Extraction and Characterization of Cellulose Nanowhiskers from Balsa Wood

Carolina Lipparelli Morelli,[1] *José Manoel Marconcini,*[2] *Fabiano Vargas Pereira,*[3] *Rosario Elida Suman Bretas,*[1] *Márcia Cristina Branciforti**[4]

Summary: In this study cellulose nanowhiskers were obtained from balsa wood. For this purpose, fibers of balsa wood were exposed to hydrolysis reactions for lignin and hemicellulose digestion and acquisition of nano-scale cellulose. Transmission electron microscopy (TEM) results demonstrated that the obtained cellulose nanocrystals had average length and thickness of 176 (±68 nm) and 7.5 (±2.9 nm), respectively. Infrared spectroscopy (FTIR) and wide angle x-ray diffraction (WAXD) showed that the process for extracting the nanowhiskers digested nearly all the lignin and hemicellulose from the balsa fiber and still preserved the aspect ratio and crystallinity satisfactory enough for future application as nanofillers in polymer nanocomposites. The thermogravimetric analysis (TGA) showed that the onset temperature of thermal degradation of the cellulose nanocrystals (226 °C) was higher than the onset temperature of the balsa fiber (215 °C), allowing its use in molding processes with polymers melts.

Keywords: balsa wood; cellulose; crystallinity; nanowhiskers; renewable resources

Introduction

Cellulose nanocrystals or nanowhiskers (CNW) consist of particles with high crystallinity and high specific surface area that can be obtained from various sources of natural fibers such as cotton, bamboo, wood and some marine animals such as tunicates.[1,2] The crystallinity and the dimensions of these nanocrystals depend on the origin of the cellulose fibers as well as the procedure used to obtain them. The theoretical elastic modulus of cellulose nanowhiskers is 167.5 GPa,[3] which makes them an interesting choice for the reinforcement of thermoplastics. In addition, CNW are biodegradable, have low density and renewable character. The increase in the stiffness of the thermoplastic matrix will also depend on the ratio between length and thickness of the nanowhiskers (aspect ratio). In this study we chose to extract CNW from balsa wood, because of its high cellulose content (52%[4]) and because it is a fast-growing tree, abundant in the Amazon region and used as a pioneer tree in the reforestation and recovery of degraded areas. One study showed that balsa tree grew 14 meters in 14 months in a plantation in a degraded pasture near Manaus, in Brazil.[5] Due to its rapid growth, the shadow of the crown of the balsa tree provides favorable conditions for the development of other plants of slow growth, contributing to reforestation and sustainable management.[6] The balsa wood (*Ochroma pyramidalis*) is the lightest wood of commercial use that exists and can weigh around 48 $kg.m^{-3}$, which is equivalent to one third of the weight of cork. The balsa wood is largely used in the manufacture of boats and wind blades and in aeromodelling.

[1] Federal University of São Carlos, São Carlos – SP, Brazil
[2] Embrapa Instrumentation, São Carlos – SP, Brazil
[3] Federal University of Minas Gerais – UFMG, Belo Horizonte – MG, Brazil
[4] University of São Paulo – USP, São Carlos – SP, Brazil
E-mail: marciacb@sc.usp.br

Experimental Part

Extraction of Cellulose Nanocrystals

Initially, the balsa wood slats were grounded into fine powder by using a Cremasco DPC-4 mill and washed with hot water (90 °C). Sequentially, the balsa powder was treated with 2 wt % of NaOH aqueous solution, at 90 °C, for 3 h, under mechanical stirring. This procedure was done four times in order to purify the cellulose pulp by removing others components present, like lignin and hemicellulose. A bleaching treatment was done later using a solution consisting of equal parts of acetate buffer solution and an aqueous sodium chloride solution (1.7 wt %). This procedure was repeated twice, at 90°C, each procedure lasting 3 h. For the extraction of cellulose nanocrystals, an aqueous solution of sulfuric acid (65 wt %) was used with constant and vigorous stirring during 75 min at 50 °C. After this period the suspension was repeatedly centrifuged at 3500 rpm for 10 min in a Heraeus Megafuge 2.0 centrifuge; the supernatant was discarded until it became cloudy, indicating the presence of the CNW in the suspension. The cloudy suspension was then submitted to dialysis with water until neutrality was attained. After this, the suspension of nanocrystals was freeze-dried for the analysis of the CNW.

Characterization of Cellulose Nanocrystals

Transmission electron microscopy (TEM) was done using a Philips CM 120 microscope with acceleration voltage of 120 kV. For this analysis, a drop of aqueous suspension with 0.01 wt % of cellulose nanocrystals was deposited on a carbon-coated grid and stained with a uranyl acetate solution (2 wt%). The length and thickness of approximately 100 nanocrystals were measured using the Image-Pro Plus 4.5 software. Infrared spectroscopy (FTIR) was made in a ThermoScientific Nicolet 6700 spectrometer, between a wavelength range of 750 to 4000 cm^{-1}, with 32 scans and resolution of 4 cm^{-1}. For this purpose, samples of CNW were grounded with liquid nitrogen and dried for 24 h at 50 °C. They were then mixed (1 wt %) with KBr previously dried during 24 h at 115 °C. Thermogravimetric analysis (TGA) was also done using equipment Q50 from TA Instruments between 28 °C and 800 °C, at a heating rate of 20 °C min^{-1}, under nitrogen atmosphere (50 mL s^{-1}). Wide angle x-ray diffraction (WAXD) was done on dried samples of CNW and balsa wood powder, in a Siemens diffractometer D5005 operating at 40 kV and 40 mA. The scans were done between 5° and 40°, with a scan rate of 2° min^{-1}.

Results and Discussion

Figure 1 presents a TEM micrograph of the cellulose nanocrystal extracted from the balsa wood and Figure 2 presents the distribution of lengths and thicknesses of the CNW. The micrographs and the measurements confirmed the nanometer dimensions of the obtained cellulose crystals, which had an average thickness (D) of 7.5 (±2.9 nm, standard deviation) and an average length (L) of 176 (±68 nm, standard deviation). These values result in an aspect ratio (L/D) of 25. These values can be used to calculate the percolation volumetric fraction ϕ_v, using equation 1, given by the percolation theory:[7,8]

$$\phi_V = \frac{0.7}{L/D} \quad (1)$$

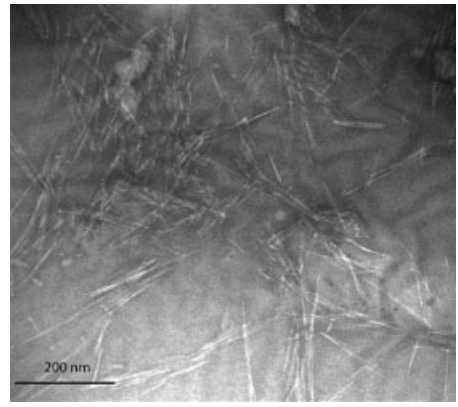

Figure 1.
TEM micrograph of the CNW obtained from balsa wood.

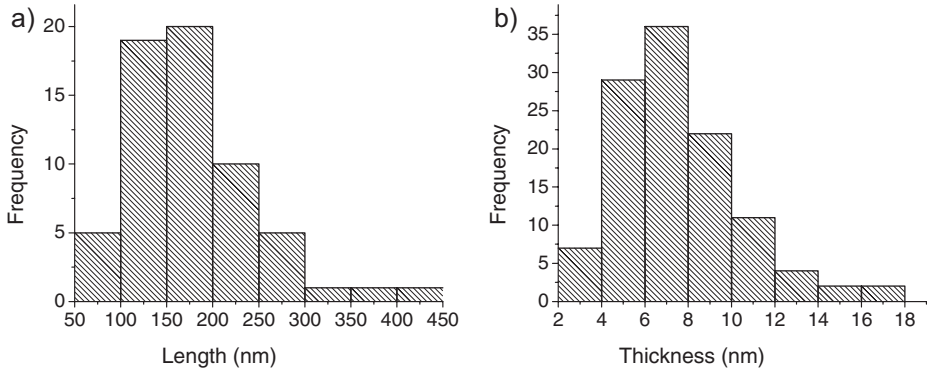

Figure 2.
Histograms of distribution of (a) lengths and (b) thicknesses of the CNW.

The density of the CNW is 1.6 g cm^{-3}[9] and the density of the most part of conventional polymer matrices lays between 0.8 and 2 g cm^{-3}; therefore, to achieve the formation of a percolating network in the polymer matrix, it would be necessary to add between 2 and 6 wt % of CNW to the polymer matrix. These values justify the application of CNW from balsa wood in polymer matrices, which will be the next step of this work.

The infrared spectra of balsa wood and CNW are shown in Figure 3. Table 1 shows the peak assignments of the main vibration bands. The presence of lignin can be identified mainly by the absorption peaks related to the C=C bond of the aromatic ring, which absorbs in the range between 1460 and 1600 cm^{-1}.[10–12] The presence of hemicellulose can be identified mainly through the peak corresponding to the C=O bond, which occurs around 1730 cm^{-1}.[10–12] In the infrared spectrum of the CNW, these peaks are not observed, which would prove the efficiency of the extraction of lignin and hemicellulose from the balsa wood.

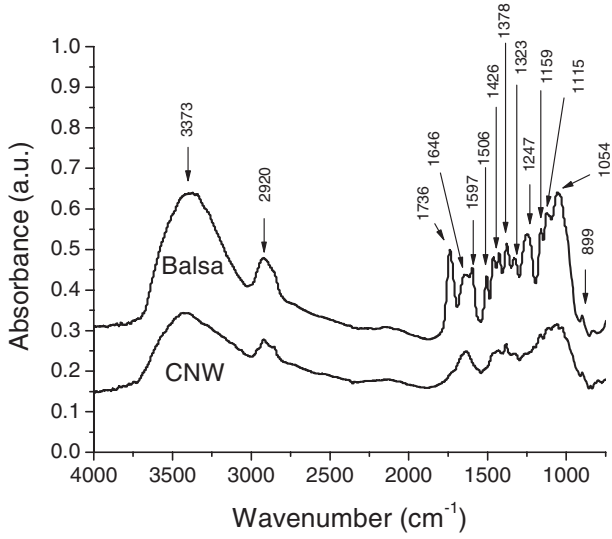

Figure 3.
Infrared spectrum of balsa wood and CNW.

Table 1.
Frequencies of vibration of the infrared spectra[10,11,12].

Wavenumber (cm^{-1})	Peak assignment	Wavenumber (cm^{-1})	Peak assignment
3373	O–H (stretching)	1378	C–H (bending)
2920	C–H (stretching)	1323	C–H (bending)
1736	C=O (stretching)	1247	C–O (stretching), related to phenol
1646	H–O–H (bending due to H_2O)	1159	C–O (stretching), related to alcohol
1597	C=C aromatic (stretching)	1115	C–O (stretching), related to alcohol
1506	C=C aromatic (stretching)	1054	C–O (stretching), related to alcohol
1462	C=C aromatic (stretching)	899	C–H (bending)
1426	C–H (bending)		

In the WAXD diffractograms of balsa wood and CNW, shown in Figure 4, diffraction peaks characteristics of cellulose I around 15° (001), 22.5° (002) and 34° (040)[13,14] can be observed. The deconvolution of the peaks allowed obtaining the degree of crystallinity by the ratio between the area corresponding to the crystalline peaks and the total area. The balsa wood powder showed a crystallinity index of 42% while the CNW had 62% of crystallinity.

Curves obtained by TGA, shown in Figure 5, indicated that the CNW had a higher onset temperature of thermal degradation (226 °C) than the balsa fibers (215 °C). This is probably due to the absence of hemicellulose in the CNW, since the hemicellulose is the component of lowest thermal resistance of the fiber, having degradation between 200 and 260 °C.[15] However, the maximum degradation temperature of balsa (357 °C) was higher than that for CNW (337 °C), what can be clearly visualized in the DTG curves. This is probably due to the presence of lignin in the balsa wood, that was extracted for the CNW acquisition. Lignin is the constituent of higher thermal stability of wood, between 300 and 500°C.[15] The first mass loss (about 6% for both samples) occurred between 28 and 100 °C and refers to the evaporation of water and volatile products. The residue obtained at 800 °C was 19% for balsa fiber and 30% for the CNW, probably relative to inorganic constituents of wood, like Ca and K. Once the

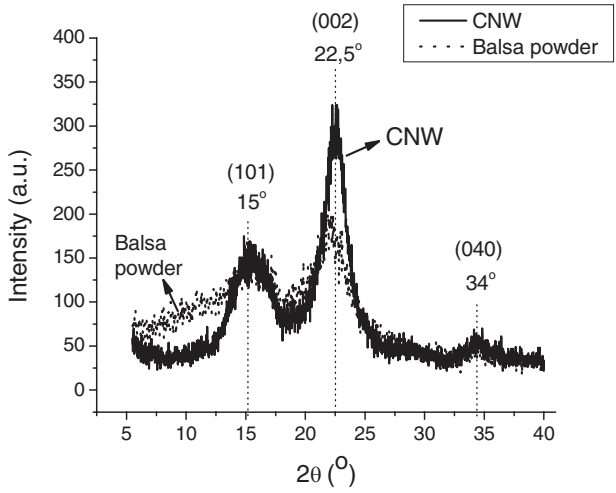

Figure 4.
X-ray diffraction patterns of balsa wood and CNW.

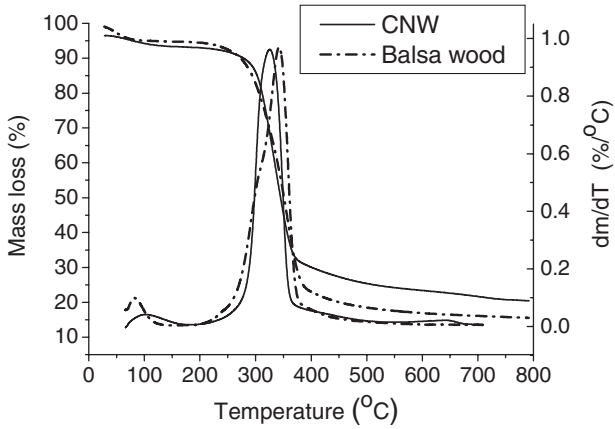

Figure 5.
TGA curves of balsa wood and CNW.

most part of constituents of balsa had already been digested in the obtaining process of CNW, it was expected that the residual mass of CNW is proportionally higher than the residual mass of the raw balsa.

Conclusion

The results showed that balsa wood can be successfully used as a source to obtain cellulose nanocrystals that can be incorporated into polymer matrices to manufacture of nanocomposites. The CNW obtained in this work had average length and thickness of 176 (±68 nm) and 7.5 (±2.9 nm), respectively, crystallinity of 62% and onset temperature of thermal degradation of 226 °C.

Acknowledgements: The authors thank CAPES for financial support (project Nanobiotec No. 13 and Ph.D. scholarship) and the company Orion Balsa Wood for supplying the balsa wood.

[1] R. Silva, S. K. Haraguchi, E. C. Muniz, A. F. Rubira, *Química Nova* **2009**, *32*, 661.
[2] K. Oksman, A. P. Mathew, M. Sain, *Plastics, Rubber and Composites* **2009**, *38*, 9/10.
[3] K. Tashiro, M. Kobayashi, *Polymer* **1991**, *32*, 1516.
[4] D. Fengel, G. Wegener, *Wood: Chemistry, Ultrastructure, Reactions*, Berlin; New York **1984**.
[5] A. Barbosa, *Instituto Nacional de Pesquisas da Amazônia* **2004**.
[6] M. C. Branciforti, A. L. Marinelli, M. Kobayashi, J. D. Ambrosio, M. R. Monteiro, A. D. Nobre, *Sustainability* **2009**, *1*, 1431.
[7] V. Favier, R. Dendievel, G. Canova, J. Y. Cavaille, P. Gilormini, *Acta Mater* **1997**, *45*, 1557.
[8] M. A. S. A. Samir, F. Alloin, A. Dufresne, *Biomacromolecules* **2005**, *6*, 612.
[9] J. Araki, M. Wada, S. Kuga, T. Okano, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1998**, *142*, 75.
[10] C. J. Pouchert, *The Aldrich Library of Infrared Spectra*, **1975**.
[11] M. F. Rosa, E. S. Medeiros, J. A. Malmonge, K. S. Gregorski, D. F. Wood, L. H. C. Mattoso, G. Glenn, W. J. Orts, S. H. Imam, *Carbohydrate Polymers* **2010**, *81*, 83.
[12] D. L. Pavia, G. M. Lampman, G. S. Kriz, *Introduction to Spectroscopy*, Saunders College Publishing, **1996**.
[13] S. Park, J. O. Bakerl, M. E. Himmel, P. A. Parilla, D. K. Johnson, *Biotechnology for Biofuels* **2010**, *3*, 10.
[14] C. J. Garvey, I. H. Parker, G. P. Simon, *Macromol. Chem. Phys.* **2005**, *206*, 1568.
[15] F. Tomczak, T. H. D. Sydenstricker, K. G. Satyanarayana, *Composites: Part A*, **2007**, *38*, 1710.

