

Cellulose nanomaterials and polymer nanocomposites

Alain Dufresne

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

ABSTRACT

The potential of nanotechnology and nanocomposites in various sectors of research and application is promising and attracts increasing investment. Unexpected and attractive properties can be observed when decreasing the size of a material down to the nanoscale. Cellulose is no exception to the rule. Cellulose nanomaterials exhibit outstanding properties and are potentially useful for a large number of industrial applications. Despite being the most available natural polymer on earth, it is only quite recently that cellulose has gained prominence as a nanostructured material. Different forms of cellulose nanomaterials can be prepared. The mechanical modulus of crystalline cellulose is the basis of many potential applications.

INTRODUCTION

Cellulose is a linear macromolecule composed of β -1,4-linked D-glucopyranose rings and it is the most abundant polymer on Earth. It is one of the most important structural elements in plants and other living species maintaining their structure. The global annual production of cellulose is estimated at 1.5×10^{12} tons¹ and it has been used for centuries in highly diverse applications. More recently, 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 has been emphasized and it opens the door to new applications. Initial concept of the chemical extraction of cellulose nanomaterials through an acid hydrolysis process was pioneered in 1947² and the first report on the mechanical deconstruction of cellulose fibers was published in 1983.^{3,4}

In nature, cellulose is a ubiquitous structural polymer that confers its mechanical properties to higher plant cells. Lignocellulosic fibers consist of a cemented cellulose microfibril aggregate. Indeed, wood and plants are cellular hierarchical biocomposites designed by nature and they basically consist of semi-crystalline cellulose microfibril reinforced amorphous matrix made of hemicellulose, lignin, waxes, extractive and trace elements. The structure of plants spans many length scales, in order to provide maximum strength with a minimum of material.

Purification of cellulose from plant fibers involves chemical treatments consisting of alkali extraction and bleaching. Owing to its hierarchical structure and semi-crystalline 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 proved for special functional nanomaterials⁵ but it is as a biobased reinforcing nanofiller that they

have attracted significant interest over the last 20 years.^{1,6-9}

CELLULOSE NANOMATERIALS

Mechanical disintegration strategy

After purification, i.e. removal of most of non-cellulosic components from the natural fiber, the resulting cellulosic material suspended in water can then be submitted to a mechanically-induced deconstructing treatment involving strong mechanical shearing actions in order to release more or less individually the nanofibrils. Different equipments such as high-pressure homogenizer, microfluidizer, ultra-fine friction grinder, high-intensity ultrasonifier, aqueous counter collision, ball milling, twin-screw extruder and refiner can be used. A detailed description of these different equipments can be found elsewhere.¹ However, these processes are highly energy-consuming and a pretreatment of the cellulosic fiber is generally necessary. Several strategies have been proposed to obtain fibers that are less stiff and cohesive, thus decreasing the energy needed for fibrillation, as detailed elsewhere.¹⁰ There are basically three alternatives: (i) limiting the hydrogen bonding in the system, and/or (ii) adding a repulsive charge, and/or (iii) decreasing the degree of polymerization (DP) or the amorphous link between individual fibrils.

This material is generally called cellulose nanofibrils (CNF), but other terminologies are used such as microfibrillated cellulose (MFC) or nanofibrillated cellulose (NFC). Regardless the source of cellulose, this material consists of long entangled filaments as shown in Figure 1a. Both individual nanofibrils and microfibril bundles can be observed, but larger fragments and unfibrillated fibers are sometimes observed. The diameter of CNF is generally in the range 2-100 nm but the length is more difficult to determine because of entanglements and difficulties in identifying both ends of individual

microfibrils. During fibrillation, the water retention increases and the suspension changes from a low to a high viscosity medium and it becomes a gel at low solid content as shown in Figure 1b. A single characterization method cannot be used to describe the properties and behavior of CNF and a multi-criteria method to characterize high quality CNF suspensions and establish a quality ranking has been proposed.¹¹ From the raw values of different tests a final and single grade called the "quality index" can be determined.

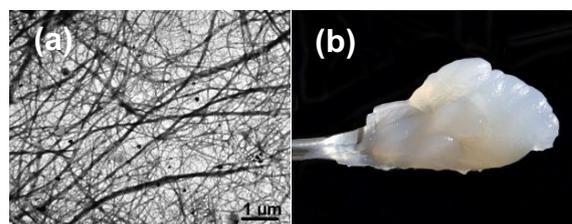


Figure 1. (a) TEM from a dilute suspension of CNF from *Opuntia ficus-indica* fibers;¹² and (b) pictures of a 2 wt% CNF suspension from eucalyptus.¹⁰

Acid hydrolysis strategy

As a semi-crystalline polymer, cellulose can be submitted to a controlled strong acid hydrolysis treatment allowing dissolution of amorphous domains and release of individual crystallites. The ensuing material is generally called cellulose nanocrystals (CNC) and consists of rod-like or needle-like nanoparticles as shown in Figures 2a. The dimensions of the nanocrystal mainly depend on the source of cellulose, the exact hydrolysis conditions and ionic strength. The average length is generally of the order of few hundreds of nanometers and the average width is of the order of few nanometers. Their surface chemistry is governed by the nature of the acid used for hydrolysis. The hydrolysis treatment of cellulose is generally performed with sulfuric acid resulting in the introduction of sulfate esters at the surface of CNC, leading to improved electrostatic stabilization of the suspension but decreased thermal stability.

When observed in polarized light between cross-nicols the CNC suspensions shows the formation of birefringent domains (Figure 2b).

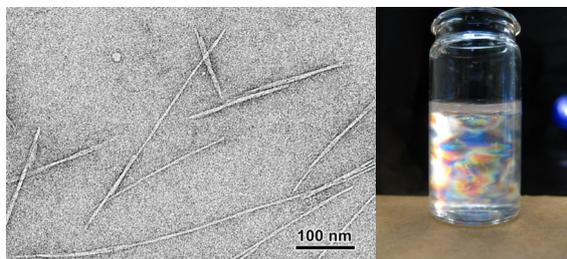


Figure 2. (a) TEM from a dilute suspension of CNC from soy hulls;¹³ and (b) photograph of an aqueous suspension of capim dourado CNC (0.50 wt%) observed between cross-nicols showing the formation of birefringent domains.¹⁴

MAIN PROPERTIES OF CELLULOSE NANOMATERIALS

When decreasing the size of a material from the microscale (cellulosic fibers) down to the nanoscale (cellulose nanomaterials) several properties change and are expected to drive new potential applications. The main properties that are impacted by this change of scale are reported as follows.

Specific surface area

Obviously, the total surface area per unit of mass, i.e. the specific surface area, increases. Its determination from gas adsorption isotherm is often incorrect because of the irreversible aggregation of the nanoparticles upon drying but it can be estimated from the average geometrical dimensions of the nanoparticles, assuming a rod-like geometry and a density of 1.5 or 1.6 $\text{g}\cdot\text{cm}^{-3}$ for crystalline cellulose. Values of 51 and 533 $\text{m}^2\cdot\text{g}^{-1}$ were reported for CNF and CNC, respectively, extracted from sisal fibers.¹⁵ This high specific surface area coupled with the low concentration of the suspensions allows the preparation of aerogels which can be used as porous templates, potentially useful in various nano-applications.

Aspect ratio

The aspect ratio is defined as the ratio of the length to the width. It determines the anisotropic phase formation and reinforcing properties of cellulose nanomaterials. It is indeed well-known that the mechanical percolation approach is highly relevant to describe the mechanical behavior of cellulose nanomaterial based composites when prepared by casting/evaporation.^{1,13} This mechanism suggests the formation of a stiff continuous network of nanoparticles linked through hydrogen bonding, which lead to an unusual and outstanding reinforcing effect. Furthermore, this phenomenon is expected to occur only above a critical volume fraction of filler phase, defined as the percolation threshold, which in turn depends on the aspect ratio of the nanoparticle. The aspect ratio is difficult to determine for CNF because of difficulties associated with the determination of their length but it is considered as very high. For CNC, the aspect ratio is easier to determine and it is found to depend on both the source of cellulose and hydrolysis conditions. The aspect ratio varies between 10 for cotton and 67 for tunicin or capim dourado (golden grass),^{1,14} and can be higher than 100 for soy hulls.¹³

Stiffness

The mechanical modulus of cellulose nanomaterials is probably their main asset. Indeed, cellulose is a ubiquitous structural polymer that confers its mechanical properties to higher plant cells. The tensile modulus of single cellulose I (native cellulose) crystal has been estimated both experimentally and theoretically. Values ranging between 56 and 220 GPa were reported with an average value of 130 GPa,¹⁶ with a tensile strength around 10 GPa. As expected, the lower crystallinity of CNF results in a lower modulus, which average value was estimated around 100 GPa.¹⁶ Moreover, crystalline cellulose with a density around 1.5-1.6 $\text{g}\cdot\text{cm}^{-3}$ can be considered as a lightweight material. The specific tensile modulus, which is the ratio

of the tensile modulus to the density, was estimated around 85 and 65 J.g⁻¹ for CNC and CNF, respectively, whereas it is around 25 J.g⁻¹ for steel.¹⁷

Thermal properties

When a cellulose nanomaterial suspension is dried, a film forms, which thermal expansion coefficient (TEC) is very low because of both its high crystallinity and strength of the cellulose nanomaterial network interactions.¹⁸ However, the low thermal stability of cellulose nanomaterials may limit their use and manufacturing conditions of its nanocomposites at high temperatures. This issue is particularly important for sulfuric acid-hydrolyzed CNC that exhibits a significantly reduced thermal stability compared to the raw starting material or other forms of nanocellulose. It is attributed to the sulfate ester groups that are introduced on the surface of the nanoparticles during the hydrolysis reaction.¹⁹

Rheological properties

Cellulose nanomaterials exhibit both a high specific surface area and high density of surface hydroxyl groups. These properties influence their interactions with the surrounding suspending liquid. After mechanical disintegration, the CNF suspension becomes a gel at low solid content as shown in Figure 1b, and it exhibits a pseudoplastic, shear-thinning behavior, i.e. its fluidity increases when stirred at high shear rate.

Optical properties

Due to their nanosize dimensions, CNF or CNC can be optically transparent if densely packed, and the interstices between the fibers are small enough to avoid light scattering. This type of flexible, transparent and renewable substrate is usually referred to as nanopaper. Transparent composite films can also be obtained by impregnating the CNF/CNC film with a transparent resin if the difference in refractive index between both components is small and/or that the

domain sizes in the different phases are smaller than the wavelength of visible light.

Furthermore, at sufficiently high concentrations, CNCs self-align to form a chiral nematic liquid crystalline phase in equilibrium with isotropic phase in aqueous medium.²⁰ Figure 3 shows a suspension of cotton CNCs which has formed a chiral nematic liquid crystal phase. Phase separation is observed with the isotropic phase in the upper part of the suspension and chiral nematic liquid crystalline phase in the lower part. The contrasting areas in the textures correspond to domains where the liquid crystalline nanoparticles are oriented in different directions. Within a domain, however, the nanoparticles are well ordered.

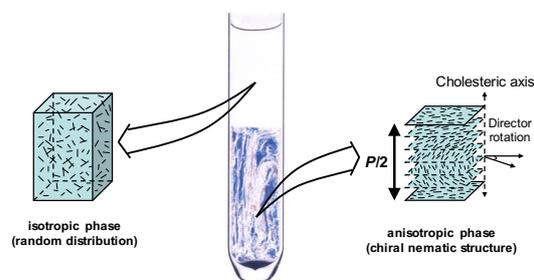


Figure 3. Typical biphasic suspension of cotton CNCs in water, viewed between partially crossed polarizers. The concentration in the upper isotropic phase is about 6.9% (w/v) and in the lower chiral nematic liquid crystalline phase, the concentration is 8.7% (w/v). The organization of each phase is schematically illustrated and half a chiral nematic pitch, $P/2$, is shown.¹

Slow evaporation of the suspension produces semi-translucent films that retain the self-assembled chiral nematic liquid crystalline order formed in the suspension, and then CNCs can form chiral nematic, iridescent, colored films. The chiral nematic organization of CNCs is always left-handed and thus, chiral nematic CNC films selectively reflect left-handed light, and appear colorful when the helicoidal pitch (P) is on the order of magnitude of the

wavelength of visible light. P can be controlled through ionic strength, temperature, concentration, exposure to magnetic field and US treatment, and it is therefore relatively straightforward to modulate film color. This structure-color phenomenon is similar to iridescence observed in nature, for example in morpho butterfly wings, seed hull of the *Margaritaria nobilis* fruit or beetle shells.

Barrier properties

Because of their small size resulting in high specific surface area, low permeability of cellulose enhanced by high crystallinity, and ability to form dense percolating networks, cellulose nanomaterials exhibit increased tortuosity towards diffusing gases (barrier property). They can provide improved barrier properties against moisture and oxygen when used as self-standing films, coating for polymers and paper, or reinforcement in polymer composites. Cellulose nanomaterials are generally poor moisture barrier but good oxygen barrier below 70% relative humidity (RH). The barrier performance can be further improved by optimizing the morphology and surface chemistry of cellulose nanomaterials, or sandwiching them with high moisture-resistant polymers.

Functionalization

Cellulose nanomaterials can be used as such or their properties can be tuned using physical or chemical methods. The inherent high reactivity of cellulose and the pervasive surface hydroxyl groups associated with the nanoscale dimensions of cellulose nanomaterials provide the possibility of modification via a chemical reaction strategy and open up opportunities to develop new functional nanomaterials.⁵ The objective of these modifications is to produce cellulose nanomaterials that can be used as reinforcing agents in composite materials or can contribute to specific functions for the development of new nanomaterials, with the target of expanding their applications in the field of functional

nanomaterials. A wide variety of chemical modification methods, including coupling hydrophobic small molecules, grafting polymers and oligomers, and adsorbing hydrophobic compounds to surface hydroxyl groups of cellulosic nanoparticles, can be employed.

COMPOSITE APPLICATIONS

A broad range of applications are envisioned for cellulose nanomaterials across many sectors.²¹

However, the addition of cellulose nanomaterials in a polymeric matrix to prepare nanocomposites is probably the major application due to the structural function of cellulose in nature. From the pioneering work on this topic²² it has been clearly demonstrated that the possible reinforcement of a polymeric matrix is not attributed to the intrinsic mechanical properties of cellulose nanomaterials. The strong interactions between cellulose nanoparticles through hydrogen bonding are beneficial to exploit their full potential and reach the highest mechanical reinforcement effect that can be obtained from these nanoparticles. At the same time, it limits their dispersion within the polymeric matrix. Moreover, because of the nano-size of the reinforcing phase, very thin polymer films with good mechanical properties and functionality can be obtained. The main issue with nanoparticles is their homogeneous dispersion in a continuous medium resulting from the high surface energy of these particles at the nano scale, associated with the polar nature of cellulose that tend to lead to aggregation, mainly when considering an apolar dispersing medium. Cellulose nanomaterials form stable dispersion in water or any polar liquid medium, and for this reason never-dried nanoparticles have been broadly used to process nanocomposites to ensure a proper level of dispersion in the polymeric matrix. However, the dispersion of cellulose nanomaterials in polymer melts and the

development of suitable processing technologies for large scale production have been addressed in the literature to broaden their applicability.²³

CONCLUSION

Nanosized materials can be extracted from any cellulosic source in the form of cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC) using a mechanical or acid hydrolysis treatment, respectively. Both nanomaterials exhibit the intrinsic properties of cellulose, i.e. renewability, non-toxicity, biodegradability, biocompatibility, and low density. Its transformation down to the nanoscale endow cellulose with new properties such as increased specific surface area and ensuing greater impact of surface functionalization, high aspect ratio, and enhanced mechanical, thermal, rheological, optical and barrier properties. These properties give cellulose many industrial applications in different sectors including the processing of polymer nanocomposites due to the structural function of cellulose in nature.

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