (Fig. 7.6). In fact, they appear like white dots in which concentration is a direct function of the particles content in the composite. These shiny dots correspond to the transverse sections of the cellulose whiskers, but their diameter determined by SEM microscopy is much higher than the whiskers diameter. This results from a charge concentration effect due to the emergence of cellulose whiskers from the observed surface (Anglès and Dufresne 2000).

The dispersion of nanoparticles in the nanocomposite film strongly depends on the processing technique and conditions. SEM comparison between either cast and evaporated or freeze-dried and subsequently hot-pressed composites based on poly (S-co-BuA) reinforced with wheat straw whiskers demonstrated that the former were less homogeneous and displayed a gradient of whiskers concentration between the upper and lower faces of the composite film (Helbert et al. 1996a; Dufresne et al. 1997). It was suggested that the casting/evaporation technique results in more homogenous films, where the whiskers have a tendency to orient randomly into horizontal planes. A two-dimensional in-plane random network of tunicin whisker reinforced epoxy was also reported from Raman spectroscopy experiments (Šturcova et al. 2005).

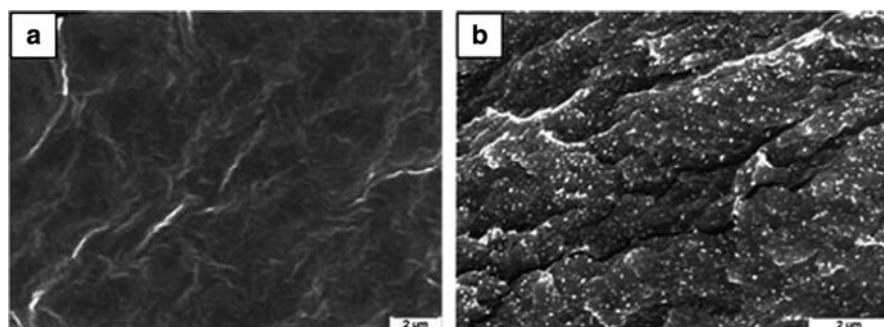


Fig. 7.6 Scanning electron micrographs from the fractured surfaces of (a) unfilled plasticized starch matrix and related composites filled with (b) 25 wt% tunicin whiskers (Anglès and Dufresne 2000) (copyright (2000) American Chemical Society)

TEM observations can be performed to investigate the microstructure and dispersion of the nanoparticles in the nanocomposite film. Casting/evaporation was reported to be an efficient processing technique to obtain a high dispersion level (Favier et al. 1995a; Matos Ruiz et al. 2001; Noishiki et al. 2002; Zimmerman et al. 2004b; Kvien et al. 2005). Small angle X-ray Scattering (SAXS) and small angle neutron scattering (SANS) are other ways to check the dispersion of cellulosic whiskers into the matrix. This latter technique was used to conclude to an isotropic dispersion of tunicin whiskers in plasticized PVC (Chazeau et al. 1999a). AFM imaging has been used to investigate the microstructure of cellulose nanocrystals reinforced polymer nanocomposites (Kvien et al. 2005; Zimmermann et al. 2005). A comparison between field emission (FE) SEM, AFM, and bright-field (BF) TEM for structure determination of cellulose whiskers and their nanocomposites with PLA was performed (Kvien et al. 2005). It was found that AFM overestimated the width of the whiskers due to the tip-broadening effect. FESEM allowed for a quick examination giving an overview of the sample but with limited resolution for detailed information. Detailed information was obtained from TEM, but this technique requires staining and suffers in general from limited contrast and beam sensitivity of the material.

7.7.2 Thermal Properties

The glass–rubber transition temperature, T_g , of cellulose whisker filled polymer composites is an important parameter, which controls different properties of the resulting composite such as its mechanical behavior, matrix chain dynamics, and swelling behavior. Its value depends on the interactions between the polymeric matrix and cellulosic nanoparticles. These interactions are expected to play an important role because of the huge specific area inherent to nanosize particles. For semicrystalline polymers, possible alteration of the crystalline domains by the cellulosic filler may indirectly affect the value of T_g .

No modification of T_g was reported for cellulose whiskers reinforced poly (S-co-BuA) (Favier et al. 1995a, b; Hajji et al. 1996; Dufresne et al. 1997), PHO (Dubief et al. 1999; Dufresne 2000), PVC (Chazeau et al. 1999a), POE (Azizi Samir et al. 2004a, c), PP (Ljungberg et al. 2005), and NR (Bendahou et al. 2009; Siqueira et al. 2010a). In glycerol plasticized starch-based composites, peculiar effects of tunicin whiskers on the T_g of the starch-rich fraction were reported depending on moisture conditions (Anglès and Dufresne 2000). For low loading level (up to 3.2 wt%), a classical plasticization effect of water was reported (Fig. 7.7). However, an antiplasticization phenomenon was observed for higher whiskers content (6.2 wt% and up). These observations were discussed according to the possible interactions between hydroxyl groups on the cellulosic surface and starch, the selective partitioning of glycerol and water in the bulk starch matrix or at whiskers surface, and the restriction of amorphous starch chains mobility in the vicinity of the starch crystallite coated filler surface. For glycerol plasticized starch reinforced with

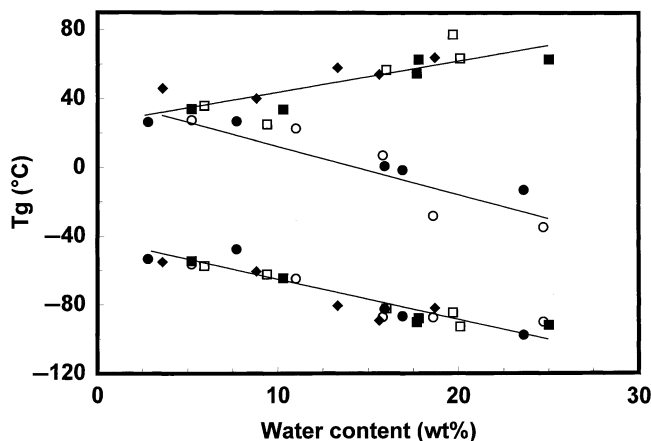


Fig. 7.7 Glass–rubber transition temperatures associated with the midpoints of the transitions versus water content for glycerol plasticized waxy maize starch filled with 0 (*filled circle*), 3.2 (*circle*), 6.2 (*filled square*), 16.7 (*square*), and 25 wt% (*filled diamond*) tunicin whiskers. Solid lines serve to guide the eye (Anglès and Dufresne 2000). Copyright (2000) American Chemical Society

cellulose crystallites prepared from cottonseed linter (Lu et al. 2005), an increase of T_g with filler content was reported and attributed to cellulose/starch interactions. For tunicin whiskers/sorbitol plasticized starch (Mathew and Dufresne 2002), T_g s were found to increase slightly up to about 15 wt% whiskers and to decrease for higher whisker loading. Crystallization of amylopectin chains upon whisker addition and migration of sorbitol molecules to the amorphous domains were proposed to explain the observed modifications. When using a PVA matrix, an increase of T_g was reported when the cellulose whiskers content increased (Garcia de Rodriguez et al. 2006; Roohani et al. 2008b). A similar observation was reported for CMC reinforced with cotton cellulose whiskers (Choi and Simonsen 2006b).

Melting temperature, T_m , values were reported to be nearly independent of the filler content in plasticized starch (Anglès and Dufresne 2000; Mathew and Dufresne 2002) and in POE-based materials (Azizi Samir et al. 2004a, c, e) filled with tunicin whiskers. The same observation was reported for CAB reinforced with native bacterial cellulose whiskers (Grunnert and Winter 2002). However, for the latter system, T_m values were found to increase when the amount of trimethylsilylated whiskers increased. The authors ascribed this difference to the stronger filler–matrix interaction in the case of chemically modified whiskers. A decrease of both T_m and degree of crystallinity of PVA was reported when adding cellulose nanocrystals (Roohani et al. 2008b). However, for electrospun cellulose whiskers reinforced PVA nanofibres, the crystallinity was found to be reduced upon filler addition (Peresin et al. 2010).

A significant increase in crystallinity of sorbitol plasticized starch (Mathew and Dufresne 2002) was reported when increasing the cellulose whiskers content. This phenomenon was ascribed to an anchoring effect of the cellulosic filler, probably

acting as a nucleating agent. For POE-based composites, the degree of crystallinity of the matrix was found to be roughly constant up to 10 wt% tunicin whiskers (Azizi Samir et al. 2004a, c, e) and to decrease for higher loading level (Azizi Samir et al. 2004c). It seems that the nucleating effect of cellulosic nanocrystals is mainly governed by surface chemical considerations (Ljungberg et al. 2006). It was shown from both X-ray diffraction and DSC analysis that the crystallization behavior of films containing unmodified and surfactant-modified whiskers displayed two crystalline forms (α and β), whereas the neat matrix and the nanocomposite reinforced with nanocrystals grafted with maleated polypropylene only crystallized in the α form. It was suspected that the more hydrophilic the whisker surface, the more it appeared to favor the appearance of the β phase. Grunnert and Winter (2002) observed from DSC measurements that native bacterial fillers impede the crystallization of the CAB matrix, whereas silylated ones help to nucleate the crystallization. The crystallinity of *N*-octadecyl isocyanate-grafted sisal whisker reinforced PCL was found to increase upon filler addition, whereas no influence of *N*-octadecyl isocyanate-grafted sisal MFC was reported (Siqueira et al. 2009). This difference was ascribed to the possibility of entanglement of MFC that tends to confine the polymeric matrix and restricts its crystallization.

For tunicin whisker-filled semi-crystalline matrices such as PHO (Dufresne et al. 1999) and glycerol plasticized starch (Anglès and Dufresne 2000), a transcrystallization phenomenon was reported. For glycerol plasticized starch-based systems, the formation of the transcrystalline zone around the whiskers was assumed to be due to the accumulation of plasticizer in the cellulose/amylopectin interfacial zones, improving the ability of amylopectin chains to crystallize. This transcrystalline zone could originate from a glycerol–starch V structure. In addition, the inherent restricted mobility of amylopectin chains was put forward to explain the lower water uptake of cellulose/starch composites for increasing filler content. Transcrystallization of PP at cellulose nanocrystal surfaces was evidenced and it was found to result from enhanced nucleation due to some form of epitaxy (Gray 2008).

The presence of sulfate groups introduced at the surface of the whiskers during hydrolysis with H_2SO_4 promotes their thermal decomposition (Roman and Winter 2004; Li et al. 2009). Thermogravimetric analysis (TGA) experiments were performed to investigate the thermal stability of tunicin whiskers/POE nanocomposites (Azizi Samir et al. 2004a, c). No significant influence of the cellulosic filler on the degradation temperature of the POE matrix was reported. Cellulose nanocrystal content appeared to have an effect on the thermal behavior of CMC plasticized with glycerin (Choi and Simonsen 2006b) suggesting a close association between the filler and the matrix. The thermal degradation of unfilled CMC was observed from its melting point (270°C) and had a very narrow temperature range of degradation. Cellulose nanocrystals were found to degrade at a lower temperature (230°C) than CMC, but showed a very broad degradation temperature range. The degradation of cellulose whisker reinforced CMC was observed between these two limits, but of interest was the lack of steps. Composites were reported to degrade as a unit.

7.7.3 Mechanical Properties

Nanoscale dimensions resulting in a very high surface area-to-volume ratio and impressive mechanical properties of rod-like cellulose whiskers have attracted significant interest in the last 15 years. These characteristics, along with the remarkable suitability for surface functionalization, make them ideal candidates to improve the mechanical properties of the host material.

The first demonstration of the reinforcing effect of cellulose whiskers in a poly (S-*co*-BuA) matrix was reported by Favier et al. (1995a, b). The authors measured, by dynamic mechanical analysis (DMA), a spectacular improvement in the storage modulus after adding tunicin whiskers even at low content into the host polymer. This increase was especially significant above the T_g of the thermoplastic matrix because of its poor mechanical properties in this temperature range. Figure 7.8 shows the isochronal evolution of the logarithm of the relative storage shear modulus ($\log G'_T/G'_{200}$, where G'_{200} corresponds to the experimental value measured at 200 K) at 1 Hz as a function of temperature for such composites prepared by water evaporation. In the rubbery state of the thermoplastic matrix, the modulus of the composite with a loading level as low as 6 wt% is more than two orders of magnitude higher than the one of the unfilled matrix. Moreover, the introduction of 3 wt% or more cellulosic whiskers provides an outstanding thermal stability of the matrix modulus up to the temperature at which cellulose starts to degrade (500 K). Since this pioneer work, many publications report the reinforcing capability of cellulose nanoparticles.

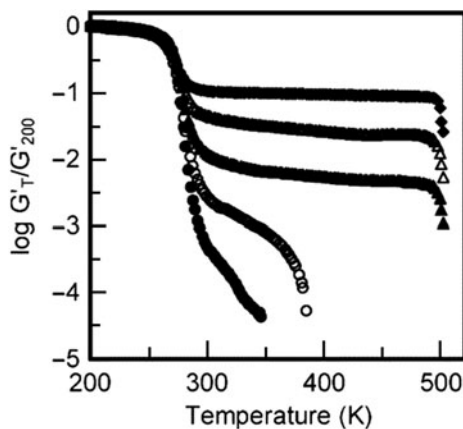


Fig. 7.8 Logarithm of the normalized storage shear modulus ($\log G'_T/G'$, where G' corresponds to the experimental value measured at 200 K) versus temperature at 1 Hz for tunicin whiskers reinforced poly(S-*co*-BuA) nanocomposite films obtained by water evaporation and filled with 0 (filled circle), 1 (circle), 3 (filled triangle), 6 (triangle), and 14 wt% (filled diamond) of cellulose whiskers (reprinted with permission from (Azizi Samir et al. 2005a). Copyright (2005) American Chemical Society

This outstanding reinforcing effect was ascribed to a mechanical percolation phenomenon (Favier et al. 1995a, b).

A good agreement between experimental and predicted data was reported when using the series-parallel model of Takayanagi modified to include a percolation approach. It was suspected that the stiffness of the material was due to infinite aggregates of cellulose whiskers. Above the percolation threshold, the cellulosic nanoparticles can connect and form a tri-dimensional continuous pathway through the nanocomposite film. For rod-like particles such as tunicin whiskers with an aspect ratio of 67, the percolation threshold is close to 1 vol% (Favier et al. 1997b). The formation of this cellulose network was supposed to result from strong interactions between whiskers, like hydrogen bonds (Favier et al. 1997a). This phenomenon is similar to the high mechanical properties observed for a paper sheet, which result from the hydrogen-bonding forces that hold the percolating network of fibers. This mechanical percolation effect explains both the high reinforcing effect and the thermal stabilization of the composite modulus for evaporated films. Any factor that affects the formation of the percolating whiskers network or interferes with it changes the mechanical performances of the composite (Dufresne 2006). Three main parameters were reported to affect the mechanical properties of such materials, viz. (1) the morphology and dimensions of the nanoparticles, (2) the processing method, and (3) the microstructure of the matrix and matrix/filler interactions.

1. For cellulose nanocrystals occurring as rod-like nanoparticles, the geometrical aspect ratio is an important factor because it determines the percolation threshold value. This factor is linked to the source of cellulose and whiskers preparation conditions. Higher reinforcing effect is obtained for nanocrystals with high aspect ratio. For instance, the rubbery storage tensile modulus was systematically lower for wheat straw whiskers/poly(S-co-BuA) composites than for tunicin whiskers-based materials (Dufresne 2006). Also, the flexibility and tangling possibility of the nanofibers plays an important role (Azizi Samir et al. 2004b; Bendahou et al. 2009; Siqueira et al. 2009). It was reported that entangled MFC induces a higher reinforcing effect than straight whiskers, whereas the elongation at break was lower.
2. The processing method conditions present the possibility of the formation of a continuous whiskers network and determine the final properties of the nanocomposite material. Slow processes such as casting/evaporation were reported to give the highest mechanical performance materials compared to freeze-drying/molding and freeze-drying/extruding/molding techniques. During slow water evaporation, because of Brownian motions in the suspension or solution (whose viscosity remains low, up to the end of the process when the latex particle or polymer concentration becomes very high), the rearrangement of the nanoparticles is possible. They have significant time to interact and connect to form a continuous network, which is the basis of their reinforcing effect. The resulting structure is completely relaxed and direct contacts between nanoparticles are then created. Conversely, during the freeze-drying/hot-pressing process, the nanoparticle arrangement in the suspension is first frozen, and then, during

the hot-pressing stage, because of the polymer melt viscosity, the particle rearrangements are strongly limited.

3. The microstructure of the matrix and the resulting competition between matrix/filler and filler/filler interactions also affect the mechanical behavior of cellulose nanocrystals reinforced nanocomposites. Classical composite science tends to favor matrix/filler interactions as a fundamental condition for optimal performance. But, for cellulose whisker-based composite materials, the opposite trend is generally observed when the material is processed via casting/evaporation method. This unusual behavior is ascribed to the originality of the reinforcing phenomenon of cellulosic nanoparticles resulting from the formation of a H-bonded percolating network. However, when using another processing route than casting/evaporation in aqueous medium, the dispersion of the hydrophilic filler in the polymeric matrix is also involved (de Menezes et al. 2009) and improved filler/matrix interactions generally lead to higher mechanical properties. In nonpercolating systems, for instance for materials processed from freeze-dried cellulose nanocrystals, strong matrix/filler interactions enhance the reinforcing effect of the filler (Ljungberg et al. 2005). The transcrystallization phenomenon reported for PHO (Dufresne et al. 1999) and plasticized starch (Anglès and Dufresne 2000) on cellulose whiskers resulted in a decrease of the mechanical properties (Anglès and Dufresne 2001) because of the coating of the nanoparticles with crystalline domains. When using unhydrolyzed cellulose microfibrils extracted from potato pulp rather than cellulose nanocrystals to reinforce glycerol plasticized thermoplastic starch, a completely different mechanical behavior was reported (Dufresne and Vignon 1998; Dufresne et al. 2000) and a significant reinforcing effect was observed. It was suspected that tangling effect contributed to this high reinforcing effect (Anglès and Dufresne 2001).

7.7.4 *Swelling Properties*

Swelling, or kinetics of solvent absorption, is a method that can highlight specific interactions between the filler and the matrix. It consists generally in first drying and weighing the sample, and then immersing it in the liquid solvent or exposing it to the vapor medium. The sample is then removed at specific intervals and weighed until an equilibrium value is reached. The swelling rate of the sample can be calculated by dividing the gain in weight by the initial weight. Generally, the short-time behavior displays a fast absorption phenomenon, whereas at longer times, the kinetics of absorption is low and leads to a plateau, corresponding to the solvent uptake at equilibrium. The diffusion coefficient can be determined from the initial slope of the solvent uptake curve as a function of time. For cellulosic particle reinforce composites, it is generally of interest to investigate the water absorption of the material because of the hydrophilic nature of the reinforcing phase. When a nonpolar polymeric matrix is used, the absorption of a nonaqueous liquid can be investigated.

A higher resistance of thermoplastic starch to water was reported when increasing the cellulose nanoparticle content (Anglès and Dufresne 2000; Lu et al. 2005; Svagan et al. 2009). Both the water uptake and the diffusion coefficient of water were found to decrease upon nanoparticle addition. These phenomena were ascribed to the presence of strong hydrogen bonding interactions between particles and between the starch matrix and cellulose whiskers. The hydrogen bonding interactions in the composites tend to stabilize the starch matrix when it is submitted to highly moist atmosphere. Moreover, the high crystallinity of cellulose also might be responsible for the decreased water uptake at equilibrium and diffusion coefficient of the material. A lower water uptake and dependence on cellulose whiskers content were reported when using sorbitol rather than glycerol as plasticizer for the starch matrix (Mathew and Dufresne 2002). An explanation was proposed based on the chemical structure of both plasticizers, more accessible end hydroxyl groups in glycerol being about twice those compared to sorbitol. Similar results were reported for cellulose whisker reinforced SPI (Wang et al. 2006) and CMC (Choi and Simonsen 2006b). Sisal whisker addition was found to stabilize PVA-based nanocomposites with no benefit seen when increasing the whisker content beyond the percolation threshold (Garcia de Rodriguez et al. 2006). A lower water uptake was observed when using MFC instead of cellulose whiskers as a reinforcing phase in NR (Bendahou et al. 2010). This observation was explained by the difference in the structure and composition of both nanoparticles, and in particular by the presence of residual lignin, extractive substances and fatty acids at the surface of MFC that limits, comparatively, the hydrophilic character of the filler. In addition, assuming that the filler/matrix compatibility was consequently lower for whiskers-based nanocomposites, one can imagine that water infiltration could be easier at the filler/matrix interface. For MFC-based nanocomposites, despite higher amorphous cellulose content, the higher hydrophobic character of the filler favors the compatibility with NR and restricts therefore the interfacial diffusion pathway for water.

Swelling experiments of PVC reinforced with tunicin whiskers were conducted in methyl ethyl ketone (MEK) (Chazeau et al. 1999b). A significant decrease in swelling was observed when increasing the cellulose whiskers content. It was assumed to be due to the existence of an interphase making a link between nanoparticles, thus allowing the formation of a flexible network. The swelling behavior in toluene of poly(S-co-BuA) reinforced with cellulose fibrils from *Opuntia ficus-indica* cladodes was reported by Malainine et al. (2005). They observed a strong toluene resistance even at very low filler loading. While the unfilled matrix completely dissolved in toluene, only 27 wt% of the polymer was able to dissolve when filled with only 1 wt% of cellulose microfibrils. This phenomenon was ascribed to the presence of a three-dimensional entangled cellulosic network which strongly restricted the swelling capability and dissolution of the matrix. For higher microfibrils content, no significant evolution was observed because of both the overlapping of the microfibrils restricting the filler-matrix interfacial area and the decrease of the entrapping matrix fraction due to the densification of the microfibrils network. Similar experiments were conducted

with cellulose microfibrils obtained from sugar beet pulp reinforced poly (S-co-BuA) (Dalmás et al. 2006). Toluene resistance of nanocomposites was found to be less significant than for microfibrils from *Opuntia ficus-indica* cladodes and to evolve with filler content. It was observed that the cohesion of composites prepared by evaporation was higher than the one of freeze-dried/hot-pressed materials. This difference was ascribed to the presence of a H-bonded network in the former samples. It was concluded that the solvent did not have any effect on the hydrogen bonds of the cellulose network present in evaporated composites. On the contrary, for freeze-dried/hot-pressed materials, lower interactions were supposed to create between fibrils and polymer chains were able to be more easily disentangled and dissolved by the solvent. The swelling behavior of cellulose whiskers reinforced NR in toluene was also reported (Bendahou et al. 2010). It was found to strongly decrease even with only 1 wt% of cellulose nanoparticles and to be almost independent of filler content and nature (MFC or whiskers).

7.7.5 Barrier Properties

Petrochemical-based polymers predominate in packaging of foods due to their easy processing, excellent barrier properties, and low cost. However, there is currently an increasing interest in replacing conventional synthetic polymers by more sustainable materials. One promising application area of cellulosic nanoparticles is barrier membranes, where the nano-sized fillers impart enhanced mechanical and barrier properties. Research in this area is burgeoning but is evolving rapidly to enhance the barrier properties and to overcome certain limitations. In addition, it is well known that molecules penetrate with difficulty in the crystalline domains of cellulose microfibrils. Moreover, the ability of cellulosic nanoparticles to form a dense percolating network held together by strong inter-particles bonds suggest their use as barrier films.

This suggestion, that the bond network has a significant effect on barrier properties, has been shown by comparing the water vapor transmission rate (WVTR) of cast films of NFC and hand sheets produced from the unprocessed pulps. The processing of bleached hardwood was shown to reduce the WVTR 4.6-fold, while the processing of bleached softwood reduced the WVTR 3.7-fold (Spence et al. 2010). The oxygen permeability of paper was considerably reduced when coated with MFC layer (Syverud and Stenius 2009). The WVTR of cotton nanocrystal reinforced CMC (Choi and Simonsen 2006b) and PVA (Paralikar et al. 2008) films were reported to decrease. Cellulose nanoparticles prepared by drop-wise addition of ethanol/HCl aqueous solution into a NaOH/urea/H₂O suspension of MCC were found to decrease the water vapor permeability of glycerol plasticized starch films (Chang et al. 2010). The water vapor barrier of mango puree-based edible (Azeredo et al. 2009) and chitosan films (Azeredo et al. 2010) were successfully improved by adding cellulose whiskers

7.8 Conclusions and Outlooks

The potential of nanocomposites in various sectors of research and application is promising and attracting increasing investment. Due to their abundance, high strength and stiffness, low weight and biodegradability, nanoscale cellulose fiber materials serve as promising candidates for the preparation of bionanocomposites. A broad range of applications of nanocellulose exists even if a high number of unknown remains to date. Tens of scientific publications and experts show its potential even if most of the studies focus on their mechanical properties as reinforcing phase and their liquid crystal self-ordering properties. Packaging is one area in which nanocellulose-reinforced polymeric films can be of interest because of the possibility to produce films with high transparency and improved mechanical and barrier properties. However, although there have been many promising achievements at the laboratory and pilot scale, there are several challenges to overcome in order to be able to produce cellulose-based nanocomposites at the industrial scale.

Two important programs have recently started on the production of nanocellulose. One is the creation in 2008 in Finland of the “Suomen Nanoselluloosakeskus” Centre or “Finnish Centre for Nanocellulosic Technologies.” One of the challenges is to produce large quantities of microfibrils of even quality. The forest industry in Finland is going through a major transition, and the utilization of new technologies is expected to provide a means for strengthening the competitiveness in the sector. The other program, supported by the Canadian government and represented by FPInnovations, is the creation of the ArboraNano network. The objective of this program for the valorization of nanocellulose (as cellulose nanocrystals) is also to revive the forestry sectors in Canada, strongly affected by the growing competition from emerging countries in Asia and South America.

However, it is worth noting that there are many safety concerns about nanomaterials, as their size allows them to penetrate into cells and eventually remain in the system. There is no consensus about categorizing nanomaterials as new materials.

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