



Cellulose nanomaterial reinforced polymer nanocomposites



Alain Dufresne

Univ. Grenoble Alpes, CNRS, Grenoble INP, LGP2, F-38000, Grenoble, France

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ABSTRACT

Several forms of cellulose nanomaterials, notably cellulose nanocrystals and cellulose nanofibrils, exhibit attractive properties and are potentially useful for a large number of industrial applications. These include the paper and cardboard industry, use as reinforcing filler in polymer nanocomposites, basis for low-density foams, additive in adhesives and paints, as well as a wide variety of filtration, electronic, food, hygiene, cosmetic, and medical products. This entry focuses on cellulose materials as filler in polymer nanocomposites. The ensuing mechanical properties obviously depend on the type of nanomaterial used, but the crucial point is the processing technique. The emphasis is on the melt processing of such nanocomposite materials that has not yet been properly resolved and remains a challenge.

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1. Introduction

There is an explosion of interest in the use of biomass as a source of renewable energy and materials. A promising source of biomass is cellulose, the most abundant polymer on Earth, which has been used for centuries in highly diverse applications. A recent 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 any naturally occurring sources of cellulose. The terms “nanocellulose” or “cellulose nanomaterial” are now used to cover the range of materials derived from cellulose with at least one dimension in the nanometer range. This material has been described as a new ageless bionanomaterial [14], as it exists in nature since the dawn of time but was only extracted rather recently. Isolation of crystalline cellulosic regions, in the form of monocrystals, by an acid hydrolysis process was first reported in 1947 [30]. The first report on the mechanical deconstruction of cellulose fibers was published latter in 1983 in two companion papers [20,33]. Nanocellulose-based materials have a low carbon footprint, are sustainable, renewable, recyclable, and nontoxic; they thus have the potential to be truly green nanomaterials with many useful and unexpected properties. How not to love them?

With a Young's modulus in the range 100–130 GPa and a surface area of several hundred $\text{m}^2\cdot\text{g}^{-1}$, new promising properties can be considered for cellulose. The potential of this nanomaterial has been proved for special functional nanomaterials [21] but it is as a biobased reinforcing nanofiller that it has attracted significant interest during

the last 20 years [5,13,15,27]. Indeed, nanocomposites show unique properties, because of the nanometric size effect, compared to conventional composite even at low filler content. Nanofillers have strong reinforcing effects and studies have also shown their positive impact in barrier packaging. However, the processing of the material plays a crucial role since it determines its morphology (spatial arrangement of the phases).

2. Cellulose nanomaterials

The possibility for preparing nanomaterials or nanoparticles from cellulose or other polysaccharides such as chitin or starch results from a common feature, viz. 1) they are semicrystalline polymers, and 2) they display a hierarchical multiscale nanostructure. After purification, nanoparticles can be extracted from these naturally occurring polymers mainly using a top-down mechanically- or chemically-induced deconstructing strategy. Even if considered as cellulose nanomaterial, bacterial cellulose results from a different strategy since it involves a bottom-up procedure, and will consequently not be addressed in this entry.

2.1. Cellulose nanofibrils

The mechanically-induced deconstruction strategy consist in applying severe multiple mechanical shearing actions to a cellulosic fiber slurry to release more or less individually the constitutive microfibrils. Different shearing equipments such as homogenizer, microfluidizer or ultra-fine friction grinder are generally used. This material is usually called microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC) or cellulose nanofibrils (CNF) and is obtained as an aqueous suspension.

E-mail address: alain.dufresne@pagora.grenoble-inp.fr.

Recently, TAPPI (Technical Association of the Pulp and Paper Industry) has proposed to standardize the terminology (Standard Terms and Their Definition for Cellulose Nanomaterial WI 3021) and below a given degree of deconstruction, the term CNF should be used.

This production route is normally associated to high energy consumptions for fiber delamination and different pretreatments have been therefore proposed to facilitate this process, e.g. mechanical cutting, acid hydrolysis, enzymatic pretreatment, and introduction of charged groups through carboxymethylation or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation. CNF appears as flexible filaments consisting of both individual and aggregated nanofibrils made of alternating crystalline and amorphous cellulose domains (Fig. 1a). 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 . It is worth noting that hydrophobic compounds are still present at the surface of CNF and that the surface charge is fixed by the pretreatment step.

2.2. Cellulose nanocrystals

The chemically-induced deconstruction strategy consists generally in applying a controlled strong acid hydrolysis treatment to cellulosic fibers allowing dissolution of amorphous domains and therefore longitudinal cutting of the microfibrils. The ensuing nanoparticles are generally called cellulose nanocrystals (CNCs) according to TAPPI (Standard Terms and Their Definition for Cellulose Nanomaterial WI 3021) and are obtained as an aqueous suspension. These nanoparticles occur as high aspect ratio rod-like nanocrystals, or whiskers (Fig. 1b). Their geometrical dimensions depend on the origin of the cellulose substrate and hydrolysis conditions. Sulfuric acid is classically used for the preparation of CNC and this process induces the formation of negatively charged sulfate groups at its surface. The average length is generally of the order of a few hundred nanometers and the width is of the order of a few nanometers. An important parameter for CNCs is the aspect ratio, which is defined as the ratio of the length to the width.

Several applications have been envisaged for these nanoparticles. However, owing to the structural function of cellulose in nature, the application of cellulose nanomaterials as a reinforcing phase for nanocomposite applications is the most prominent and broadly investigated end use.

3. Stiffness of the cellulose nanomaterial

Cellulose is a ubiquitous structural semicrystalline polymer and cellulose crystals give trees and plants their strength and light weight. In nature, cellulose is found in the crystalline form of cellulose I (native cellulose) which is a mixture of two polymorphs, cellulose I α and I β . These two crystalline forms have the same conformation of the heavy

atom skeleton, but differ in their hydrogen bonding patterns. The I α form represents a triclinic phase with one-chain-per-unit cell, while the I β form represents a monoclinic phase with two-chains-per-unit cell. The ratio of the two allomorphs I α and I β differs greatly depending on the species. The I α phase is mainly found in celluloses produced by primitive organisms such as algae or bacteria while cellulose I β lies mainly in the cellulose produced by higher plants (cotton, wood,...) and animals such as in the envelope of marine animals.

The elastic modulus E_L of the crystalline regions of cellulose I in the direction parallel to the chain axis was measured both experimentally and through atomistic molecular dynamics simulations. Some values are reported in Fig. 2 and Table 1. These values were determined at room temperature and considering intramolecular hydrogen bonding. Much lower values were reported when intramolecular hydrogen bonding was not taken into account, evidencing their important role in the determination of the crystallite modulus and chain deformation mechanism. Nevertheless, a broad range of values is observed and the average experimental and predicted tensile modulus of cellulose I crystal depicted by horizontal lines in Fig. 2 is 124 GPa and 134 GPa, respectively. It is therefore reasonable to consider that the tensile modulus of crystalline cellulose I is around 130 GPa. The modulus of cellulose microfibrils is expected to result from a mixing rule of the modulus of the crystal, the amorphous regions of cellulose and defects/air in the sample. Its average value is around 100 GPa [13].

Cellulose nanomaterials should therefore act as excellent reinforcing nanomaterial in a polymeric matrix which modulus is around few GPa in the best conditions, i.e. in its glassy state. However, homogeneously blending this nanomaterial with a polymeric matrix is challenging.

4. Processing of polymer nanocomposites

Both CNC and CNF are generally obtained as diluted aqueous (or at least polar liquid) dispersions. The stability of the colloidal suspension results from the presence of residual hemicelluloses for CNF and charged sulfate groups in the case of sulfuric acid-hydrolyzed CNC. The pioneering works on the preparation of nanocellulose reinforced polymer nanocomposites consequently involved an aqueous medium to keep this natural dispersion of the nanoparticles. This mode of processing allows preserving the individualization state of the nanoparticles resulting from their colloidal dispersion in water. Water-soluble polymers or polymer aqueous dispersions (latex) are therefore and continue to be favorable systems for such application.

Processing of nanocomposite materials from cellulosic nanoparticles and polymer latex was historically the first one reported in the literature [16]. The nanocomposite system reported in this study consisted of CNC extracted from tunicate and the polymeric matrix was obtained by the statistical copolymerization of styrene and butyl acrylate (poly(S-co-BuA)). Solid nanocomposite films were obtained by mixing

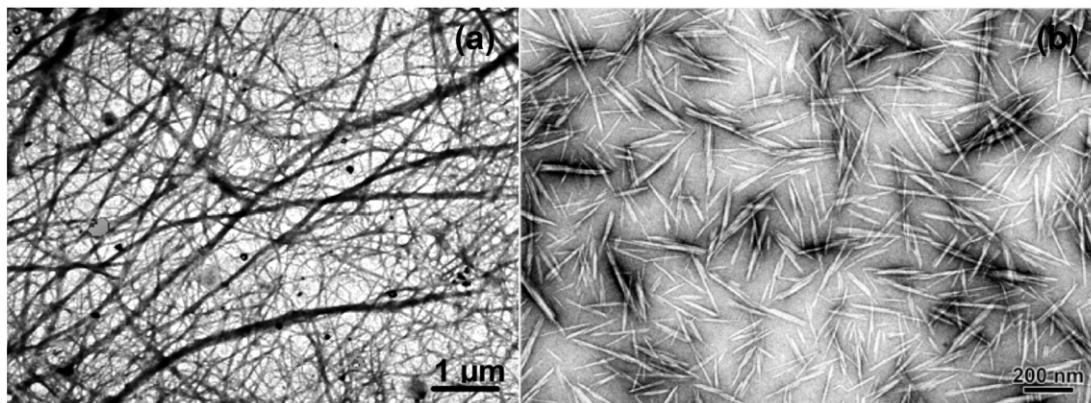


Fig. 1. Transmission electron micrographs from a dilute suspension of (a) cellulose nanofibrils prepared from *Opuntia ficus-indica* fibers [23], and (b) cellulose nanocrystals extracted from ramie fibers [18].

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