Nanocellulose: a new ageless bionanomaterial

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Owing to the hierarchical structure of cellulose, nanoparticles can be extracted from this naturally occurring polymer. Multiple mechanical shearing actions allow the release of more or fewer individual microfibrils. Longitudinal cutting of these microfibrils can be achieved by a strong acid hydrolysis treatment, allowing dissolution of amorphous domains. The impressive mechanical properties, reinforcing capabilities, abundance, low density, and biodegradability of these nanoparticles make them ideal candidates for the processing of polymer nanocomposites. With a Young's modulus in the range 100–130 GPa and a surface area of several hundred $m^2 \, g^{-1}$, new promising properties can be considered for cellulose.

Introduction

Wood and plants are cellular hierarchical biocomposites produced by nature, and are essentially semicrystalline cellulose microfibril-reinforced amorphous matrices made of hemicellulose, lignin, waxes, extractive and trace elements [1]. Lignocellulosic fibers consist therefore of a cemented microfibril aggregate. As a consequence, the structure of plants spans many length scales, to provide maximum strength with a minimum of material. Wood, which is approximately 40–50 wt% cellulose (half in nanocrystalline form and half in amorphous form), provides an example (Fig. 1). While the whole tree is on the scale of meters, centimeters describe structures within the cross-section, millimeters describe growth rings, tens of micrometers describe the cellular anatomy, micrometers describe the layer structure within cell walls, tens of nanometers describe the configuration of cellulose fibrils in a matrix mainly composed of hemicellulose and lignin, and nanometers describe the molecular structures of cellulose, hemicellulose, and lignin and their chemical interactions [2].

In nature, cellulose is a ubiquitous structural polymer that confers its mechanical properties to higher plant cells. The hierarchical structure of natural fibers, based on their elementary nanofibrilar components, leads to the unique strength and high performance properties of different species of plants. Indeed, the most important attributes of wood and other lignocellulosic materials are their mechanical properties, in particular their unusual ability to provide high mechanical strength and high strength-to-weight ratio while allowing for flexibility to counter large dimensional changes due to swelling and shrinking. In all terrestrial and aquatic plant species, the primary cell wall is a dynamic structure and its constituent material must be synthesized in a form that can undergo extension.

There is an increasing demand for products made from renewable and sustainable non-petroleum based resources. Cellulose, the most abundant polymer on Earth, is renewable, biodegradable, as well as non-toxic. Purification of cellulose from plant fibers involves chemical treatments consisting of alkali extraction and bleaching. Owing to its hierarchical structure and semicrystalline nature, nanoparticles can be extracted from this naturally occurring polymer using a top-down mechanically or chemically induced deconstructing strategy.

The potential of cellulosic nanoparticles or nanocellulose has been demonstrated for special functional nanomaterials [3] but it is as a biobased reinforcing nanofiller that such nanomaterials have attracted significant interest over the past 20 years [4–7]. However, the main challenge with nanoparticles is related to their homogeneous dispersion within a polymeric matrix. Moreover, cellulose nanoparticles have a strong tendency for self-association because of the omnipresence of interacting surface hydroxyl

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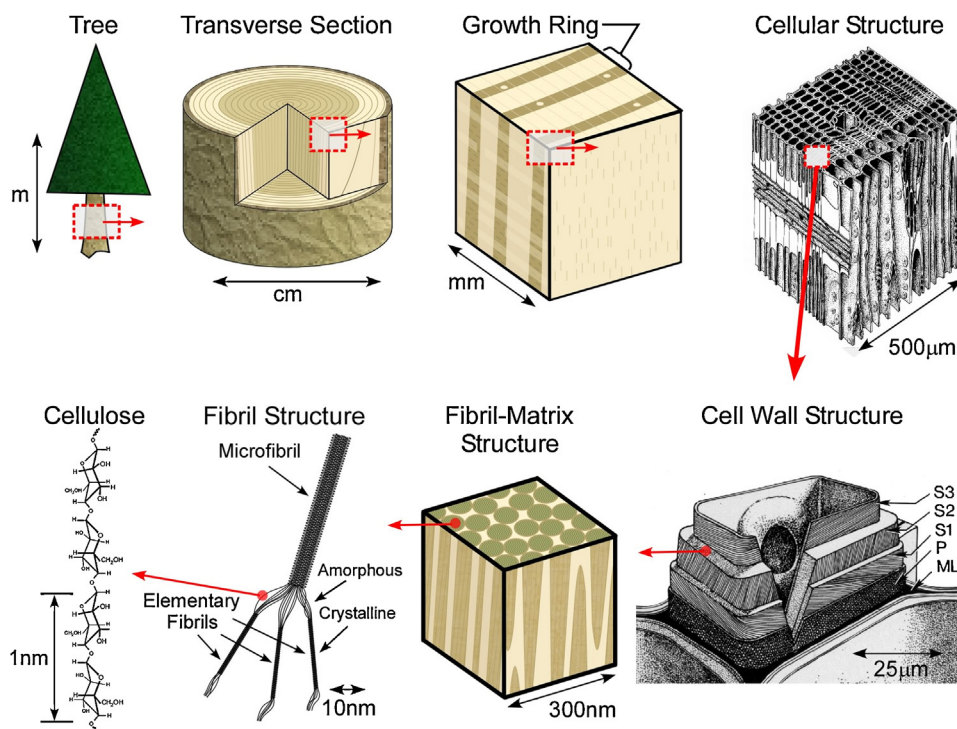
FIGURE 1

Wood hierarchical structure: from tree to cellulose. Reproduced with permission from [2].

groups. This property, which is the basis of the strength of paper sheets, is a desirable feature for the formation of load-bearing percolating architectures within the host polymer matrix. However, these inter-particle interactions can cause aggregation during the preparation of the nanocomposite and limit the potential of mechanical reinforcement. This phenomenon is magnified when the size of the particle decreases.

Mechanically induced destructuring strategy

Multiple mechanical shearing actions applied to cellulosic fibers release more or fewer individual microfibrils. This material is usually called microfibrillated cellulose (MFC). Different mechanical treatment procedures have been reported to prepare MFC. They mainly consist of high-pressure homogenization and/or grinding [7]. However, this production route is normally associated with high energy consumption for fiber delamination [8–10]. Therefore, different pretreatments have been proposed to facilitate this process, for example, mechanical cutting [11], acid hydrolysis [12], enzymatic pretreatment [13,14], and the introduction of charged groups through carboxymethylation [15] or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation [16].

After disintegration, MFC is typically obtained as a suspension in liquid, usually water. During homogenization, the suspension changes from a low viscosity to a high viscosity medium. Normally a 2 wt% fiber suspension is used for the preparation of MFC. At higher concentrations, the increased viscosity during processing becomes too high, such that the suspension cannot be moved forward by the pumping system. The MFC aqueous suspensions display a gel-like behavior as shown in Fig. 2.

The production of MFC from wood pulp and various non-wood sources has been reported in the literature. The morphology of constitutive nanoparticles is generally characterized using microscopic techniques. Fig. 3 shows MFC obtained from *Opuntia ficus-indica*. MFC consists of both individual and aggregated nanofibrils made of alternating crystalline and amorphous cellulose domains. Although image analysis can provide information on fibril width, it is more difficult to determine the length because of entanglement and difficulties in identifying both ends of individual nanoparticles. Indeed, the observation scale for length and

FIGURE 2

Picture of a 2 wt% microfibrillated cellulose aqueous suspension from eucalyptus, enzymatically pretreated. Reproduced with permission from [17]. Copyright 2012, Elsevier.

FIGURE 3

Transmission electron micrograph showing MFC obtained after high-pressure mechanical treatment of *Opuntia ficus-indica* fibers. Reproduced with permission from [18]. Copyright 2003, Elsevier.

FIGURE 4

Photograph of an aqueous dispersion of capim dourado cellulose nanocrystals (0.50 wt%) observed between cross-nicols showing the formation of birefringent domains. Reproduced with permission from [19], Copyright 2010, Springer.

diameter is quite different. The width is generally in the range 3–100 nm depending on the source of cellulose, defibrillation process and pretreatment and the length is considered to be higher than 1 μm [7].

Chemically induced destructuring strategy

A controlled strong acid hydrolysis treatment can be applied to cellulosic fibers allowing dissolution of amorphous domains and therefore longitudinal cutting of the microfibrils. The ensuing nanoparticles are generally called cellulose nanocrystals (CNCs) and are obtained as an aqueous suspension. When observed between crossed-Nicols the CNC dispersion shows the formation of birefringent domains (Fig. 4). During the acid hydrolysis process, the hydronium ions penetrate the cellulose chains in the amorphous regions promoting the hydrolytic cleavage of the glycosidic bonds and releasing individual crystallites after mechanical treatment (sonication). Different strong acids have been shown to successfully degrade cellulose fibers, but hydrochloric and sulfuric acids have been extensively used. However, phosphoric [20], hydrobromic [21,22] and nitric acids [23] have also been reported for the preparation of crystalline cellulosic nanoparticles. One of the main reasons for using sulfuric acid as hydrolyzing agent is its reaction with the surface hydroxyl groups via an esterification process allowing the grafting of anionic sulfate ester groups. The presence of these negatively charged groups induces the formation of a negative electrostatic layer covering the nanocrystals and promotes their dispersion in water. However, it compromises the thermostability of the nanoparticles [24]. To increase the thermal stability of H_2SO_4-prepared nanocrystals, neutralization of the nanoparticles by sodium hydroxide (NaOH) can be carried out [25].

These nanoparticles occur as high aspect ratio rod-like nanocrystals, or whiskers. Their geometrical dimensions depend on the origin of the cellulose substrate and hydrolysis conditions. Fig. 5 shows CNCs obtained from two different cellulosic sources. Each rod can be considered as a cellulose crystal with no apparent defect. CNCs generally present a relatively broad distribution in
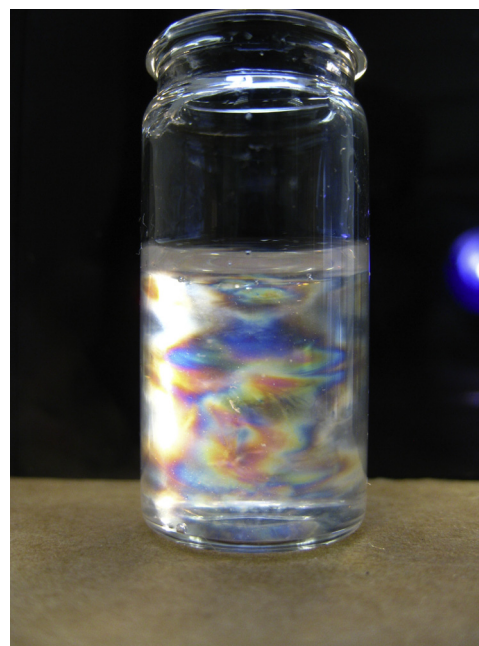
length because of the diffusion-controlled nature of the acid hydrolysis. The average length is generally of the order of a few hundreds nanometers and the width is of the order of a few nanometers [6]. An important parameter for CNCs is the aspect ratio, which is defined as the ratio of the length to the width. It varies between 10 for cotton [27] and 67 for tunicin [26] or capim dourado (golden grass) [19].

Acid hydrolysis is the classical way of preparing CNCs. However, other processes allowing the release of crystalline domains from cellulosic fibers have more recently been reported, including enzymatic hydrolysis treatment [28], TEMPO oxidation [29], hydrolysis with gaseous acid [30], and treatment with ionic liquids [31].

Mechanical properties of cellulose nanoparticles

Cellulose has been used by our society as an engineering material for thousands of years. However, even if cellulose confers its mechanical properties to higher plant cells, the mechanical properties of natural fibers are strongly influenced by many factors, particularly chemical composition and location in plants. Other factors that may affect the fiber properties are maturity, separating processes, microscopic and molecular defects such as pits and nods, type of soil and weather conditions under which they were grown. Further improved fibers and composites can be obtained by disintegrating the natural grown fibers, and separating the almost defect free highly crystalline fibrils.

The mechanical properties of cellulose microfibrils should be higher and less dispersed than those of lignocellulosic fibers from which they are released from because of a more homogeneous nature. Different strategies, both theoretical and experimental, have been used to determine the longitudinal modulus of cellulose microfibrils (or bundles) [7]. A broad range of values has been
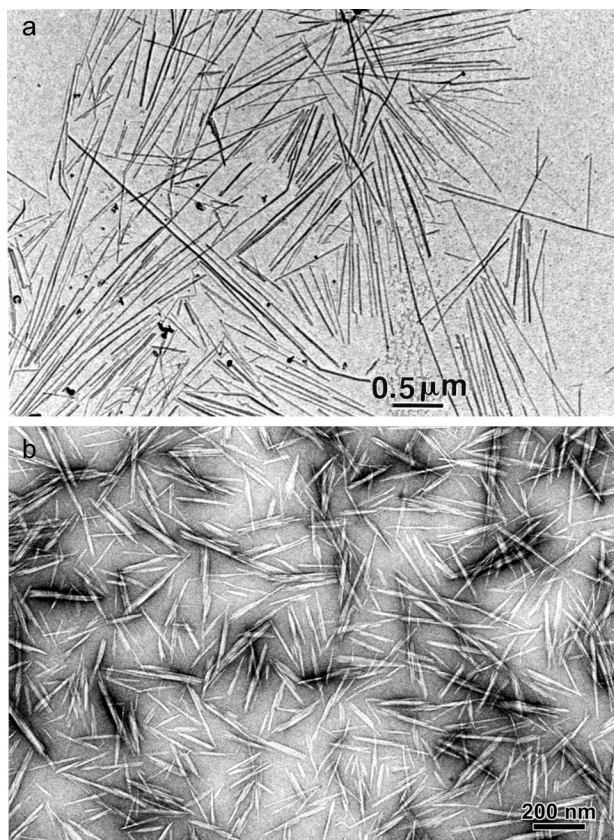
FIGURE 5

Transmission electron micrographs from a dilute suspension of (a) tunicin, and (b) ramie nanocrystals. Reproduced with permission from [26,25]. Copyright 2000, American Chemical Society, and copyright 2008, Royal Society of Chemistry.

reported. However, the average value is around 100 GPa, that is, much higher than for cellulose fibers.

The modulus of cellulose microfibrils is expected to result from a mixing rule between the modulus of the crystalline domains and the amorphous fraction. Therefore, it should be higher for more crystalline CNCs. Again a broad range of values was reported [7]. However, the average value is around 130 GPa, that is, much higher than for cellulose microfibrils as expected.

These impressive mechanical properties make cellulose nanoparticles ideal candidates for the processing of reinforced polymer composites. The Young's modulus of nanocellulose with a density for crystalline cellulose of around 1.5–1.6 g cm^{-3} is much higher than the one of glass fibers, around 70 GPa [32] with a density around 2.6 g cm^{-3}, which are classically used in composite applications. It is similar to Kevlar (60–125 GPa, density around 1.45 g cm^{-3}) [33] and potentially stronger than steel (200–220 GPa, density around 8 g cm^{-3}) [34]. Indeed, the specific Young's modulus, which is the ratio between the Young's modulus and the density, of nanocellulose is around 65 J g^{-1} for microfibrils and 85 J g^{-1} for nanocrystals whereas it is around 25 J g^{-1} for steel.

Processing of polymer nanocomposites

Cellulose nanoparticles have a strong tendency for self-association because of the omnipresence of interacting surface hydroxyl groups. This property, which is the basis of the strength of paper sheets, is a desirable feature for the formation of load-bearing percolating architectures within the host polymer matrix. However, these inter-particle interactions can cause aggregation during the preparation of the nanocomposite thus inducing the loss of the nanoscale and limit the potential of mechanical reinforcement. This aggregation phenomenon is magnified when the specific surface area increases and then when the size of the particle decreases. Different strategies have been reported in the literature to homogeneously mix cellulose nanoparticles with a polymeric matrix. These different strategies are summarized in Fig. 6 and detailed information can be found elsewhere [35].

Because of the good dispersion level of cellulose nanoparticles in water, it is obviously the most suitable processing medium. Both water-soluble polymers and polymer aqueous dispersions (latex) can be used. After mixing the cellulose nanoparticle dispersion with the polymer solution/dispersion, a solid nanocomposite film can be obtained by simple casting and water evaporation. This mode of processing allows the preservation of the individualization state
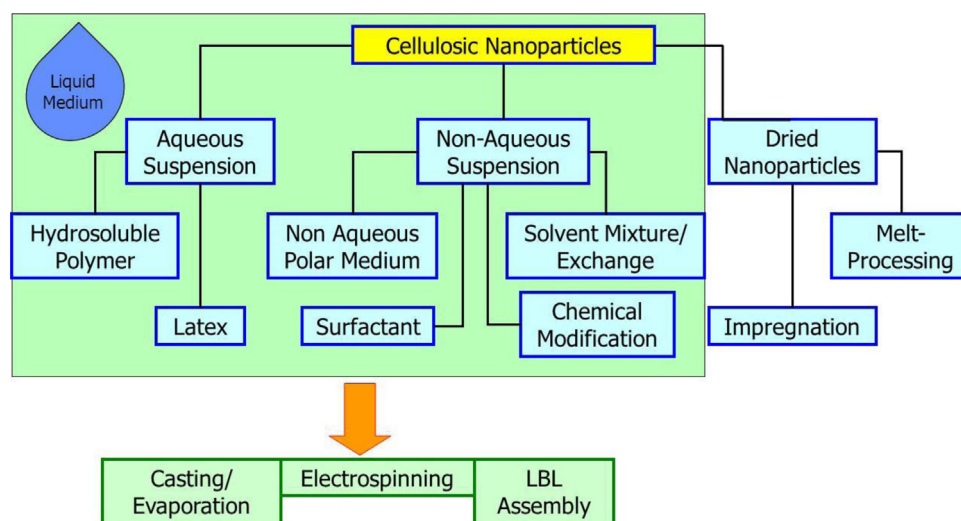
FIGURE 6

The different strategies applied for the processing of nanocellulose reinforced polymer nanocomposites.

of the nanoparticles resulting from their colloidal dispersion in water. A copolymer of styrene and butyl acrylate (poly(S-co-BuA)) in latex form and tunicin nanocrystals were used in the pioneering work [36].

Water has been extensively used as a processing medium but stable suspensions of CNCs with negatively charged surface groups, commonly produced by hydrolysis of the native cellulose with sulfuric acid, can be obtained in various polar liquid media. For instance, stable CNC suspensions have been prepared in N,N-dimethyl sulfoxide (DMF) [37], dimethyl sulfoxide (DMSO), N-methyl pyrrolidine (NMP), formic acid and m-cresol [38]. Casting from a mixture of solvents can also be used to prepare nanocellulose-reinforced nanocomposites. By this method, the aqueous suspension of nanoparticles is mixed with a polymer solution involving a solvent miscible with water, for example, tetrahydrofuran (THF) [39]. A solvent exchange procedure can be applied to suspend cellulosic nanoparticles in the proper liquid medium for further surface chemical modification, or mixing with a polymer solution or monomer for subsequent *in situ* polymerization [40]. The aqueous suspension is progressively solvent exchanged in

liquids of decreasing polarity by several successive centrifugation and redispersion operations, using sonication after each solvent exchange step to avoid aggregation. Acetone is routinely used for the first solvent exchange step.

Stable cellulose nanoparticle dispersions in apolar or low polarity solvent can be obtained by physically coating the surface with a surfactant [41,42] or chemically grafting apolar moieties onto the surface. Both methods allow the tuning of the surface and a decrease of the surface energy of the nanoparticle. The surface chemical modification of cellulose nanoparticles obviously involves the ample surface hydroxyl groups resulting from their nanoscale dimensions and ensuing high surface area. Experimental conditions should avoid swelling media and the peeling effect of surface-grafted chains inducing their dissolution in the reaction medium. Therefore, the chemical grafting process has to be mild to preserve the integrity of the nanoparticle. The most common surface chemical modifications of CNCs are summarized in Fig. 7. They can be categorized into three distinctive groups, namely (1) substitution of hydroxyl groups with small molecules (as indicated with red arrows in Fig. 7), (2) polymer grafting based
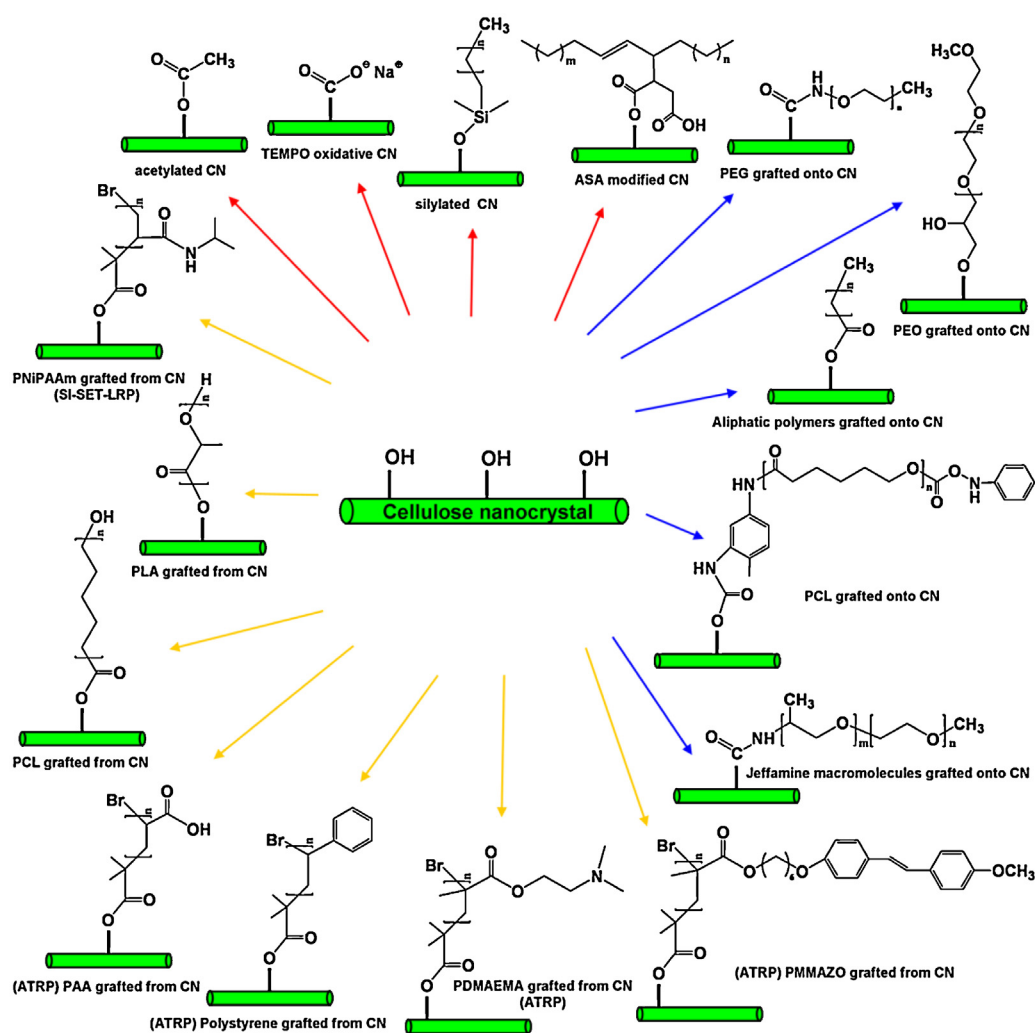

FIGURE 7

Common surface covalent chemical modifications of cellulose nanocrystals. PEG: poly(ethylene glycol); PEO: poly(ethylene oxide); PLA: poly(lactic acid); PAA: poly(acrylic acid); PNiPAAm: poly(*N*-isopropylacrylamide); PDMAEMA: poly(*N*,*N*-dimethylaminoethyl methacrylate). Reproduced with permission from [3]. Copyright 2012, Royal Society of Chemistry.

on the 'grafting onto' strategy with different coupling agents (as indicated with blue arrows in Fig. 7), and (3) polymer grafting based on the 'grafting from' approach with a radical polymerization involving ring opening polymerization (ROP), atom transfer radical polymerization (ATRP) and single-electron transfer living radical polymerization (SET-LP) (as indicated with yellow arrows in Fig. 7). The chemically modified nanoparticles can be dispersed in organic liquids of low polarity and mixed with a polymer solution or eventually directly added into the polymer melt after drying. However, two conflicting effects arise from this procedure. On the one hand, it allows an improvement in the dispersion of the modified nanoparticles in the continuous apolar medium which is beneficial to optimize the mechanical properties of the ensuing nanocomposite. On the other hand, it restricts the interactions between nanoparticles through hydrogen-bonding which is the basis of the outstanding mechanical properties of nanocellulose based nanocomposites.

The previous processing techniques used mainly a liquid as the processing medium and are mainly restricted to wet processing methods such as casting/evaporation, which has been extensively used. The main advantage of this strategy relies in the fact that it allows preserving the dispersion state of the nanoparticles in the liquid. However, it limits the number of polymer matrices that can be used in association with cellulose nanoparticles. Moreover, this procedure is both non-industrial and non-economic. It should be used for niche applications. Several organizations have announced nanocellulose demonstration plants [7]. Therefore, more industrial nanocomposite processing techniques should be developed. Melt-compounding techniques, such as extrusion or injection molding, are commonly used to process thermoplastic polymers. They are 'green' (solvent-free), and industrially and economically viable. However, these conventional processing techniques are infrequently employed for the preparation of cellulose nanoparticle reinforced polymer nanocomposites. This is ascribed to inherent incompatibility and thermal stability issues. 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 nanoparticles. Few solutions have been proposed to address this challenge. A glance at the literature shows the different strategies [38].

Mechanical properties of polymer nanocomposites

Outstanding mechanical properties can be obtained by blending nanocellulose and a polymer matrix even at low filler loading [7,36]. Such properties originate from the high stiffness of crystalline cellulose that provides the strength to higher plants, the nanoscale dimensions and high aspect ratio of the nanoparticles, and the high reactivity of cellulose. In suitable conditions, a mechanically percolating stiff network of nanoparticles can form within the polymer matrix that supports the mechanical solicitation. The formation of this network is conditioned by the homogeneous dispersion of the filler, the percolation threshold that depends on the aspect ratio of the nanoparticles, and the strength of the filler/filler interactions. This mechanical percolation phenomenon has been extensively reported in the literature [46–48]. The stiffness of the percolating CNC was found to increase with the aspect ratio of the nanocrystals [46]. It therefore means that the use of higher aspect ratio CNC is more interesting from a

mechanical point of view because it first induces a decrease of the critical percolation threshold and also stiffens the formed continuous network.

In these conditions, the host polymeric matrix does not play any role in the mechanical stiffness of the material. It corresponds to the highest mechanical reinforcement effect that can be obtained from these nanoparticles. However, many parameters can affect this phenomenon [44]. When the formation of this percolating nanoparticle network is inhibited, only the high stiffness of crystalline cellulose, nanoscale dimensions, high aspect ratio and dispersion of the nanoparticles, and filler/matrix interactions are involved in the reinforcing phenomenon.

Optical properties of nanocellulose films

The optical properties of nanocellulose films can be investigated by determining the regular light transmittance with a UV-visible spectrometer. Measurements are performed in the wavelength range 200–1000 nm. The regular light transmittance at 600 nm wavelength, which is in the middle of the visible wavelength range, is generally reported [47].

Films made only from MFC can be optically transparent if the cellulose nanofibers are densely packed, and the interstices between the fibers are small enough to avoid light scattering [48]. However, it was shown that mechanical compression performed on freeze-dried MFC did not result in transparency (Fig. 8). It was suggested that the nanofibers were deformed under load but recovered after unloading, and the spaces created resulted in light scattering. Films prepared by slow filtration, drying and compression were much more densely packed, and were not optically transparent but translucent (Fig. 8), probably because of surface light scattering. The films formed by filtration, presented a high transparency thanks to a polishing step with emery paper. The transparency of the MFC sheet (thickness 55 μm) reached 71.6% at a wavelength of 600 nm (Fig. 8). The transmittance at 600 nm of softwood and hardwood TEMPO-oxidized MFC films was found to be around 90% and 78%, respectively [49]. The lower light transmittance of hardwood cellulose was ascribed to the presence of xylan that was supposed to interfere in part with complete dispersion of the nanofibrils in water.

Owing to their anisotropic rod-like morphology, CNCs display a specific property. In suspension, these nanoparticles have a
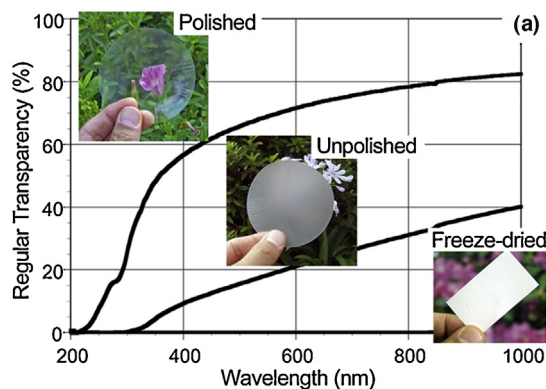

FIGURE 8

Light transmittance of microfibrillated cellulose films. Reproduced with permission from [48]. Copyright 2009, WILEY-VCH Verlag GmbH & Co. KGaA.
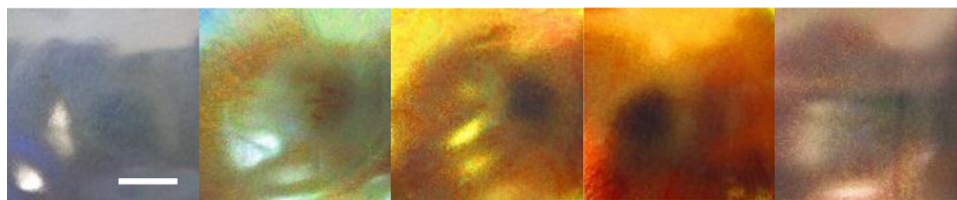
FIGURE 9

Cellulose nanocrystal films produced from suspensions treated with increasing applied ultrasonic energy (0, 250, 700, 1800, and 7200 J g^{-1} of CNC) from left to right. Viewing is normal to the film surface under diffuse lighting. Scale marker 1 cm. Samples of CNC suspension were sonicated using a Sonics vibra-cell 130 W 20 kHz ultrasonic processor with a 6 mm diameter probe: typically, 15 mL of a 2–3 wt% CNC suspension was placed in a 50 mL plastic tube and sonicated at 60% of the maximum power. Prolonged sonication (to an energy input of over 3600 J/g CNC) was performed in an ice bath to prevent desulfation caused by heating of the suspension. Reproduced with permission from [53]. Copyright 2011, American Chemical Society.

lyotropic liquid crystalline behavior, that is, a phase transition from an isotropic liquid to an ordered liquid crystal when changing the concentration [50–52]. Indeed, above a given concentration, a chiral nematic phase forms. Under certain conditions, the suspension may be slowly evaporated to obtain semi-translucent films that maintain the chiral nematic liquid crystal order formed in the suspension. These films exhibit iridescence reflecting polarized light in a narrow wavelength range determined by the chiral nematic pitch and the refractive index of the film. These optical properties are likely to generate new applications for CNC films.

Ultrasound treatment was found to increase the chiral nematic pitch in suspension and red-shift the reflection wavelength of CNC films as the applied energy increased [53]. Fig. 9 shows solid films cast from aliquots of 2.8 wt% CNC suspensions prepared by sulfuric acid hydrolysis from bleached softwood kraft pulp and sonicated with increasing (left to right) energy inputs. The energy was measured in J g^{-1} of CNC. The films exhibit reflected iridescence with colors ranging from blue-violet to red. By combining sonication and electrolyte addition the reflective properties of the film can be predictably tuned. The effects of sonicating a CNC suspension were shown to be cumulative and permanent. Moreover, suspensions sonicated with different energy inputs can be mixed to prepare films having a reflection band intermediate between those obtained from the individual suspensions. It was suggested that the ultrasound-induced red-shift is electrostatic in nature.

Barrier properties of nanocellulose films

There is an increasing interest in the barrier properties of nanocellulose films or related nanocomposites due to increased tortuosity provided by nanoparticles. Indeed, because of their small size, the surface-to-volume ratio of the nanoparticles is significantly greater than that for microparticles [17]. Most materials used for food packaging are practically non-degradable petrochemical based polymers, representing a serious environmental problem. The main reason for their use is due to their easiness of processability, low cost and excellent barrier properties. Barrier properties using bio-based materials are becoming increasingly desirable in our society to develop environmentally friendly efficient materials in different applications. Moreover, the low permeability of cellulose can be enhanced by the highly crystalline nature of cellulose nanoparticles and their ability to form a dense percolating network. Provided that strong particle-polymer molecular interactions exist, the smaller particles have a greater

ability to bond to the surrounding polymer material, thereby reducing the chain segmental mobility and thus the penetrant diffusivity.

Cellulose is a hydrophilic polymer and it obviously absorbs water when immersed in liquid water or conditioned in moist atmosphere. However, the water vapor permeability is decreased when the cellulose fibers are disintegrated to the nanoscale level [55]. Moreover, the sensitivity to moisture of the nanoparticles can be tuned via pre-treatment before homogenization [55,56] or post-treatment (polymer impregnation [54,57], or chemical grafting [58,59]).

The gas permeability is also reduced in dry atmospheres when decreasing the size of the cellulosic particles because of the crystalline and dense structure of the nanoparticle film [60,61]. However, this property is lost in moist atmosphere [62]. To improve the gas barrier properties of nanocellulose films at high relative humidity (RH) level, hybrid clay-MFC films can be prepared [63,64] or chemical modification of the nanoparticles can be performed [59]. Coating of polymer films with MFC layers has also been investigated as a new way to produce good barrier materials and as possible solution to retain the advantages of both cellulosic nanoparticles and polymers [49,65]. Whatever the treatment or the experimental conditions used to produce nanocellulose, it is seen as a new biomaterial for the creation of a good barrier for food packaging. Nanocomposite films extend food shelf-life, and also improve food quality as they can serve as carriers for active substances such as antioxidants and antimicrobials [66].

Conclusion

There has been an explosion of interest in the use of biomass as a source of renewable energy and materials. Despite being the most available natural polymer on earth, it is only quite recently that cellulose has gained prominence as a nanostructured material, in the form of nanocellulose. This term covers the range of materials derived from cellulose with at least one dimension in the nanometer range. It mainly consists of chemically (cellulose nanocrystals – CNCs) or mechanically extracted nanoparticles (microfibrillated cellulose – MFC). After intensive research, several initiatives have emerged in the perspective of producing nanocellulose on a large scale. Nanocellulose-based materials are carbon-neutral, sustainable, recyclable and non-toxic. They thus have the potential to be truly green nanomaterials, with many useful and unexpected properties.

References

[1] D. Fengel, G. Wegener, Wood: Chemistry, Ultrastructure, Reactions, Walter de Gruyter, 1984.

[2] R.J. Moon, McGraw-Hill Yearbook in Science & Technology, McGraw-Hill, 2008, pp. 225–228.

[3] N. Lin, J. Huang, A. Dufresne, Nanoscale 4 (2012) 3274–3294.

[4] M.A.S. Azizi Samir, F. Alloin, A. Dufresne, Biomacromolecules 6 (2005) 612–626.

[5] S.J. Eichhorn, et al. J. Mater. Sci. 45 (2010) 1–33.

[6] R.J. Moon, et al. Chem. Soc. Rev. 40 (2011) 3941–3994.

[7] A. Dufresne, Nanocellulose: From Nature to High Performance Tailored Materials, Walter de Gruyter GmbH & Co. KG, 2012.

[8] A.N. Nakagaito, H. Yano, Appl. Phys. A: Mater. Sci. Process. 78 (2004) 547–552.

[9] Ø. Eriksen, K. Syverud, Ø. Gregersen, Nord. Pulp Paper Res. 23 (2008) 299–304.

[10] T. Zimmermann, N. Bordeanu, E. Strub, Carbohydr. Polym. 79 (2010) 1086–1093.

[11] F.W. Herrick, et al. J. Appl. Polym. Sci. Polym. Symp. 37 (1983) 797–813.

[12] A. Boldizar, et al. Int. J. Polym. Mater. 11 (1987) 229–262.

[13] M. Henriksson, et al. Eur. Polym. J. 43 (2007) 3434–3441.

[14] M. Pääkkö, et al. Biomacromolecules 8 (2007) 1934–1941.

[15] L. Wågberg, et al. Langmuir 24 (2008) 784–795.

[16] A. Isogai, T. Saito, H. Fukuzumi, Nanoscale 3 (2011) 71–85.

[17] N. Lavoine, et al. Carbohydr. Polym. 90 (2012) 735–764.

[18] M. Malainine, et al. Carbohydr. Polym. 51 (2003) 77–83.

[19] G. Siqueira, et al. Cellulose 17 (2010) 289–298.

[20] T. Okano, et al. Nisshin Oil Mills Ltd. Patent JP 98/151052.

[21] S.Y. Lee, et al. Fibers Polym. 10 (2009) 77–82.

[22] I. Filpponen, D.S. Argyropoulos, Biomacromolecules 11 (2010) 1060–1066.

[23] D. Liu, et al. Bioresource Technol. 101 (2010) 2529–2536.

[24] M. Roman, W.T. Winter, Biomacromolecules 5 (2004) 1671–1677.

[25] Y. Habibi, et al. J. Mater. Chem. 18 (2008) 5002–5010.

[26] M.N. Anglès, A. Dufresne, Macromolecules 33 (2000) 8344–8353.

[27] T. Ebeling, et al. Langmuir 15 (1999) 6123–6126.

[28] G. Siqueira, et al. Cellulose 17 (2010) 1147–1158.

[29] M. Hirota, et al. Cellulose 17 (2010) 279–288.

[30] E. Kontturi, UPM-Kymmene Corporation. Patent WO2011/114005.

[31] Z. Man, et al. J. Polym. Environ. 19 (2011) 726–731.

[32] F.T. Wallengberg, J.C. Watson, H. Li, ASM Handbook, Vol. 21: Composites, 2001, 27–34.

[33] W.Y. Yeh, R.J. Young, Polymer 40 (1999) 857–870.

[34] J. Lemaitre, et al., Mécanique des Matériaux, 3rd ed., Dunod, 2009.

[35] A. Dufresne, Int. Polym. Proc. 27 (2012) 557–564.

[36] V. Favier, et al. Polym. Adv. Technol. 6 (1995) 351–355.

[37] M.A.S. Azizi Samir, et al. Macromolecules 37 (2004) 1386–1393.

[38] O. Vand den Berg, J.R. Capadona, C. Weder, Biomacromolecules 8 (2007) 1353–1357.

[39] M. Schroers, A. Kokil, C. Weder, J. Appl. Polym. Sci. 93 (2004) 2883–2888.

[40] G. Siqueira, J. Bras, A. Dufresne, Biomacromolecules 10 (2009) 425–432.

[41] L. Heux, G. Chauve, C. Bonini, Langmuir 16 (2000) 8210–8212.

[42] I. Kvien, B.S. Tanem, K. Oksman, Biomacromolecules 6 (2005) 3160–3165.

[44] A. Dufresne, J. Nanosci. Nanotechnol. 6 (2006) 322–330.

[46] J. Bras, et al. Carbohydr. Polym. 84 (2011) 211–215.

[47] S. Iwamoto, A.N. Nakagaito, H. Yano, Appl. Phys. A: Mater. Sci. Process. 89 (2007) 461–466.

[48] M. Nogi, et al. Adv. Mater. 21 (2009) 1595–1598.

[49] H. Fukuzumi, et al. Biomacromolecules 10 (2009) 162–165.

[50] R.H. Marchessault, F.F. Morehead, N.M. Walter, Nature 184 (1959) 632–633.

[51] J.F. Revol, et al. Liq. Cryst. 16 (1994) 127–134.

[52] X.M. Dong, et al. Langmuir 12 (1996) 2076–2082.

[53] S. Beck, J. Bouchard, R. Berry, Biomacromolecules 12 (2011) 167–172.

[54] K. Spence, et al. Cellulose 17 (2010) 835–848.

[55] M. MInelli, et al. J. Membr. Sci. 358 (2010) 67–75.

[56] K. Spence, et al. Cellulose 18 (2011) 1097–1111.

[57] K. Spence, et al. Bioresources 6 (2011) 4370–4388.

[58] G. Rodionova, et al. Cellulose 18 (2011) 127–134.

[59] L.C. Tomé, et al. Cellulose 17 (2010) 1203–1211.

[60] K. Syverud, P. Stenius, Cellulose 16 (2009) 75–85.

[61] S. Belbekhouche, et al. Carbohydr. Polym. 83 (2011) 1740–1748.

[62] C. Aulin, M. Gällstedt, T. Lindström, Cellulose 17 (2010) 559–574.

[63] A. Liu, et al. Biomacromolecules 12 (2011) 633–641.

[64] A. Liu, L.A. Berglund, Carbohydr. Polym. 87 (2012) 53–60.

[65] S. Fujisawa, et al. Carbohydr. Polym. 84 (2011) 579–583.

[66] M. Andresen, et al. Biomacromolecules 8 (2007) 2149–2155.

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