

# Polymer nanocomposites reinforced with nanoparticles extracted from renewable resources

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## ABSTRACT

There has been an explosion of interest in the use of biomass as a source of renewable energy and materials. One focus of this activity has followed from the recognition that, by suitable chemical and mechanical treatments, it is possible to produce fibrous materials with one or two dimensions in the nanometer range from many naturally occurring sources of cellulose. The term nanocellulose is used to cover the range of materials derived from cellulose with at least one dimension in the nanometer range. Owing to its hierarchical structure and semicrystalline nature, nanoparticles can be extracted from naturally occurring cellulose using a top-down mechanically- or chemically-induced deconstructing strategy.

**Keywords:** nanocellulose, nanocomposite, cellulose nanocrystal, nanofibrillated cellulose, starch nanocrystal

## 1 MECHANICAL SHEARING

Multiple mechanical shearing actions applied to cellulosic fibers release more or less individually the microfibrils. This material is usually called nanofibrillated cellulose (NFC). Production of NFC from wood pulp and various non-wood sources has been reported in the literature. This production route is normally connected to high energy consumptions associated with the fiber delamination. Therefore different pretreatments have been proposed to limit this high-energy input, e.g. mechanical cutting, acid hydrolysis, enzymatic treatment, and introduction of charged groups e.g. through carboxymethylation or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation.

The morphology of constitutive nanoparticles is generally characterized using microscopic techniques. Figure 1a shows NFC obtained from *Opuntia ficus-indica*. NFC 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 diameter are 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  $\mu\text{m}$ .

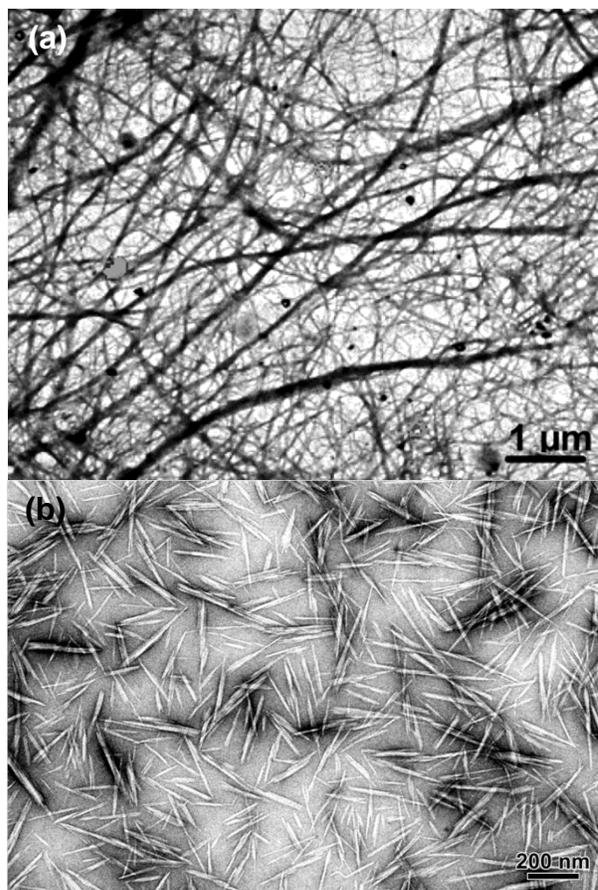


Figure 1: TEM from a dilute suspension of (a) NFC obtained after high-pressure mechanical treatment of *opuntia ficus-indica* fibers [1], and (b) CNC after acid hydrolysis of ramie fibers [2].

## 2 ACID HYDROLYSIS

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). These nanoparticles occur as high aspect ratio rod-like nanocrystals, or

whiskers. Their geometrical dimensions depend on both the origin of the cellulose substrate and hydrolysis conditions. Roughly, the length of these nanorods ranges between 100 nm and 1  $\mu\text{m}$ , and the diameter is within the range 5-20 nm. Figure 1b shows CNC obtained from ramie fibers. The rod-like nanocrystals from ramie exhibit an average diameter of 6-8 nm and a length of about 150-250 nm.

Starch can also be used to prepare highly crystalline nanoparticles. However, owing to its different function in nature they occur as platelet-like nanoparticles. Figure 2 shows transmission electron micrograph obtained from dilute suspensions of waxy maize starch nanocrystals prepared by  $\text{H}_2\text{SO}_4$  hydrolysis, respectively. They consist of 5-7 nm thick platelet-like particles with a length ranging from 20 to 40 nm and a width in the range 15-30 nm. Marked 60-65° acute angles were observed.

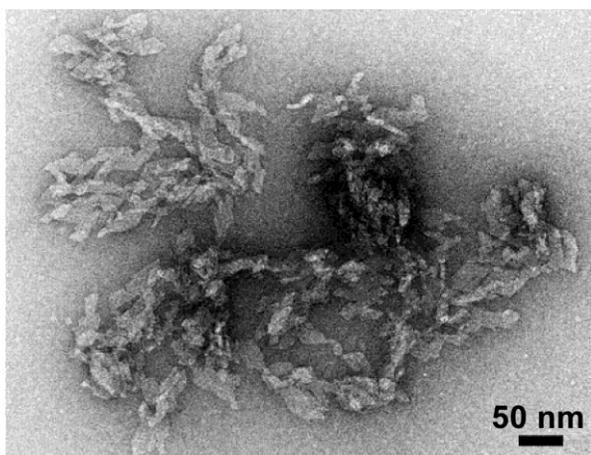


Figure 2: TEM from a dilute suspension of starch nanocrystals obtained by acid hydrolysis of waxy maize starch granules [3].

### 3 POLYMER NANOCOMPOSITES

The potential of these nanoparticles has been proved for special functional nanomaterials [4] but it is as a biobased reinforcing nanofiller that they have attracted significant interest during the last 20 years [5-8]. With a Young's modulus in the range 100-130 GPa and a surface area of several hundred  $\text{m}^2\cdot\text{g}^{-1}$ , promising properties can be considered for these nanoparticles [9]. These impressive mechanical properties make cellulose nanoparticles ideal candidate for the processing of reinforced polymer nanocomposites.

#### 3.1 Processing

Because of the good dispersion level of polysaccharide nanoparticles in water, it is obviously the most suitable processing medium. Both water-soluble polymers and polymer aqueous dispersions (latex) have been extensively used. Stable nanoparticle dispersions in apolar or low polarity solvent can be obtained by physically coating the

surface with a surfactant or chemically grafting apolar moieties onto the surface. Both methods allow tuning the surface and decreasing the surface energy of the nanoparticle. However, two conflicting effects arise from this last procedure. On the one hand, it allows improving 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 polysaccharide based nanocomposites.

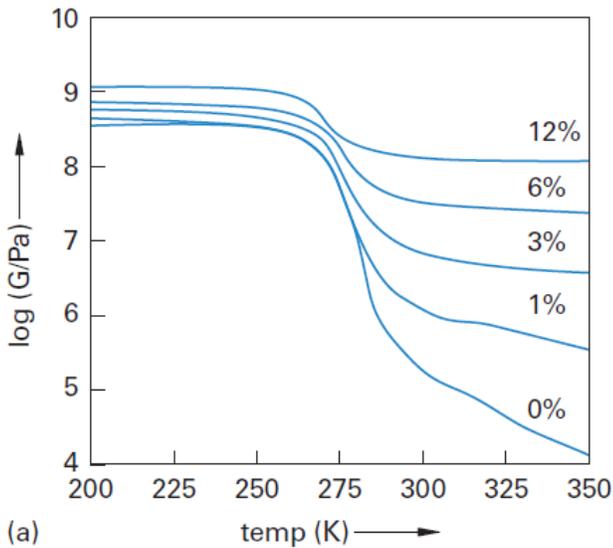
Melt-compounding techniques, such as extrusion or injection molding, are commonly used to process thermoplastic polymers. They are "green" (solvent-free), and industrially and economically viable. However, these conventional processing techniques are infrequently employed for the preparation of polysaccharide nanoparticle reinforced polymer nanocomposites. This is ascribed to inherent incompatibility and thermal stability issues. The hydrophilic nature of polysaccharides 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.

#### 3.2 Mechanical Properties

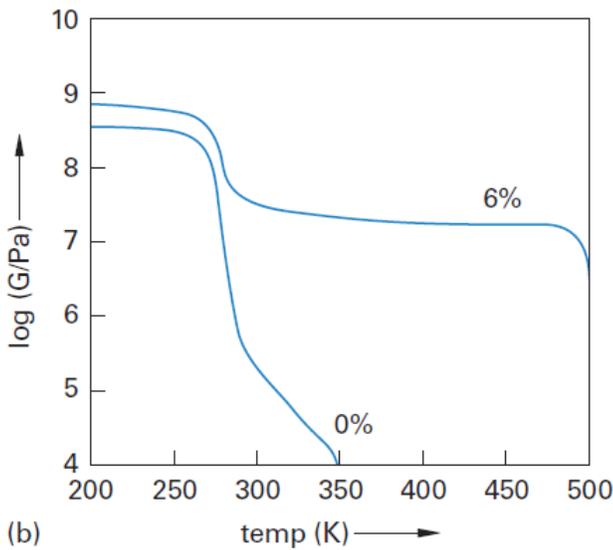
Outstanding mechanical properties can be obtained by blending polysaccharide nanoparticles and polymer matrix even at low filler loading [8]. It originates from the high stiffness of crystalline cellulose that provides the strength to higher plants, nanoscale dimensions and high aspect ratio of the nanoparticles, 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 strength of the filler/filler interactions.

A copolymer of styrene and butyl acrylate (poly(S-co-BuA)) in latex form and tunicin nanocrystals were used in the pioneering work [10]. The reinforcing effect of the nanoparticles was accessed by dynamic mechanical analysis (DMA) experiments in the shear mode (Figure 3). The authors measured a spectacular improvement in the storage modulus after adding tunicin nanocrystals into the host polymer even at low contents. This increase was especially significant above the glass-rubber transition temperature of the thermoplastic matrix because of its poor mechanical properties in this temperature range. In the rubbery state of the thermoplastic matrix, the modulus of the composite with a loading level as low as 6 wt%, i.e. 4 vol%, was more than two order of magnitude higher than the one of the unfilled matrix. Moreover, the introduction of 3 wt% or more cellulosic nanocrystals provided an outstanding

thermal stability of the matrix modulus up to the temperature at which cellulose started to degrade (500K).



(a)



(b)

Figure 3: Logarithm of the storage shear modulus as a function of temperature for poly(S-co-BuA) reinforced with tunicin CNC. Panel a shows the reinforcing effect obtained for various nanocrystal contents and panel b shows the improvement of the thermal stability of the matrix [10].

This mechanical percolation phenomenon has been extensively reported in the literature. The stiffness of the percolating CNC network was found to increase with the aspect ratio of the nanocrystals [11]. 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 on 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. 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.

### 3.3 Optical Properties

Films made only from NFC can be optically transparent if the cellulose nanofibers are densely packed, and the interstices between the fibers are small enough to avoid light scattering. Moreover, owing to their anisotropic rod-like morphology, CNCs display a specific property. In suspension, these nanoparticles have a lyotropic liquid crystalline behavior, i.e. a phase transition from an isotropic liquid to an ordered liquid crystal when changing the concentration. Indeed, above a given concentration, a chiral nematic phase forms. This is illustrated in Figure 4.

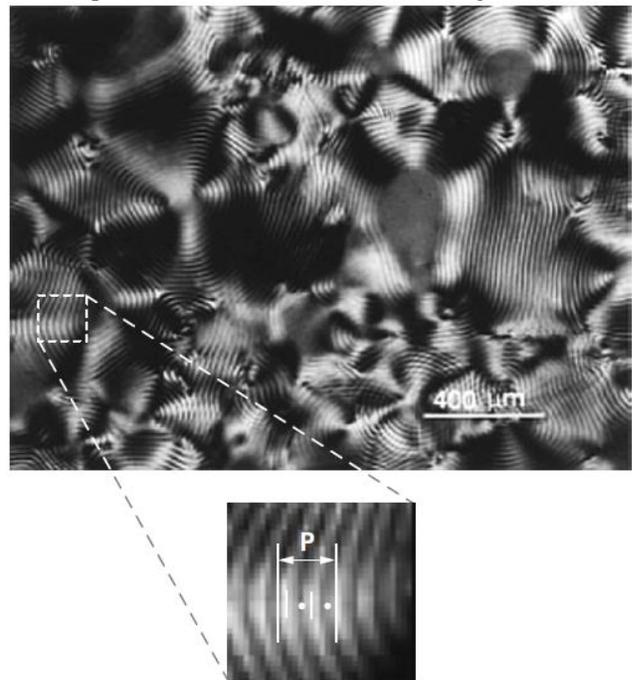


Figure 4: Chiral nematic liquid crystal texture of the anisotropic phase of a cotton CNC suspension viewed in a polarizing microscope. The nanocrystals lie parallel to the plane of the page in the light regions and perpendicular in the dark regions [8].

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.

### 3.4 Barrier Properties

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 for microparticles. 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 advisable in our society to develop environmentally friendly efficient material in different applications. Moreover, the low permeability of cellulose can be enhanced by the highly crystalline nature of cellulose nanoparticles and 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.

Polysaccharides are hydrophilic polymers and they obviously absorb 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. Moreover, the sensitivity to moisture of the nanoparticles can be tuned by performing pretreatment prior to homogenization or post-treatment (polymer impregnation, or chemical grafting).

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

## 4 CONCLUSIONS

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 (nanofibrillated cellulose - NFC). After intensive research, several initiatives have emerged in the perspective of producing nanocellulose at 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] M.E. Malainine, M. Mahrouz and A. Dufresne, *Carbohydr. Polym.* 51, 77, 2003.
- [2] Y. Habibi, A.L. Goffin, N. Schiltz, E. Duquesne, P. Dubois and A. Dufresne, *J. Mater. Chem.* 18, 5002, 2008.
- [3] H. Angelier, L. Choisnard, S. Molina-Boisseau, P. Ozil and A. Dufresne, *Biomacromolecules* 5, 1545, 2004.
- [4] N. Lin, J. Huang and A. Dufresne, *Nanoscale* 4, 3274, 2012.
- [5] M.A.S. Azizi Samir, F. Alloin and A. Dufresne, *Biomacromolecules* 6, 612, 2005.
- [6] S.J. Eichhorn et al., *J. Mater. Sci.* 45, 1, 2010.
- [7] R.J. Moon, A. Martini, J. Nairn, J. Simonsen and J. Youngblood, *Chem. Soc. Rev.* 40, 3941, 2011.
- [8] A. Dufresne, "Nanocellulose: From Nature to High Performance Tailored Materials", Walter de Gruyter GmbH & Co. KG, 2012.
- [9] A. Dufresne, *Mater. Today* 16, 220, 2013.
- [10] V. Favier, G.R. Canova, J.Y. Cavaillé, H. Chanzy, A. Dufresne and C. Gauthier, *Polym. Adv. Technol.* 6, 351, 1995.
- [11] J. Bras, D. Viet, C. Bruzzese and A. Dufresne, *Carbohydr. Polym.* 84, 211, 2011.