Nanocelluloses from Eucalyptus Wood Pulp: A Morphological Comparison

Antonio J. F. Carvalho

Department of Materials Engineering of the Engineering School of São Carlos, University of São Paulo, Av. Trabalhador São-carlense, 400 - Centro, São Carlos - SP, 13566–590, Brazil

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ABSTRACT: Two nanocelluloses from eucalyptus, namely microfibrillated cellulose (MFC) and cellulose nanocrystals (CNC), were prepared and compared by transmission electron microscopy (TEM). The MFC fibers are 20–30 nm wide and are composed of very homogeneous bundles of aligned regular elementary fibrils of 3–5 nm diameter. They show long straight portions and short flexible zones, attributed to crystalline and amorphous zones, respectively. The needle-shaped CNC was approximately 200 nm long and 10 nm wide in the wider portion. A model for the MFC structure, whose flexible zones are formed by alignment of the amorphous portion of the elementary fibrils, has been proposed. This study throws new light on the ultrastructure of cellulose microfibrils, which is not completely known.

KEYWORDS: Cellulose, microfibrillated cellulose, cellulose nanocrystals, nanocelluloses

1 INTRODUCTION

Cellulose has been one of the most important raw materials used by humans since ancient times and continues to be of great importance in various industries, such as papermaking and clothing. It has no good substitute in several applications, owing to its unique properties, especially hydrophilicity and chemical resistance. Large quantities of cellulose are produced as wood pulp for papermaking and for the production of modified cellulose materials, such as esters and ethers [1, 2]. Additionally, a strategic new area of intense research is the development of second-generation ethanol for use as a fuel. Recently, a new generation of cellulose materials, generically termed nanocelluloses, has emerged [3–5]. The most important nanocelluloses are cellulose nanocrystals (CNC) [5] and microfibrillated cellulose (MFC) [6], both prepared by top-down methods that involve chemical and physical or physicochemical extraction processes. The MFC has a diameter in the range of 20–60 nm with a length on the order of microns; termed microfibrillated cellulose due to historical facts, it is also considered a nanocellulose material.

The most widely used raw material for this purpose is pure cellulose obtained from chemical wood pulps [1, 2]. While MFCs are prepared by the delamination of wood pulp by a mechanical process before and/or after chemical or enzymatic treatment [3, 4], CNCs are prepared by acid hydrolysis, in which the amorphous regions are preferentially disintegrated [3–5].

The processing conditions and morphology of the nanocelluloses produced depend on the source of cellulose and processing parameters. Great efforts have been devoted to developing economical and practical processing methods and characterizing the morphology of these materials, since some features of their structure are still not well known. Therefore, the key factor for the technological development of such new renewable and highly technological materials depends on the availability of viable processing methods and a better understanding of their structures.

Here we describe the use of transmission electron microscopy (TEM) to compare two nanocellulose materials, cellulose nanocrystals and microfibrillated cellulose, both obtained from eucalyptus kraft wood pulp. An idealized model for microfibrillated cellulose

**Corresponding author*: toni@sc.usp.br

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is proposed based on the structure and dimensions of the common-source nanocelluloses produced.

2 EXPERIMENTAL SECTION

2.1 Materials

Bleached cellulose wood pulp from *Eucalyptus* was supplied by Aracruz Celulose S.A. (Brazil). The other reagents were purchased from Synth (Brazil) and were used as received.

2.2 Preparation of Cellulose Nanocrystals

The wood pulp was dispersed in water with an Ultra-Turrax grinder (IKA, Germany) and stirred in a 2% NaOH solution at 80°C for 2 hours. The treated pulp was filtered and a new cycle of washing was performed twice. The pulp was then rinsed with water until neutral washings, dewatered to 35% solid and added to a sulfuric acid solution at 64 wt% (160 mL of sulfuric acid 96% and 90 mL of water), cooled to 2°C and kept in an ice bath. For each 1 g of cellulose pulp, 8.75 mL of 64 wt% sulfuric acid was used. The temperature of the mixture was adjusted to 45°C and the system was stirred for 60 minutes and then poured into a mixture of water and ice to interrupt the hydrolysis. The suspension was centrifuged at 10,000 rpm at 10°C for 10 min and half of the upper portion was removed. Distilled water was added and mixed with the remaining mixture, which was centrifuged once again. This washing was repeated until the pH of the liquid in the centrifuge was almost neutral. The suspension was then dialyzed against water in cellophane bags to ensure its neutrality, homogenized by dispersion in an Ultra-Turrax IKA T25 at 13,600 rpm for 3 min, sonicated at 400 W and 22 KHz, and filtered in a sintered glass filter.

2.3 Preparation of Cellulose Nanofibers

The pulp was stirred in a 2 wt% potassium hydroxide solution at 85°C for 1 h and filtered and washed to neutrality. It was then suspended in water (7 mg/mL) and sonicated with a high-power Hielscher 400 W sonicator operating at 24 kHz and set to 80% of its maximum power. The pulp suspension was cooled in an ice bath in order to keep the temperature below 40°C.

2.4 TEM Characterization

The samples were prepared on a 400 mesh copper grid (Ted Pella, Inc. – Prod. No. 01822 – Ultrathin Carbon Type-A) covered with carbon and formvar and stained with a 2 wt% uranyl acetate solution. They were analyzed with a FEI Tecnai G2 F20 HR transmission electron microscope.

3 RESULTS AND DISCUSSION

The term "microfibrils," commonly used to define microfibrillated cellulose (MFC), may generate some confusion since other terms such as elementary fibrils, protofibrils and nanofibers have also been used in the literature [7]. Microfibrils are formed by arrangements of cellulose chains that display the shape of ribbons of approximately 0.5 x 1.0 nm [1], aligned in planes spaced by 0.39 nm [7, 8]. Such arrangements are produced by the self-assembly of cellulose chains into subunits whose structure varies with the plant source. For trees formed out of six-membered rosettes, each subunit produces a linear sheet of 6 cellulose chains [4], totaling 36 cellulose chains for each rosette. These structures, termed elementary fibrils, have a cross-section diameter of 3–5 nm [9–11] and are composed of both amorphous and crystalline regions. The amorphous regions are responsible for their flexibility. The self-assembly of these elementary fibrils give rise to larger fibers, named cellulose fibrils, composed of 1000–2000 cellulose chains, whose cross-section ranges from 15 to 20 nm [3, 4, 12]. Finally, the self-assembly of these microfibrils produces the micro- or macrofibers that form the cellular tissue of the plant cell. Figure 1 shows the structures formed from the cellulose chains.

The micrograph in Figure 2 shows cellulose microfibrils with elementary fibrils separating from the main microfibril structure. The image suggests that the total length of the microfibril could reach 6 µm.

Figure 3 shows the TEM image of a microfibril of approximately 100–150 nm width. The elementary

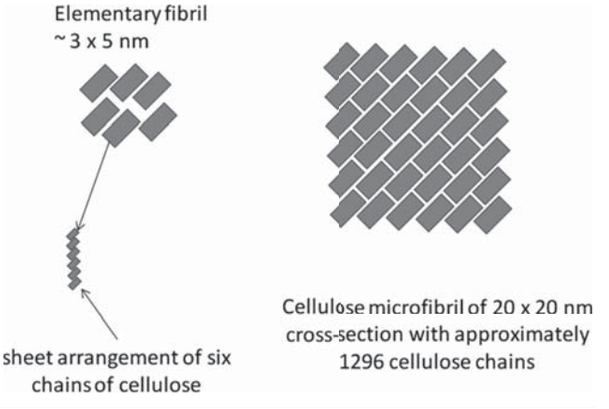

Figure 1 Sketch of cellulose structures at different levels from cellulose chains to microfibrils.

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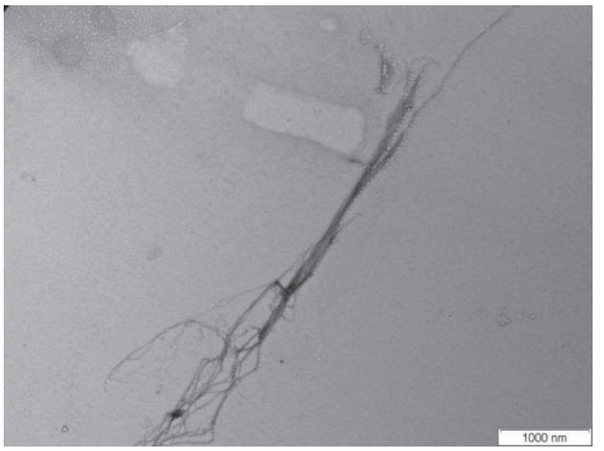


Figure 2 TEM image of MFC from eucalyptus.

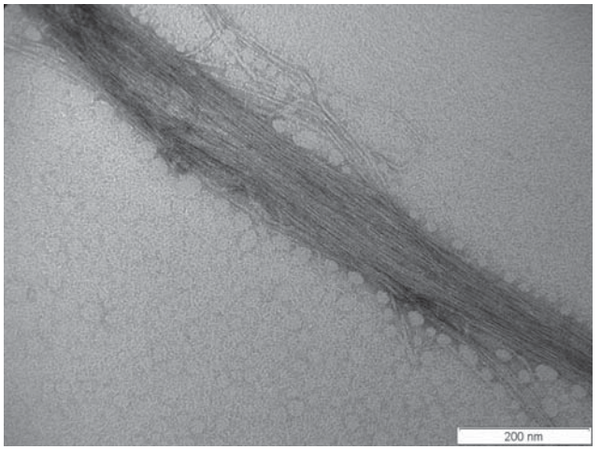


Figure 3 TEM image of MFC formed by the self-assembly of elementary microfibrils.

fibrils are aligned in the axial direction and are being detached from the microfibril. They show very regular dimensions of an approximately 5 nm diameter.

Figure 4 shows microfibrils of 20–30 nm width formed by the disintegration of the larger microfibrils showed in Fig. 3. Here again, only a few elementary fibrils are isolated. Both microfibrils and elementary fibrils are flexible, however most of the microfibrils are straight. Examples of the straight and flexible points are indicated by arrows in Figure 4. The images of Figures 3 and 4 show that elementary fibrils are longer than 1000 nm (Fig. 2).

Figure 5 shows TEM images of very regular needle-shaped CNC at two magnifications. The black arrows in the bottom image indicate the width of the CNC at

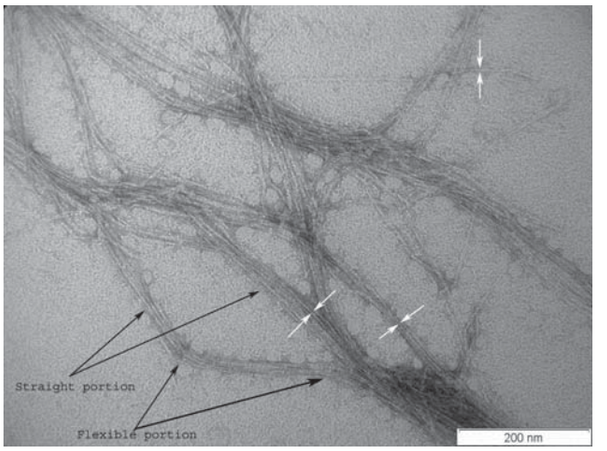
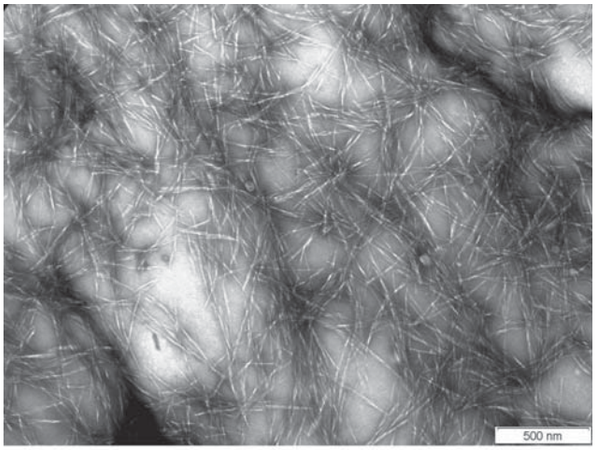


Figure 4 TEM image of MFC produced from larger fibrils showing rigid and flexible regions.



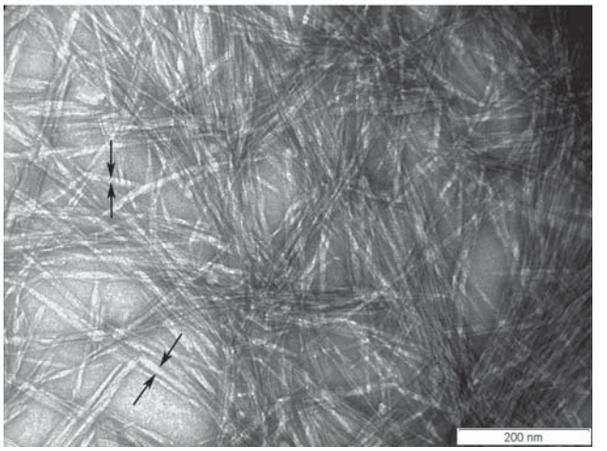


Figure 5 TEM image of CNC produced from eucalyptus wood pulp.

its middle point, where it is thicker. The average length of the CNC is 500 nm.

A remarkable feature of the elementary fibrils is that they are flexible but very regular. Their thickness is constant throughout their length with a mean cross-section of 3–4 nm. On the other hand, the rigid cellulose nanocrystals are thicker in the central portion with a cross-section of 8–12 nm, which is between the values for microfibrils and elementary fibrils (Fig. 6). This result shows that CNC are not formed by the dissolution of amorphous portions of single elementary fibrils, but by the scission of cellulose microfibrils formed by 10 to 15 elementary fibrils. The scission occurs in regions where the microfibrils are predominantly or completely amorphous. A possible model that explains this process is based on the assumption that there are zones in which the amorphous portions of cellulose elementary fibrils coincide. The needle shape can be explained by the fact that external elementary fibrils are more affected than internal ones, which leads to the detachment of crystalline portions mainly at the ends. This model is depicted in Figure 6.

The flexible sites on the cellulose fibrils shown in Figure 4 may indicate that those portions are composed of mostly amorphous cellulose and responsible for the scission points during acid hydrolysis. Since MFC is composed of elementary fibrils with approximately 36 cellulose chains each, the MFC can generate more than one CNC structure. The model for CNC formation indicates that hydrolytic conditions will play a significant role in the morphology of CNC, whereas the morphology of MFC and elementary fibrils are decided by the structure of a plant source.

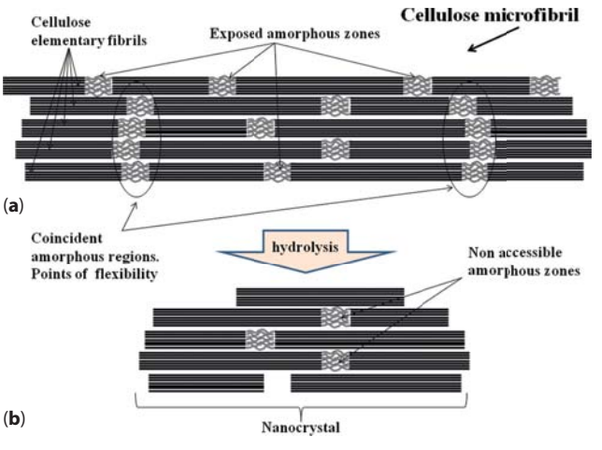


Figure 6 Schematic model for cellulose microfibrils and their hydrolysis product; **(a)** before hydrolysis and **(b)** after hydrolysis of the most accessible amorphous cellulose.

4 CONCLUSIONS

The study of eucalyptus cellulose microfibrils and nanocrystals has shown that typical cellulose microfibrils of 20–30 nm width compose large straight fibrils of 100–200 nm width. Microfibrils are progressively detached from the larger fibrils and elementary fibrils of 3–5 nm width are observed. The elementary fibrils can easily be visualized both in larger fibrils and in the microfibrils' structures. The 20–30 nm cellulose microfibrils formed by the aggregation of aligned elementary fibrils are composed of long straight portions at least 200 nm long and shorter flexible regions. Cellulose nanocrystals produced by acid hydrolysis with H_2SO_4 are at least 500 nm long and are needle-shaped, being 10 to 15 nm wide in the middle. These results suggest that the flexible portions in the microfibrils are mostly amorphous and dissolution gives rise to the long aligned portions of elementary fibrils, which correspond to the straight rigid portions of microfibrils. The differences in the morphology of CNC and MFC suggest that elementary fibrils are assembled in such a way that the long highly crystalline regions and the alternating short portions of amorphous regions of fibrils coincide with each other, this being responsible for the flexibility of microfibrils and the points of scission during acid hydrolysis.

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