

A review of cellulose nanocrystals and nanocomposites

ELAINE C. RAMIRES AND ALAIN DUFRESNE

ABSTRACT: Aqueous suspensions of cellulose nanocrystals can be obtained by acid hydrolysis of lignocellulosic fibers. Cellulose nanocrystals correspond to defect-free rod-like nanoparticles that present remarkable properties such as light weight, low cost, availability of raw material, renewability, nanoscale dimension, and unique morphology. Because of these properties, cellulose nanocrystals have been largely applied as reinforcing fillers in nanocomposite materials. This paper discusses the preparation, morphological features, and physical properties of cellulose nanocrystals, as well as their incorporation in nanocomposite materials.

Application: Cellulose nanocrystals can be used to prepare nanocomposites with improved mechanical and barrier properties.

Cellulose whiskers have attracted significant interest in the 15 last years because of their impressive mechanical properties and nanoscale dimensions, which result in very high surface area-to-volume ratios [1]. Their characteristics, along with their remarkable suitability for surface functionalization, make cellulose nanoparticles ideal for improving the mechanical properties of the host material in the preparation of nanocomposites.

Aqueous suspensions of cellulose nanoparticles can be prepared by a mechanical treatment (leading to the production of microfibrillated cellulose) or acid hydrolysis of the biomass. Our review only deals with acid-hydrolyzed nanoparticles. This treatment dissolves regions of low lateral order so that the water-insoluble, highly crystalline residue can be converted into a stable suspension by subsequent vigorous mechanical shearing action. The resulting nanocrystals occur as rod-like particles or whiskers, with dimensions that depend on the nature of the substrate, but range in the nanometer scale. The whiskers contain only a small number of defects and their axial Young's modulus, which is limit derived from theoretical chemistry, is 167.5 GPa—close to that of steel (200 GPa). The stiffness of the nanoparticles makes them suitable for processing green nanocomposite materials.

Cellulose is a high-molecular-weight homopolysaccharide composed of β -1,4-anhydro-D-glucopyranose [2]. One of the most specific characteristics of cellulose is that each of its monomers bears three hydroxyl groups that, along with their hydrogen bonding ability, play a major role in directing crystalline packing and in governing important physical properties of these highly cohesive materials. The cellulose obtained from nature is referred to as cellulose I, or native cellulose.

The potential of cellulose-based composites lies in the Young's modulus of the cellulose crystallite, which was first studied in 1962 from the crystal deformation of cellulose I using highly oriented fibers of bleached ramie [3]. A value of 137 GPa was reported, which differed from the theoretical

estimate of 167.5 GPa reported by Tashiro and Kobayashi [4]. More recently, Raman spectroscopy technique was used to measure the elastic modulus of native cellulose crystals [5], and a value of about 143 GPa was reported. The elastic modulus of single microfibrils from tunicate was measured by atomic force microscopy (AFM) using a three-point bending test [6]. Values of 145 and 150 GPa were reported for single microfibrils prepared by 2,2,6,6-tetramethylpiperidinyl-oxyl radical (TEMPO)-oxidation and sulfuric acid hydrolysis, respectively. These values were much higher than the Young's modulus of cellulosic fibers (e.g., 35–45 GPa for flax fibers).

PREPARATION OF CELLULOSE NANOCRYSTALS

Ranby [7] and Battista et al. [8] were the first to produce stable suspensions of colloidal-sized cellulose crystals by sulfuric acid hydrolysis. This process was later optimized [9, 10]. The extraction or isolation of crystalline cellulosic regions, in the form of rod-like nanocrystals, is a simple process based on acid hydrolysis [11]. The biomass first undergoes purification and bleaching processes and after removal of noncellulose constituents (e.g., lignin and hemicelluloses), the bleached material undergoes 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 disrupts the amorphous regions surrounding and embedding cellulose microfibrils while leaving the crystalline segments intact. It is ascribed to the faster hydrolysis kinetics of amorphous domains compared with crystalline ones. The hydronium ions penetrate the cellulosic material in the amorphous domains, promoting the hydrolytic cleavage of the glycosidic bonds that releases individual crystallites. The resulting suspension is subsequently diluted with water and washed by successive centrifugations. Dialysis against distilled water is then performed to re-

move free acid in the dispersion. A sonication step produces disintegration of aggregates and complete dispersion of the whiskers, which are refrigerated after filtration to remove residual aggregates. This general procedure has to be adapted according to the nature of the substrate.

Dong et al. were among the first researchers to study the effect of hydrolysis conditions on the properties of resulting cellulose nanocrystals [12]. They proved that longer hydrolysis time leads to shorter nanocrystals and also increases their 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. [13]. Beck-Candanedo et al. reported the properties of cellulose nanocrystals obtained by hydrolysis of softwood and hardwood pulps and investigated the influence of hydrolysis time and acid-to-pulp ratio [14]. The reaction time was found to be one of the most important parameters to consider in the acid hydrolysis of wood pulp. Moreover, they reported that reaction time that is too long will completely digest the cellulose into its component sugar molecules while lower reaction time will only yield large, undispersable fibers and aggregates. Also, it was reported that increased hydrolysis time of pea-hull fibers resulted in decreased length and diameter, while the aspect ratio first increased and then decreased [15].

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 [16]. That reaction was carried out in an acid mixture composed of hydrochloric acid (HCl) and an organic acid (acetic acid and butyric acid). Resulting nanocrystals were of similar dimensions compared with those obtained by HCl hydrolysis alone. The resulting surface-modified cellulose whiskers were dispersible in ethyl acetate and toluene, indicating increased hydrophobicity and presumably higher compatibility with hydrophobic polymers.

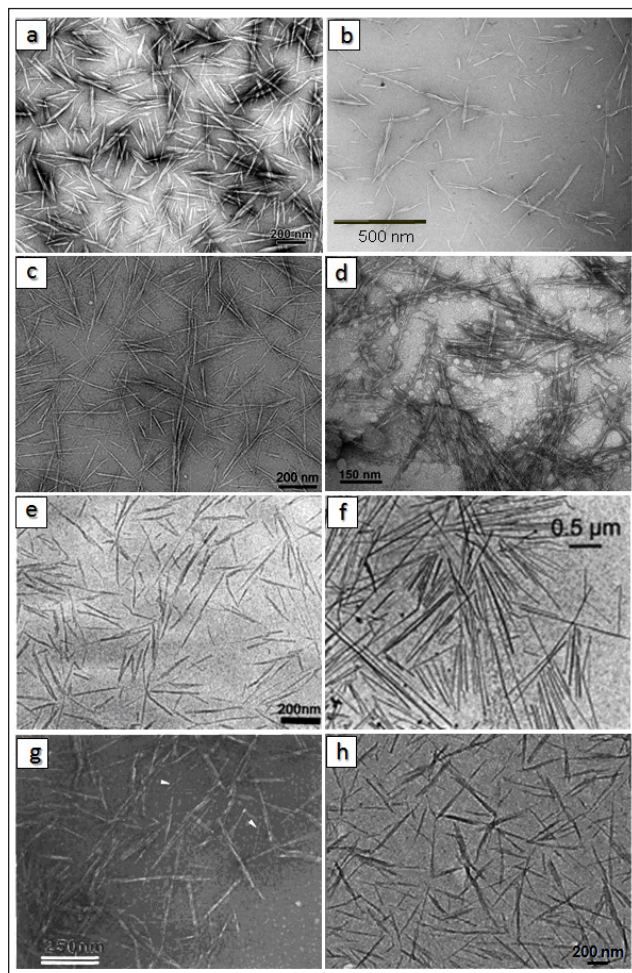
The use of sulfuric acid (H_2SO_4) to prepare cellulose nanocrystals leads to a more stable aqueous suspension than that prepared using hydrochloric acid [17, 18]. The H_2SO_4 -prepared nanoparticles were shown to present a negatively charged surface while the HCl-prepared nanoparticles were not charged. During acid hydrolysis using H_2SO_4 , 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.

If the cellulose nanocrystals are prepared by HCl hydrolysis, then their aqueous suspensions tend to flocculate. Habibi et al. performed TEMPO-mediated oxidation of cellulose whiskers obtained from HCl hydrolysis of cellulose nanoparticles from tunicin (cellulose extracted from tunicate) to introduce negative charges on their surfaces [19]. After hydrolysis and TEMPO-mediated oxidation, the nanoparticles kept their initial morphological integrity and native crystallinity. At their surfaces, however, the hydroxymethyl groups were selectively converted to carboxylic groups, thus imparting a negative

surface charge to the whiskers. These oxidized cellulose nanocrystals did not flocculate when dispersed in water, and their suspensions appeared birefringent.

MORPHOLOGICAL PROPERTIES OF CELLULOSE NANOPARTICLES

Cellulose nanocrystals can be prepared from any botanical source containing cellulose. Regardless of the source, cellulose nanocrystals occur as elongated nanoparticles (**Fig. 1**). The persistence of the spot diffractogram when the electron probe is scanned along the rod during transmission electron microscopy (TEM) observation shows the monocrystalline nature of the cellulosic fragment [20]. Therefore, each fragment can be considered as a cellulosic crystal with no apparent defect. Their dimensions depend on several factors, in-



1. Transmission electron micrographs from dilute suspension of cellulose nanocrystals from (a) ramie [21], (b) luffa cylindrica [22], (c) sisal [23], (d) microcrystalline cellulose (MCC) [24], (e) sugar-beet pulp [13], (f) tunicin [25], (g) wheat straw [26], and (h) cotton [27]. (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 © 2008 American Chemical Society; and (g) reproduced by permission of John Wiley & Sons Inc.

CELLULOSE NANOCOMPOSITES

The first report of the effect of using cellulose whiskers in nanocomposite materials was done by Favier et al. [20, 46]. A spectacular increase of the storage modulus of the styrene/butyl acrylate copolymer (poly[S-co-BuA]) matrix was reported upon adding tunicin whiskers even at low content. Measurements were carried out using dynamic mechanical analysis (DMA).

The outstanding reinforcing effect was ascribed to a mechanical percolation phenomenon [20, 46]. Above the percolation threshold, the cellulosic nanoparticles could connect and form a tridimensional continuous pathway through the nanocomposite film. The formation of this cellulose network was supposed to result from strong interactions between whiskers, such as hydrogen bonds [47]. This phenomenon was similar to the high mechanical properties observed for a paper sheet, which resulted from the hydrogen-bonding forces that held the percolating network of fibers. This mechanical percolation effect explained 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 [48]. Three main parameters were reported to affect the mechanical properties of such materials: (1) the morphology and dimensions of the nanoparticles, (2) the processing method, and (3) the microstructure of the matrix and matrix/filler interactions.

By considering the morphology and dimensions, a higher reinforcing effect was 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 materials based on tunicin whiskers [48]. Also, the flexibility and tangling possibility of the nanofibers played an important role [13, 49, 50].

Slow processing methods such as casting/evaporation were reported to give the highest mechanical performance materials compared with freeze-drying/molding and freeze-drying/extruding/molding techniques. During slow water evaporation, rearrangement of the nanoparticles is possible because of Brownian motions in the suspension or solution (in which viscosity remains low, up to the end of the process when the latex particle or polymer concentration becomes very high). The nanoparticles have enough time to interact and connect to form a continuous network, which is the basis of their reinforcing effect. Conversely, during the freeze-drying/hot-pressing process, the nanoparticle arrangement in the suspension is first frozen and then the particle rearrangements are limited during the hot-pressing stage because of the polymer melt viscosity.

The microstructure of the matrix and the resulting competition between matrix/filler and filler/filler interactions also affect the mechanical behavior of cellulose nanocrystal-reinforced nanocomposites. Classical composite science tends to favor matrix/filler interactions as a fundamental condition for

Source	L (nm)	D (nm)	Ref.
Alfa	200	10	[28]
Algal (Valonia)	> 1000	10-20	[29, 30]
Bacterial	100-several 1000	5-10 x 30-50	[31-33]
Cotton	85-300	5-18	[12,34-38]
Cottonseed linter	170-490	40-60	[39]
Flax	100-500	10-30	[40]
Luffa cylindrica	242	5.2	[22]
Microcrystalline cellulose (MCC)	150-350	3-8	[24, 41]
Ramie	200-300	10-15	[21, 42]
Sisal	100-500	3-5	[23]
Sugar beet pulp	210	5	[13]
Tunicin	100-several 1000	10-20	[20]
Wheat straw	150-300	5	[43]
Wood	100-300	3-5	[14, 17, 34]

I. Geometrical characteristics of cellulose nanocrystals from various sources: length (L) and cross-section (D).

cluding the source of the cellulose, the exact hydrolysis conditions, and ionic strength. The length and width of hydrolyzed cellulose nanocrystals are generally on the order of few hundred nanometers and a few nanometers, respectively (**Table I**).

The aspect ratio is an important parameter for cellulosic whiskers. The aspect ratio is the ratio of the length to the width, and it determines the anisotropic phase formation and reinforcing properties. 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 they are extensively referred to in the literature. The shape and dimensions of cellulose whiskers can be determined from microscopic observations or scattering techniques. The cross-sections of microfibrils observed by TEM are square, whereas their atomic force microscopy (AFM) topography shows a rounded profile due to convolution with the shape of the AFM tip [30]. Scattering techniques include small-angle light [44] and neutron [45] scattering.

NANOCOMPOSITES

optimal performance. For composite materials based on cellulose whiskers, the opposite trend is generally observed when the material is processed via the casting/evaporation method. This unusual behavior is ascribed to the originality of the reinforcing phenomenon of cellulosic nanoparticles resulting from the formation of hydrogen-bonded percolating network. However, when using a processing route other than casting/evaporation in water medium, the dispersion of the hydrophilic filler in the polymeric matrix is also involved [51] and improved filler/matrix interactions generally lead to higher mechanical properties. In nonpercolating systems, such as for materials processed from freeze-dried cellulose nanocrystals, strong matrix/filler interactions enhance the reinforcing effect of the filler [52].

PROCESSING OF CELLULOSE NANOCOMPOSITES

Polymer latexes

This mode of processing allows for the preservation of the individualized state of the nanoparticles resulting from their colloidal dispersion in water. The first publication reporting the preparation of cellulose nanocrystal-reinforced polymer nanocomposites was carried out using a latex of (poly[S-co-BuA]) and tunicin whiskers [20]. The same copolymer was used in association with wheat-straw [26] or sugar-beet [13] cellulose nanocrystals. Other latexes, such as poly(β -hydroxyoctanoate) (PHO) [53–55], polyvinylchloride (PVC) [56–59], waterborne epoxy [60], natural rubber (NR) [49, 61–63], and polyvinyl acetate (PVAc) [23], were also used as matrices. Recently, stable aqueous nanocomposite dispersions containing cellulose whiskers and a poly(styrene-co-hexyl-acrylate) matrix were prepared via miniemulsion polymerization [28]. Addition of a reactive silane was used to stabilize the dispersion. Solid nanocomposites films were obtained by mixing and casting the two aqueous suspensions followed by water evaporation. Alternative methods were to freeze dry and hot press or freeze dry, extrude, and hot press the mixture.

Hydrosoluble or hydrodispersible polymer

The preparation of cellulosic particles-reinforced starch [25, 45, 64–67], silk fibroin [68], poly(oxyethylene) (POE) [13, 69–72], polyvinyl alcohol (PVA) [73–77], hydroxypropyl cellulose (HPC) [73, 74], carboxymethyl cellulose (CMC) [78], or soy protein isolate (SPI) [79] has been reported in the literature. The hydrosoluble or hydrodispersible polymer was first dissolved in water and the solution was then mixed with the aqueous suspension of cellulose nanocrystals. The ensuing mixture would generally be evaporated to obtain a solid nanocomposite film, or it could be freeze dried and hot pressed.

Nonaqueous systems

An alternative way to process nonpolar polymer nanocomposites reinforced with cellulose nanocrystals is to disperse them in an adequate (with regard to matrix) organic medium. Coat-

ing with a surfactant or surface chemical modification of the nanoparticles can be considered. With this process, the global objective is to reduce their surface energy to improve their dispersibility or compatibility with nonpolar media.

Coating of cotton and tunicin whiskers with a surfactant such as a phosphoric ester of polyoxyethylene (13) nonylphenyl ether was found to lead to stable suspensions in toluene and cyclohexane [80] or chloroform [24]. Coated tunicin-whiskers reinforced atactic polypropylene (aPP) [52], isotactic polypropylene (iPP) [81], or poly(ethylene-co-vinyl acetate) (EVA) [82] were obtained by solvent casting using toluene. The same procedure was used to disperse cellulosic nanoparticles in chloroform and process composites with polylactic acid (PLA) [24, 83].

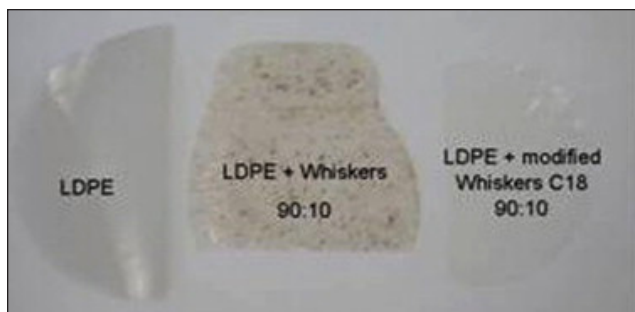
Surface chemical modification of cellulosic nanoparticles is another way to decrease their surface energy and disperse them in organic low-polarity liquids. That process generally involves reactive hydroxyl groups from the surface. The chemical grafting has to be mild to preserve the integrity of the nanoparticle. Goussé et al. stabilized tunicin microcrystals in tetrahydrofuran (THF) by a partial silylation of their surface [84]. Araki et al. prepared original sterically stabilized aqueous rod-like cellulose microcrystals suspensions through 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 [85]. The PEG-grafted microcrystals displayed drastically enhanced dispersion stability evidenced through resistance to addition of 2M sodium chloride. The microcrystals also showed ability to redisperse into either water or chloroform from the freeze-dried state.

Preparation of stable cellulose whiskers suspensions in dimethylformamide (DMF) [86, 87], and dimethyl sulfoxide (DMSO) or N-methyl pyrrolidine (NMP) [88] without either addition of a surfactant or any chemical modification was also reported.

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 to increase the apolar character of the nanoparticle, and 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.

Nanocomposite materials were processed from polycaprolactone (PCL)-grafted cellulose whiskers using the grafting-onto [89] and grafting-from [21] approaches. The grafting-onto approach mixed the nanoparticles with a polymer and a

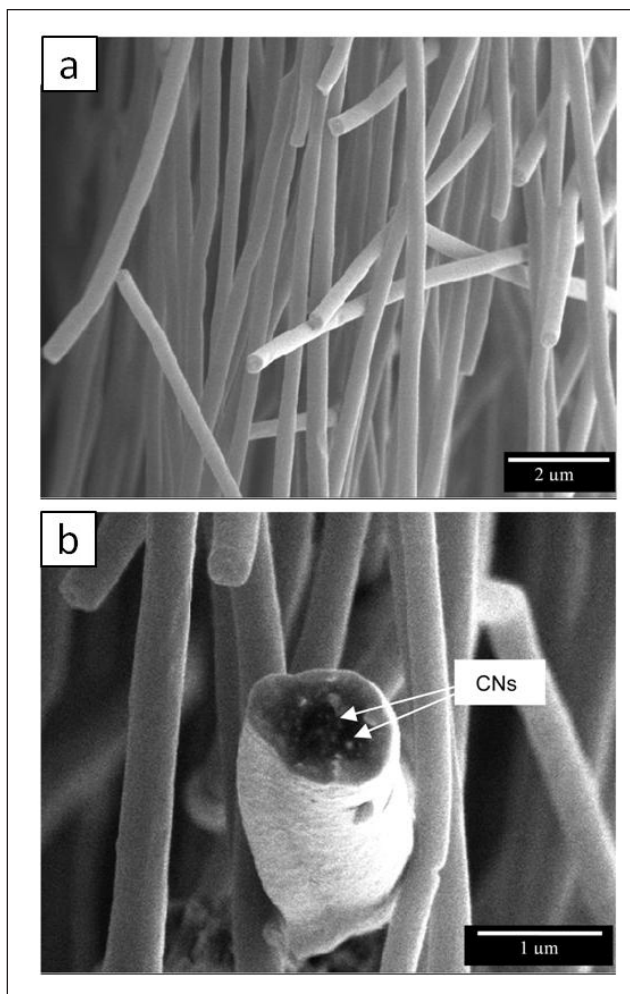


2. Photographs of the neat low-density polyethylene film and extruded nanocomposite films reinforced with 10 wt% of unmodified and C18 acid chloride-grafted cellulose whiskers [51]. Reproduced by permission of Elsevier.

coupling agent to graft the existing polymer onto the surface of the filler. The grafting-from approach mixed the nanoparticles with a monomer and an initiator and the polymer directly grew on the surface of the filler. The ensuing nanoparticles were used to process nanocomposites using PCL as 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 that were incorporated into PLA as matrix [90]. The surfaces of cellulose whiskers were also chemically modified by grafting organic acid chlorides presenting different lengths of the aliphatic chain by an esterification reaction [51]. These functionalized nanoparticles were extruded with low-density polyethylene (LDPE) to prepare nanocomposite materials. Cellulose whiskers-reinforced waterborne polyurethane nanocomposites were synthesized via in situ polymerization using the casting/evaporation technique [91]. The grafted chains formed a crystalline structure on the surface of the nanoparticles and induced the crystallization of the matrix. Cellulose nanoparticles were modified with *n*-octadecyl isocyanate (C18H37NCO) using two different methods, one of which was an in situ solvent exchange procedure [92]. Phenol was also enzymatically polymerized in the presence of TEMPO-oxidized cellulosic nanoparticles to prepare nanocomposites under ambient conditions [93].

Extrusion and impregnation

Very few studies have been reported concerning the processing by extrusion methods of cellulose nanocrystals-reinforced nanocomposites. The hydrophilic nature of cellulose causes irreversible agglomeration during drying and aggregation in nonpolar matrices because additional hydrogen bonds form between amorphous parts of the cellulose nanoparticles. Therefore, the preparation of cellulose whiskers-reinforced PLA nanocomposites by melt extrusion was carried out by pumping the suspension of nanocrystals into the polymer melt during the extrusion process [94]. An attempt to use PVA as a compatibilizer to promote the dispersion of cellulose



3. Cryoscanning electron microscopy micrographs of electrospun polyvinyl alcohol loaded with 15% cellulose nanocrystals [100, 103]. ©2000 American Chemical Society.

whiskers within the PLA matrix was reported [95]. Organic acid chlorides-grafted cellulose whiskers were extruded with LDPE [51]. The homogeneity of the ensuing nanocomposite was found to increase with the length of the grafted chains (**Fig. 2**).

Electrospinning

Electrostatic fiber spinning, or electrospinning, is a versatile method for preparing fibers with diameters ranging from several microns to 100 nm through the action of electrostatic forces [96, 97]. Electrospinning uses an electrical charge to draw a positively charged polymer solution from an orifice to a collector and shares characteristics of both electrospraying and conventional solution dry spinning of fibers. It is a noninvasive process that does not require the use of coagulation chemistry or high temperatures to produce solid threads from solution, which makes it particularly suitable to the production of fibers using large and complex molecules.

Bacterial cellulose whiskers were incorporated into POE nanofibers with a diameter of less than 1 μm by the electro-

pinning process to enhance the mechanical properties of the electrospun fibers [98]. 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. 3**), with diameters in the nanoscale range and enhanced mechanical properties, were successfully produced [99, 100].

Electrospun polystyrene (PS) [101], and PCL [102] 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.

Multilayer films

The use of the layer-by-layer (LBL) technique is expected to maximize the interaction between cellulose whiskers and a polar polymeric matrix, such as chitosan [104]. It also allows the incorporation of large amounts of cellulose whiskers, presenting a dense and homogeneous distribution in each layer.

Podsiadlo et al. reported the preparation of cellulose whiskers multilayer composites with a polycation, poly-(dimethyldiallylammonium chloride) (PDDA), using the LBL technique [37]. The authors concluded that the multilayer films presented high uniformity and dense packing of nanocrystals. The preparation of thin films composed of alternating layers of orientated rigid cellulose whiskers and flexible polycation chains was reported [105]. 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 [106]. More recently, biodegradable nanocomposites were obtained from the LBL technique using highly deacetylated chitosan and cellulose whiskers [104]. Hydrogen bonds and electrostatic interactions between the negatively charged sulfate groups on the nanoparticle surfaces and the ammonium groups of chitosan were the driving forces for the growth of the multilayered films. Self-organized films were also obtained using only charge-stabilized dispersions of cellulose nanoparticles with opposite charges [107] from the LBL technique.

BARRIER PROPERTIES

One promising application of cellulosic nanoparticles is barrier membranes, where the nanosized fillers impart enhanced mechanical and barrier properties, because molecules penetrate with difficulty in the crystalline domains of cellulose nanoparticles. Moreover, the ability of cellulosic nanoparticles to form a dense percolating network held together by strong interparticle bonds reinforces their use as barrier films.

Cellulose nanoparticles prepared by drop-wise addition of ethanol/HCl aqueous solution into an NaOH/urea/H₂O solution of MCC were found to decrease the water vapor permeability of glycerol plasticized-starch films [108]. The water vapor barriers of mango puree-based edible [109] and chito-

san films [110] were successfully improved by adding cellulose whiskers. The water vapor transmission rate of cotton nanocrystals-reinforced CMC [78] and PVA [76] films were reported to decrease.

CONCLUSIONS

The potential of nanocomposites in various sectors of research and application is attracting increasing investment. Due to their abundance, high strength and stiffness, low weight, and biodegradability, nanoscale cellulose fiber materials show promise as candidates for the preparation of bionanocomposites. There is a broad range of nanocellulose applications, even though much is still unknown. Numerous scientific publications and experts have shown the potential of nanocomposites, even if most of the studies focused on their mechanical properties as a reinforcing phase and their liquid crystal self-ordering properties. Packaging is one area in which nanocellulose-reinforced polymeric films is of interest because films can be produced with high transparency and improved mechanical and barrier properties. However, although there have been many promising achievements at the laboratory or pilot scale, several challenges need to be solved and investigated before cellulose-based nanocomposites can be produced at the industrial scale. **TJ**

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Capes Foundation for the postdoctoral fellowship for E.C.R. (Proc. 5184-09-6).

LITERATURE CITED

1. Eichhorn, S.J., Dufresne, A., Aranguren, M., et al., *J. Mater. Sci.* 45(1): 1(2010).
2. Klemm, D., Heublein, B., Fink, H.-P., et al., *Angew. Chem., Int. Ed.* 44(22): 3358(2005).
3. Sakurada, I., Nukushina, Y., and Ito, T., *J. Polym. Sci.* 57(165): 651(1962).
4. Tashiro, K., and Kobayashi, M., *Polym.* 32(8): 1516(1991).
5. Sturcova, A., Davies, G.R., and Eichhorn, S.J., *Biomacromolecules* 6(2): 1055(2005).
6. Iwamoto, S., Kai, W., Isogai, A., et al., *Biomacromolecules* 10(9): 2571(2009).
7. Ranby, B.G., *Discuss. Faraday Soc.* 11(1): 158(1951).
8. Battista, O.A., Coppick, S., Howsmon, J.A., et al., *Ind. Eng. Chem.* 48(2): 333 (1956).
9. Bondeson, D., Mathew, A., and Oksman, K., *Cellulose* 13(2): 171(2006).
10. Hamad, W.Y. and Hu, T.Q., *Can. J. Chem. Eng.* 88(3): 392(2010).
11. Roman, M. and Winter, W.T., *TAPPI Int. Conf. Nanotechnol., Proc.*, TAPPI PRESS, Atlanta, GA, USA, 2006, 06NANO09 (Conf. CD).
12. Dong, X.M., Revol, J.-F., and Gray, D.G., *Cellulose* 5(1): 19(1998).
13. Azizi Samir, M.A.S., Alloin, F., Paillet, M., et al., *Macromolecules* 37(11): 4313(2004).
14. Beck-Candanedo, S., Roman, M., and Gray, D.G., *Biomacromolecules* 6(2): 1048(2005).
15. Chen, G., Dufresne, A., Huang, J., et al., *Macromol. Mater. Eng.*

- 294(1): 59(2009).
16. Braun, B., and Dorgan, J.R., *Biomacromolecules* 10(2): 334(2009).
17. Araki, J., Wada, M., Kuga, S., et al., *Colloids Surf. A* 142(1): 75(1998).
18. Corrêa, A.C., Teixeira, E.M., Pessan, L.A., et al., *Cellulose* 17(6): 1183(2010).
19. Habibi, Y., Chanzy, H., and Vignon, M.R., *Cellulose* 13(6): 679(2006).
20. Favier, V., Canova, G.R., Cavaille, J.Y., et al., *Polym. Adv. Technol.* 6(5): 351(1995).
21. Habibi, Y., Goffin, A.-L., Schiltz, N., et al., *J. Mater. Chem.* 18(41): 5002(2008).
22. Siqueira, G., Bras, J., and Dufresne, A., *BioResources* 5(2): 727(2010).
23. de Rodriguez, N.L.G., Thielemans, W., and Dufresne, A., *Cellulose* 13(3): 261(2006).
24. Kvien, I., Tanem, B.S., and Oksman, K., *Biomacromolecules* 6(6): 3160(2005).
25. Anglès, M.N. and Dufresne, A., *Macromolecules* 33(22): 8344(2000).
26. Helbert, W., Cavaille, J.Y., and Dufresne, A., *Polym. Compos.* 17(4): 604(1996).
27. Fleming, K., Gray, D., Prasannan, S., et al., *J. Am. Chem. Soc.* 122(21): 5224(2000).
28. Ben Elmabrouk, A., Wim, T., Dufresne, A., et al., *J. Appl. Polym. Sci.* 114(5): 2946(2009).
29. Revol, J.F., *Carbohydr. Polym.* 2(2): 123(1982).
30. Hanley, S.J., Giasson, J., Revol, J.F., et al., *Polym.* 33(21): 4639(1992).
31. Grunert, M. and Winter, W.T., *J. Polym. Environ.* 10(1-2): 27(2002).
32. Tokoh, C., Takabe, K., Fujita, M., et al., *Cellulose* 5(4): 249(1998).
33. Roman, M., and Winter, W.T., *Biomacromolecules* 5(5): 1671(2004).
34. Fengel D. and Wegener G., *Wood, Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, New York, 1983, p. 613.
35. Ebeling, T., Paillet, M., Borsali, R., et al., *Langmuir* 15(19): 6123(1999).
36. Araki, J., Wada, M., Kuga, S., et al., *Langmuir* 16(6): 2413(2000).
37. Podsiadlo, P., Choi, S.-Y., Shim, B., et al., *Biomacromolecules* 6(6): 2914(2005).
38. Teixeira, E.M., Corrêa, A.C., Manzoli, A., et al., *Cellulose* 17(3): 595(2010).
39. Lu, Y., Weng, L., and Gao, X., *Macromol. Biosci.* 5(11): 1101(2005).
40. Cao, X., Dong, H., and Li, C.M., *Biomacromolecules* 8(3): 899(2007).
41. Boluk, Y. and Zhao, L., *TAPPI Int. Conf. Nanotechnol. For. Prod. Ind., Proc.*, TAPPI PRESS, Atlanta, 2009, p. 980.
42. Habibi, Y., Foulon, L., Aguié-Béghin, V., et al., *J. Colloid. Interface. Sci.* 316(2): 388(2007).
43. Helbert, W., Cavaille, J.Y., and Dufresne, A., *Polym. Compos.* 17(4): 604(1996).
44. Lima, M.M.D., Wong, J.T., Paillet, M., et al., *Langmuir* 19(1): 24(2003).
45. Orts, W.J., Godbout, L., Marchessault, R.H., et al., *Macromolecules* 31(17): 5717(1998).
46. Favier, V., Chanzy, H., and Cavaille, J.Y., *Macromolecules* 28(18): 6365(1995).
47. Favier, V., Canova, G.R., Shrivastavas, C., et al., *Polym. Eng. Sci.* 37(10): 1732(1997).
48. Dufresne, A., *J. Nanosci. Nanotechnol.* 6(2): 322(2006).
49. Bendahou, A., Habibi, Y., Kaddami, H., et al., *J. Biobased Mater. Bioenergy* 3(1): 81(2009).
50. Siqueira, G., Bras, J., and Dufresne, A., *Biomacromolecules* 10(2): 425(2009).
51. de Menezes, A.J., Siqueira, G., Curvelo, A.A.S., et al., *Polym.* 50(19): 4552(2009).
52. Ljungberg, N., Bonini, C., Bortolussi, F., et al., *Biomacromolecules* 6(5): 2732(2005).
53. Dubief, D., Samain, E., and Dufresne, A., *Macromolecules* 32(18): 5765(1999).
54. Dufresne, A., Kellerhals, M.B., and Witholt, B., *Macromolecules* 32(22): 7396(1999).
55. Dufresne, A., *Compos. Interfaces* 7(1): 53(2000).
56. Chazeau, L., Cavaille, J.Y., Canova, G., et al., *J. Appl. Polym. Sci.* 71(11): 1797(1999).
57. Chazeau, L., Cavaille, J.Y., and Terech, P., *Polym.* 40(19): 5333(1999).
58. Chazeau, L., Paillet, M., and Cavaille, J.Y., *J. Polym. Sci., Part B: Polym. Phys.* 37(16): 2151(1999).
59. Chazeau, L., Cavaille, J.Y., and Perez, J., *J. Polym. Sci., Part B: Polym. Phys.* 38(3): 383(2000).
60. Ruiz, M.M., Cavaille, J.Y., Dufresne, A., et al., *Macromol. Symp.* 169(1): 211(2001).
61. Bendahou, A., Kaddami, H., and Dufresne, A., *Eur. Polym. J.* 46(4): 609(2010).
62. Siqueira, G., Abdillahi, H., Bras, J., et al., *Cellulose* 17(2): 289(2010).
63. Bras, J., Hassan, M.L., Bruzesse, C., et al., *Ind. Crops Prod.* 32(3): 627(2010).
64. Mathew, A.P., and Dufresne, A., *Biomacromolecules* 3(3): 609(2002).
65. Mathew, A.P., Thielemans, W., and Dufresne, A., *J. Appl. Polym. Sci.* 109(6): 4065(2008).
66. Kvien, I., Sugiyama, J., Votrubec, M., et al., *J. Mater. Sci.* 42(19): 8163(2007).
67. Svagan, A.J., Hedenqvist, M.S., and Berglund, L., *Compos. Sci. Technol.* 69(3-4): 500(2009).
68. Noishiki, Y., Nishiyama, Y., Wada, M., et al., *J. Appl. Polym. Sci.* 86(13): 3425(2002).
69. Azizi Samir, M.A.S., Alloin, F., Gorecki, W., et al., *J. Phys. Chem. B* 108(30): 10845(2004).
70. Azizi Samir, M.A.S., Alloin, F., Sanchez, J.-Y., et al., *Polym.* 45(12): 4149(2004).
71. Azizi Samir, M.A.S., Mateos, A.M., Alloin, F., et al., *Electrochim. Acta* 49(26): 4667(2004).
72. Azizi Samir, M.A.S., Alloin, F., and Dufresne, A., *Compos. Interfaces* 13(4-6): 545(2006).
73. Zimmermann, T., Pohler, E., and Geiger, T., *Adv. Eng. Mater.* 6(9): 754(2004).
74. Zimmermann, T., Pohler, E., and Schwaller, P., *Adv. Eng. Mater.* 7(12): 1156(2005).
75. Lu, J., Wang, T., and Drzal, L.T., *Composites, Part A* 39(5): 738(2008).

76. Paralikara, S.A., Simonsen, J., and Lombardi, J., *J. Membr. Sci.* 320(1-2): 248(2008).
77. Roohani, M., Habibi, Y., Belgacem, N.M., et al., *Eur. Polym. J.* 44(8): 2489(2008).
78. Choi, Y. and Simonsen, J., *J. Nanosci. Nanotechnol.* 6(3): 633(2006).
79. Wang, Y., Cao, X., and Zhang, L., *Macromol. Biosci.* 6(7): 524(2006).
80. Heux, L., Chauve, G., and Bonini, C., *Langmuir* 16(21): 8210(2000).
81. Ljungberg, N., Cavallé, J.-Y., and Heux, L., *Polym.* 47(18): 6285(2006).
82. Chauve, G., Heux, L., Arouini, R., et al., *Biomacromolecules* 6(4): 2025(2005).
83. Petersson, L. and Oksman, K., *Compos. Sci. Technol.* 66(13): 2187(2006).
84. Gousse, C., Chanzy, H., Excoffier, G., et al., *Polym.* 43(9): 2645(2002).
85. Araki, J., Wada, M., and Kuga, S., *Langmuir* 17(1): 21(2001).
86. Azizi Samir, M.A.S., Alloin, F., Sanchez, J.-Y., et al., *Macromolecules* 37(4): 1386(2004).
87. Marcovich, N.E., Auad, M.L., Bellesi, N.E., et al., *J. Mater. Res.* 21(4): 870(2006).
88. van den Berg, O., Capadona, J.R., and Weder, C., *Biomacromolecules* 8(4): 1353(2007).
89. Habibi, Y., and Dufresne, A., *Biomacromolecules* 9(7): 1974(2008).
90. Lin, N., Chen, G., Huang, J., et al., *J. Appl. Polym. Sci.* 113(5): 3417(2009).
91. Cao, X., Habibi, Y., and Lucia, L.A., *J. Mater. Chem.* 19(38): 7137(2009).
92. Siqueira, G., Bras, J., and Dufresne, A., *Langmuir* 26(1): 402(2010).
93. Li, Z., Renneckar, S., and Barone, J.R., *Cellulose* 17(1): 57(2010).
94. Oksman, K., Mathew, A.P., Bondeson, D., et al., *Compos. Sci. Technol.* 66(15): 2776(2006).
95. Bondeson, D., and Oksman, K., *Composites, Part A* 38(12): 2486(2007).
96. Huang, Z.M., Zhang, Y.Z., Kotaki, M., et al., *Compos. Sci. Technol.* 63(15): 2223(2003).
97. Greiner, A., and Wendorff, J.H., *Angew. Chem., Int. Ed.* 46(30): 5670(2007).
98. Park, W.-I., Kang, M., Kim, H.-S., et al., *Macromol. Symp.* 249/250(1): 289(2007).
99. Medeiros, E.S., Mattoso, L.H.C., Ito, E.N., et al., *J. Biobased Mater. Bioenergy* 2(3): 231(2008).
100. Peresin, M.S., Habibi, Y., Zoppe, J.O., et al., *Biomacromolecules* 11(3): 674(2010).
101. Rojas, O.J., Montero, G.A., and Habibi, Y., *J. Appl. Polym. Sci.* 113(2): 927(2009).
102. Zoppe, J.O., Peresin, M.S., Habibi, Y., et al., *ACS Appl. Mater. Interfaces* 1(9): 1996(2009).
103. Peresin, M.S., Zoppe, J.O., Habibi, Y., et al., *TAPPI Int. Conf. Nanotechnol. For. Prod. Ind., Proc.*, TAPPI PRESS, 2009, Atlanta, p. 189.
104. de Mesquita, J.P., Donnici, C.L., and Pereira, F.V., *Biomacromolecules* 11(2): 473(2010).
105. Jean, B., Dubreuil, F., Heux, L., et al., *Langmuir* 24(7): 3452(2008).
106. Jean, B., Heux, L., Dubreuil, F., et al., *Langmuir* 25(7): 3920(2009).
107. Aulin, C., Varga, I., Claesson, P.M., et al., *Langmuir* 24(6): 2509(2008).
108. Chang, P.R., Jian, R., Zheng, P., et al., *Carbohydr. Polym.* 79(2): 301(2010).
109. Azeredo, H., Mattoso, L.H.C., Wood, D., et al., *J. Food. Sci.* 74(5): N31(2009).
110. Azeredo, H.M.C., Mattoso, L.H.C., Avena-Bustillos, R.J., et al., *J. Food. Sci.* 75(1): N1(2010).

ABOUT THE AUTHORS

Recent environmental concerns have led to increased use of materials obtained from biomass as raw materials for the production of biofuels, bioenergy, biomolecules, and biobased products. Cellulose nanocrystals can be prepared from any botanical source containing cellulose. Apart from their renewable nature, the cellulose nanocrystals have generated interest from the scientific community because of their biodegradability, strength, availability throughout the world, low density, and other characteristics. These characteristics, along with their remarkable suitability for surface functionalization, make cellulose nanocrystals ideal candidates for improving the mechanical properties of the host material in the preparation of nanocomposites.

Because of the nanometric size effect, nanocomposites have some unique properties with respect to their conventional microcomposite counterparts. However, although there have been many promising achievements at laboratory or pilot scale, several

challenges must be overcome to be able to produce cellulose-based nanocomposites at the industrial scale. The processing of nanocomposite materials with conventional techniques

such as extrusion (solvent-free) is also challenging.



Ramires



Dufresne

Ramires is a postdoctoral researcher at Grenoble Institute of Technology, The International School of Paper, Print Media and Biomaterials (Pagora) with a fellowship from Capes Foundation, Ministry of Education, Brazil. Dufresne is professor at Grenoble Institute of Technology, The International School of Paper, Print Media and Biomaterials (Pagora). Email Dufresne at alain.dufresne@pagora.grenoble-inp.fr.