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PROPERTIES AND APPLICATIONS OF NANOCELLULOSE POLYMER COMPOSITES. A SHORT REVIEW

Magdalena Silvia RODEANU, Marian BASTIUREA,
Gabriel ANDREI, Dumitru DIMA
”Dunărea de Jos” University of Galati, 47, Domneasca Street, RO-800008, Galati, Romania
email: magda.bastiurea@ugal.ro

ABSTRACT

This paper covers some aspects related to the structure of natural cellulose fibers as well the sources, obtaining methods, properties and their applications. In contrast with aramide and other materials resulted from fossil fuels, nanocellulose is completely renewable. The tensile strength of crystalline cellulose is similar to aluminum's. Its stiffness has been shown to be in the order of magnitude which is similar to aramide and better than glass fibers. Nananocellulose may be prepared as films which are expected to show high strength, high stiffness and high strain. Its strength/weight ratio is 8 times greater than that of stainless steel.

KEYWORDS: nanocellulose, polymer, nanocomposites

1. Introduction

Cellulose is the most widespread biopolymer on earth, having an annual production that is estimated to be over 7.5 × 10^{10} tons [3, 17]. Cellulose is the major component of most plant fibers, about 40% to 50% of the plant [19]. Nature creates amazing materials under modest conditions, i.e., neutral pH and ambient temperature and pressure [13]. In biosynthesis, approximately 36 individual cellulose molecule chains connect with each other through hydrogen bonding to form larger units known as elementary fibrils, which are packed into larger microfibrils with 5-50 nm in diameter and several micrometers in length [8], which in turn aggregate to form cellulose fibers. By applying effective methods these fibers can be disintegrated into cellulose substructures with micro- or nano-size dimensions [3]. Generally, cellulose is a linear natural macromolecular substance of carbohydrates class, consisting of D-anhydroglucose repeating units joined by β-1,4-glycosidic linkages (Figure 1), with molecular formula of $(C_6H_{10}O_5)_n$, where 'n' is the degree of polymerization ranging from 10,000 to 15,000) [3, 8, 9, 13], fiber with high strength, height stiffness, and low density, insoluble in water, forming the plant cells walls and giving the plant strength and elasticity. Cellulose fibers can be classified according to their origin and grouped as cellulose fibers extracted from wood fiber (hardwood, softwood); and from non-wood lignocellulosic fibre: leaves (abaca, cantala, curaua, palm, henequen, pineapple, sisal, banana), from seeds: cotton; from bast (flax, hemp, jute, ramie); from fruit (coir, kapok, oil palm); from grass: alpha, bagasse, bamboo; from stalk/straw (cereal: corn, wheat, rice), from tunicate and bacteria [7, 8, 11].

Plant fibers are constituted of cellulose fibers, consisting of helically wound cellulose microfibrils, bound together by an amorphous lignin/ hemicellulose matrix. Lignin keeps the water in fibers, acts as a protection against biological attack and as a stiffener to give stem its resistance against gravity forces and wind [7]. Hemicelluloses are believed by many researchers to act as interfacial coupling agents between the polar surface of cellulose and the relatively nonpolar lignin matrix. In principle, the plant cell wall composite is designed much like a synthetic fiber-reinforced polymer composite [11, 13].

The plant cell wall fiber is a heterogeneous membrane [1]. It is built up of two sections: the primary cell wall and the secondary cell wall, which is further divided into three layers (S1, S2 and S3) like in Figure 2 [7, 11, 13].

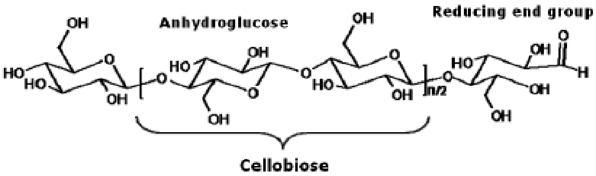

Fig. 1. *Chemical structure of cellulose [3]*

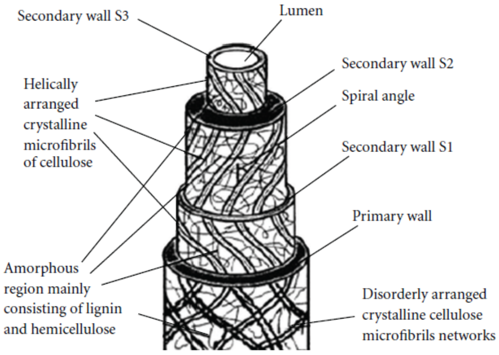

Fig. 2. *Structural constitution of a natural vegetable fiber cell, in which the secondary wall S2 makes up ~80% of the total thickness and thus acts as the main load bearing component [7, 11, 12]*

2. Synthesis of cellulose nanofibers

Cellulose nanofiber are not yet commercially available, instead micro-crystalline cellulose (MCC), a closely related item, is available, material widely used as a rheology control agent and as a binder in the pharmaceutical industry [9]. MCC is formed by particles of hydrolysed cellulose consisting of a very large amount of cellulose microcrystals together with amorphous areas.

MCC is prepared by removing part of the amorphous regions by acid degradation leaving the less accessible crystalline regions as fine crystals of typically 200–400nm in length and an aspect ratio of about 10. Degree of polymerization (DP) is about 140–400, depending on the cellulose source and treatment procedure [14].

There are several methods for cellulose nanofibers isolation that have been reported till now. Cellulose nano-fibers have been synthesized from acetobacter xyllinium by enzymatic hydrolysis, from potato tuber cells through alkali hydrolysis and from sugar beets. Cellulose nano-fibers were prepared from MCC by application of a high pressure homogenizer (20,000 psi) and treatment consisting of different passes (0, 1, 2, 5, 10, 15 and 20).

Cellulose nanofibers have been extracted from the agricultural residues, wheat straw and soy hulls by chemomechanich technique.

The size of the obtained cellulose nano-fibers depends on several factors, a particular importance having the source of cellulose and the applied treatment [3, 7].

Each microfibril from the cellulose fiber is formed by aggregation of elementary fibrils, which are made up of crystalline and amorphous parts.

The crystalline parts, which can be isolated by several treatments, are the whiskers, also known as nanowhiskers, nanocrystals, cellulose nanocrystals, nanocrystaline cellulose (NCC), nanofibrils, cellulose crystallites, nanorods, rodlike cellulose microcrystals or microcrystals (in spite of their nanoscale dimension), with lengths ranging from 500nm up to 1–2μm, and about 8–20nm or less in diameter (Azizi Samir et al., 2004; Lima & Borsali, 2004), resulting in high aspect ratios. Each microfibril can be considered a string of whiskers, linked along it by amorphous domains (which act as structural defects) [1 - 18].

2.1. Mechanical methods

Mechanical methods such as high pressure homogenization, milling/ refining, cryocrushing, microfluidization were used to extract nanocellulose of wood fibers and plant fibers that have eliminated already hemicellulose and lignin matrix by pretreatment, from microcrystalline cellulose, invertebrate marine animals tunicates, algae and bacteria [5].

2.1.1. Crushing

This method has some drawbacks on the water retention capacity, which tends to increase during the process of refining and high energy requirement needed in the refining cellulosic materials and decreased cellulosic material crystallinity, and also to increase the solubility of the polymer [3].

2.1.2. Cryocrushing

A subclass of the previous method is the "cryocrushing", which involves water-swollen cellulosic material immersed in liquid nitrogen, followed by crushing the material with a mortar and pestle. This method has already been successfully used for craft fibers after refining.

Homogenization method has been applied by many researchers and involves cellulosic material passing through a small nozzle at very high pressure (20,000 psi). When frozen fibers are subjected to high impact forces, ice crystals exert pressure on the cell walls, breaking them and releasing the microfibrils [3].

2.2. Physical methods

2.2.1. Ultrasonication

Through this environmental friendly method, ultrasonication alone or combined with other methods eg. the acid hydrolysis, have been obtained nanofibers only in laboratory tests.

Thus Filson and Daeson-Andoh obtained by ultrasonication and acid hydrolysis nano-fibers with an average diameter between 9- 23nm [18], see TEM image in Figure 3.

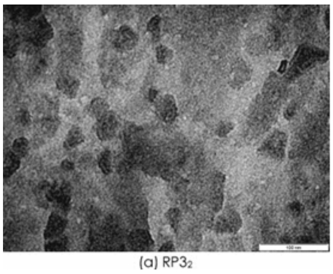

Fig. 3. *TEM image of cellulose nanocrystals produced from ultrasonication of recycled pulp for 10 min and in water [18]*

2.2.2. Microwave

The main disadvantage of this method is that the material obtained is extremely deteriorated and the strength characteristics of the nano-fibers are small.

2.2.3. Gamma rays irradiation

Using the method there is a separation of a gas due to dehydrogenation, depolymeri-zation and destruction effects of the chains glucosides, affecting not only the molecular structure but also the secondary and supramolecular structure [3].

2.3. Chemical methods

2.3.1. Acid hydrolysis

Stable aqueous suspensions of cellulose nano fibers can be prepared by acid hydrolysis. This is main method used to obtain cellulose whiskers, using mineral acids like H_2SO_4, HCl and H_3PO_4, consisting basically in removing the amorphous regions present in the fibrils, leaving the crystalline regions that have a higher resistance to acid attack intact with a high degree of crystallinity [3, 14, 17].

2.3.2. Alkaline hydrolysis

Alkaline hydrolysis determines the partial separation of the cellulose fibers from the cell wall [3, 7] and an improvement of the physical and chemical characteristics of cellulose, particularly its reactivity to other chemical agents. These treatments are usually made using diluted solutions of NaOH (1-10%) at low or high temperatures and concentrated NaOH solutions over 10% only at low temperatures.

2.3.3. Organic solvent treatments

Aqueous and non-aqueous solvents are used for pulp. Usually, all these solvents suffer from either high environmental toxicity or poor solvating power [3, 6]. Another important aspect of this technology is the easy recovery of organic solvents by distillation and the absence of residues from these treatments [3].

2.3.4. Ionic liquid treatments

Dissolving of cellulose with ionic liquids allows for the full use of cellulose by combining two major principles of green chemistry: use of preferred solvent environment and bio-renewable feed-stocks [3, 5, 6].

2.3.5. Biological treatments

Under the enzymes action cellulosic material undergoes a degradation process. Destruction is influenced by the chemical characteristics of the cellulose wich has a high stability due to its high crystallinity. Degradation of the cellulose substrate occurs in the presence of microorganisms (fungi, bacteria) or directly with cellulose enzyme preparations. Enzymatic treatment removes non-cellulose components of the cellulosic fibers may increase the crystallinity, thermal stability and the amount of hydroxil groups of fibers treated [3].

3. Structural analysis

Once isolated, crystals are often suspended in a solution. Evaporating the solution on a substrate will produce a film of nanocrystals that can be imaged and characterized using a number of techniques: 1) Optical Microscopy (OM) which is limited to imaging objects greater than about half of the wavelength of visible light (> 250nm) and therefore can only image large crystal aggregates; 2) Scanning Electron Microscopy (SEM) (Fig. 4); 3) Atomic Force Microscopy (AFM) which involves rastering a cantilever with a very fine tip (tip radius ~ 20nm) across the sample and obtaining an image by measuring the cantilever deflection (see AFM image in Figure 6); 4) Transmission Electron Microscopy (TEM), in which electrons are accelerated to a high voltage and detected after they pass through the sample, (see TEM images in Fig. 5).

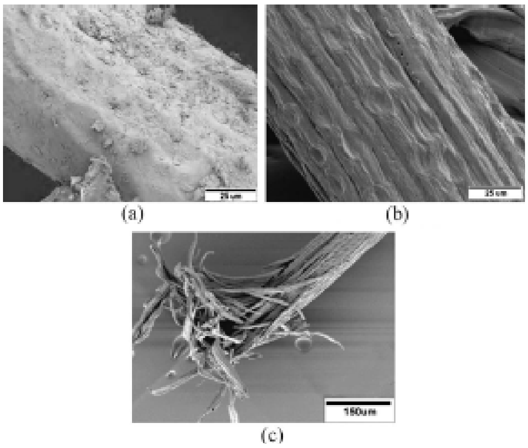

Fig. 4. *SEM micrographs of (a) untreated coconut fiber; (b) coconut fiber subjected to pre-treatment and (c) coconut fiber subjected to bleaching [2]*

Both AFM and TEM can achieve nanometer resolution and are therefore effective for imaging cellulose nanocrystals. Nuclear magnetic resonance and x-ray diffraction have also been used to further investigate crystal structure [15]. X-ray diffraction image can be seen in Figure 8. FTIR Spectra of NCC and of bamboo pulp following pretreatment with NaOH (Figure 7). As shown in this figure, the spectrum of NCC was similar to that of pretreated bamboo pulp with respect to the characteristic of cellulose peaks [15].

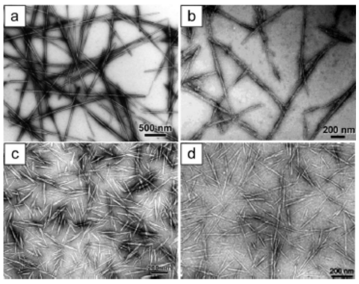

Fig. 5. *TEM images of dried dispersion of cellulose nanocrystals derived from (a) tunicate, (b) bacterial, (c) ramie, (d) sisal [17]*

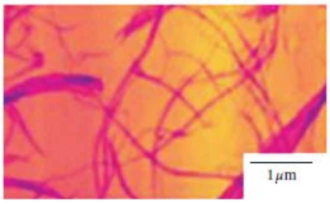

Fig. 6. *AFM image of wood cellulose nanofiber [7]*

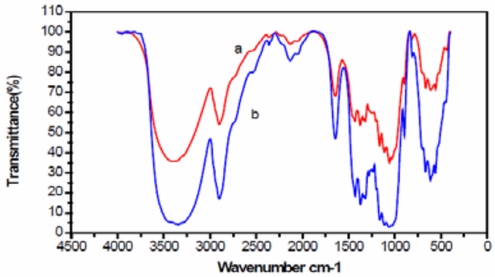

Fig. 7. *FTIR spectra of bamboo nanocristalline cellulose (a), and bamboo pulp with NaOH pretreatment (b) [15]*

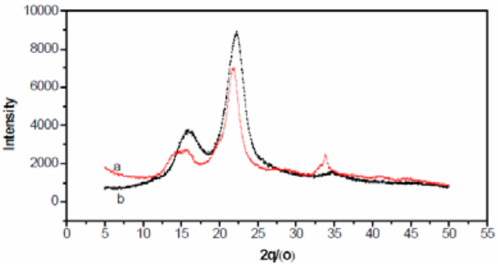

Fig. 8*. X-ray diffraction image of bamboo nanocrystalline cellulose (a) and cotton nanocrystaline cellulose (b) [15]*

4. Properties of nanocellulose

4.1. Mechanical properties

For wood nanocrystalline cellulose were determined different values of Young's modulus in the axial direction (EA = 50-100GPa) and transverse (ET = 18-50), tensile strenght σ_f = 0.3-1.4GPa, strain ε_f = 4-23% [4]. Other authors have determined that axial modulus values ranging between 110-220GPa, transverse modulus between 10-50 GPa and tensile strength between 7.5 -7.7GPa [5].

Tensile strength is greater than 200MPa, value similar to Kevlar fibers. Nanocellulose films have the same tensile strength value, strain 12% and the 20GP tensile stress [16].

4.2. Thermal properties

Thermal expansion coefficient in the axial direction was estimated at 0.1 ppm/K, value similar to quartz crystal [4].

The onset of thermal degradation occurs at 300^0C for freeze dried microcrystalline cellulose and 260^0C for nanocrystalline cellulose obtained by sulfuric acid hydrolysis of the same microcrystalline cellulose [4].

4.3. Electrical and magnetic properties

The cellulose is not electrically conductive, in native form. But it is influenced by the magnetic field when it is present, as loaded cellulose nanocrystals (CNC). CNC orientation using magnetic fields has been previously reported [16].

5. Applications

The cellulose nanofiber and composites reinforced with such fillers have found many potential applications in important areas such as electronics and electrical industry, construction, biomedicine, cosmetic, paper, packaging, building materials, textiles, solar cells, bioethanol, adsorption of heavy metal ions from aqueous solution, as filtration membranes and so on. Formulations with nanocellulose and silver nanoparticles can particularly be used as microbial medicaments, antibacterial agents in wound dressing, bandages, implants, skins replacements for burnings, face masks, artificial blood vessels, cuffs for nerve surgery, drug delivery, cell carriers and support matrices for enzyme immobilization, cosmetic tissues [4]. Surface modified cellulose nanofibers can be used for many applications such as coating, adhesives, sealings, filters, membranes, packing and cosmetics, aerospace industry, optically transparent flexible devices such as flat displays, digital cameras, cellular telephones and integrated circuits, paper or board for printing and recording information liquid crystals for transparent windows, lamps or dials of clocks and watches [4, 6, 8]. For the bacterial cellulose important examples include supports for proteins, cell cultures and microorganisms, products for temporary skin and tissue replacement. NCC use of the fiber as reinforcement phase in the composite polymer matrix, have been incorporated into a wide range of polymer matrices, including polysiloxanes, polysulfonates, poly(caprolactone), styrene-butyl acrylate latex, poly(oxyethylene), poly(styrene*co*-butyl acrylate) (poly(S-*co*-BuA)), cellulose acetate butyrate, carboxymethyl cellulose, poly(vinyl alcohol), poly(vinyl acetate), poly(ethylene-vinyl acetate) (EVA), epoxides, polyethylene, polypropylene, poly-(vinyl chloride), poly-urethane, and water-borne polyurethane. Their incorporation into biopolymers, such as starch-based polymers, soy protein, chitosan, or regenerated cellulose, and biopolymer-like poly(lactic acid), poly(hydroxyoctanoate), and polyhydroxybutyrates have also been reported [10, 17].

6. Conclusions

This paper reviews the processes developed for the production of nanocellulose which include the methods for obtaining neat cellulose as well as the nanofibrillation procedure obtained by physical, chemical, enzymatic, mechanical or combined techniques. Aspects concerning physical description and material characterization were discussed. The paper underlines methods morphological investigation and structural characterization. Moreover, mechanical, thermal and electrical properties are reviewed.

References

[1]. Dufresne A. - *Natural Polymers*, Volume 2: Nanocomposites, chapter 1 Nanocellulose:Potential Feinforcement in Composites. Royal Society of Chemistry 1-32, (2012)

[2]. Rosa M.F. et al. - *Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior*, Carbohydrate Polymers 81 (2010) 83–92

[3]. Frone A. et al. - *Some aspects concerning the isolation of cellulose micro- and nano-fibers***.** U.P.B. Sci. Bull., Series B, Vol. 73, Iss. 2, (2011)

[4]. Rebouillat S. et al. - *State of the Art Manufacturing and Engineering of Nanocellulose: A Review of Available Data and Industrial Applications*, Journal of Biomaterials and Nanobiotechnology, (2013), 4, 165-188

[5]. Moon R. et al. - *Cellulose nanomaterials review: structure, properties and nanocomposites,* Chem. Soc. Rev., (2011), **40**, 3941–3994

[6]. Liu H. et al. - *Understanding the Interactions of Cellulose with Ionic Liquids: A Molecular Dynamics Study,* The Journal of Phisical Chemistry B, (2010)

[7]. Kalia S. et al. - *Cellulose-Based Bio- and Nanocomposites: A Review***,** Hindawi Publishing Corporation International Journal of Polymer Science Volume 2011, Article ID 837875

[8]. Zhou C. et al. - *Recent Development in Applications of Cellulose Nanocrystals for Advanced Polymer-Based, Nanocrystals – Synthesis*, Characterization and Applications, (2012)

[9]. Chauhan V. et al. - *Use of nanotechnology for high performance cellulosic and papermaking products*, Cellulose chemistry and technology, (2011)

[10]. Masoodi R.et al., *Mechanical characterization of cellulose nanofiber and bio-based epoxy composite*, Materials and Design 36 (2012) 570–576

[11]. Kalia S. et al. - *Pretreatments of natural fibers and their application as reinforcing material in polymer composites-a review*, Polymer Engineering and Science, (2009), 49:1253–1272.

[12]. Rong M.Z et al. - *The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composite,* Composites Science and Technology, (2001), 61:1437–1447

[13]. Zhuo Li - *Bio-based Composites That Mimic the Plant Cell Wall*, Thesis Master of Science In Biological Systems Engineering, Virginia Polytechnic Institute and State University, (2009),

[14]. de Azeredo H. - *Nanocomposites for food packaging applications*, Food Research International 42 (2009) 1240–1253

[15]. Mengjiao Y. et al. - *Preparation and Characterisation of Bamboo nanocrystalline cellulos*, BioResources 7(2), 1802-1812, (2012)

[16]. Tummala G.K. - *A Brief Review on Electronic and Magnetic Applications of Nanocellulose.*

[17]. Habibi Y. et al. - *Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications*, American Chemical Society, (2009)

[18]. Filson P.B. et al. - *Sono-chemical preparation of cellulose nanocrystals from lignocellulose derived materials*, Bioresource Technology, vol 100, (2009), no.7, pp.2259-2264.