Preparation and Characterization of Nanocomposites of Carboxymethyl Cellulose Reinforced with Cellulose Nanocrystals

Wilson Pires Flauzino Neto,[*1] Hudson Alves Silvério,[1] Júlia Graciele Vieira,[1] Héden da Costa e Silva Alves,[1] Daniel Pasquini,[1] Rosana Maria Nascimento de Assunção,[2] Noélio Oliveira Dantas[3]*

Summary: Cellulose nanocrystals (CNC) were extracted from Kraft pulp of *Eucalyptus urograndis*. The CNC were isolated by acid hydrolysis with H_2SO_4 64% (w/w) solution, for 20 minutes at 45 °C. The morphology and crystallinity of the CNC were investigated by atomic force microscopy (AFM) and X-ray diffraction (XRD), respectively. The AFM image supports the evidence for the development of crystals of cellulose in nanometric scale. These nanoparticles were used as reinforcement material in carboxymethyl cellulose (CMC) matrix. Nanocomposites films were prepared by casting. The nanocomposites were characterized by thermal (TGA) and mechanical (DMA) analyses. A large reinforcing effect of the filler was observed. The tensile strength of nanocomposites was significantly improved by 107%, the elongation at break decreased by 48% and the thermal resistance increased slightly. The improvements in thermo-mechanical properties suggest a close association between filler and matrix.

Keywords: carboxymethyl cellulose; cellulose nanocrystals; *Eucalyptus urograndis*; nanocomposites; nanoparticles

Introduction

Facing the problems of plastic recycling and fossil resources exhaustion, there is a great interest to develop sustainable and environmentally friendly materials with enhanced performances. Several biodegradable biopolymers need to be modified to be competitive to petroleum based polymers in question of performance and cost. One way to improve the properties of biopolymers and greatly enhance their commercial potential is to incorporate nanosized reinforcement into the polymer.[1] In this context, cellulose nanocrystals (CNC), also known as ''whiskers'' have received from the materials community a high level of attention, since nanocomposites of CNC/biopolymers may have similar or superior properties compared to polymers of non-renewable sources and composites of inorganic fibers/polymers.[2]

The main features that stimulate the use of cellulose nanoparticles as reinforcement in polymer matrices are the large interfacial area and high modulus of elasticity.[3] These properties associated with a homogeneous distribution within a matrix, the strong interactions and adherence with the same, generally results in clear improvements in thermal, mechanical, and barrier properties of the nanocomposites.[4,5,6] Among other points relevant to the use of CNC can still

[1] Instituto de Química, Universidade Federal de Uberlândia, Campus Santa Mônica, Av. João Naves de Ávila, 2121, Uberlândia - Minas Gerais, Brazil
Fax: +55 (34) 3239-4208;
E-mail: wilsonpfneto@yahoo.com.br
[2] Faculdade de Ciências Integradas do Pontal, Universidade Federal de Uberlândia, Campus Pontal, Rua 20, 1600 CEP 38.304-402, Ituiutaba - Minas Gerais, Brazil
[3] Instituto de Física, Universidade Federal de Uberlândia, Av. João Naves de Ávila, n°2121, Uberlândia - Minas Gerais, Brazil

quote its biodegradable character, low density, transparency, low cost and the fact that they are derived from renewable natural sources highly abundant.[6]

Carboxymethyl cellulose (CMC) is a biopolymer with several application areas in the industrial, food and medical fields. Biodegradable films made of this material do not pose a threat to the environment, has relatively low cost and are non-toxic. However, the disadvantages of these films include poor thermomechanical properties and a strongly hydrophilic nature.[7,8]

Considering the limitations of films made of CMC, the effect of CNC as nano-sized fillers on the properties of CMC-based composites is of interest in the development of novel or improved applications for this polymer, e.g. packaging films and food coatings. The objective of the present research was to evaluate the effect of incorporation of CNC on the thermomechanical properties of CMC-based cast biodegradable films. The nanocrystals were isolated by sulfuric acid hydrolysis from wood pulp Kraft of *Eucalyptus urograndis*. The morphology and crystallinity of the CNC were investigated by Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD), respectively. Thermogravimetric and Dynamic Mechanical Analyses (TGA and DMA) were performed for evaluated the effect of CNC content on mechanical strength, thermal stability and elongation of nanocomposites.

Experimental Part

Extraction of Cellulose Nanocrystals (CNC)

The bleached Kraft pulp of *Eucalyptus urograndis*, provided by the Compacel Company, was crushed using an industrial blender, and then used for the extraction of nanocrystals by acid hydrolysis. The hydrolysis was performed at 45 °C for 20 min under vigorous and constant stirring, using 20 mL of H_2SO_4 64% for each gram of cellulose. Immediately after hydrolysis, the suspension was diluted 10 times to stop the hydrolysis reaction, and centrifuged for 3 min at 11,000 rpm to remove the excess acid. Subsequently the precipitate was dialyzed against tap water until neutral pH. The resulting suspension of dialysis process was treated using a disperser type Turrax for 10 min at 14,000 rpm, then was treated by ultrasonic for 10 min and stored under refrigeration.

Atomic Force Microscopy (AFM)

The AFM measurements were performed using a Shimadzu SPM-9600. AFM images were obtained at room temperature (~21 °C) in the dynamic mode with scan rate of 1 Hz and using Si tips with curvature radius of less than 10 nm and spring constant of 42 N m^{-1}. A drop of diluted nanoparticles aqueous suspension was deposited onto freshly cleaved mica surface and air-dried. The dimensions of CNC were calculated using the VectorScan software (software for Shimadzu's SPM-9600).

Gravimetric Analysis

The hydrolysis yield and the cellulose concentration in the final suspension were 29.58% and 2.368 g L^{-1}, respectively. These were calculated taking an aliquot of known volume of the suspension at 105 °C for 12 hours. The material resulting from drying of the suspension was used as a sample for XRD analysis.

X-Ray Diffraction (XRD)

The X-ray diffractograms of the Kraft pulp fiber and CNC were obtained at room temperature with 2θ range from 5 to 40° and a scan rate of 1 °C min^{-1}. The equipment used was a diffractometer Shimadzu LabX XRD-6000, operating at a power of 40 kV with current of 30 mA and Cu Kα radiation (1.5406 Å). The crystallinity index (CI) of the material was determined by the ratio of the peak heights of the X-ray spectrum of the crystalline peak at $2\theta = 22–23°$ and the amorphous region $2\theta = 18–19°$, using the method of Segal.[9]

Preparation of Nanocomposites

Different aliquots of the aqueous suspension of CNC, with known concentrations

were added to 10 mL of a solution of CMC 3% (w/v), in order to obtain the final concentrations of CNC, 0, 2, 4, 6, 8, 10 and 15% by weight, relative to the CMC matrix. The resulting mixture was homogenized by ultrasonication and deposited on Petri dishes and left at rest to the total evaporation of water, forming the films. The CMC used in the preparation of films, was the carboxymethyl cellulose sodium of food grade, with molecular weight 70,000 to 90,000 and degree of substitution 0.8 (Denvercel Company).

Thermogravimetric Analysis (TGA)

Thermal stability of the films were evaluated using a Shimadzu DTG-60H. The analysis conditions were: a nitrogen atmosphere with flow 30 mL min^{-1}, heating rate of 10 °C min^{-1}, temperature range of 25 to 600 °C, sample mass between 5 and 7 mg and aluminum pans.

Dynamic Mechanical Analysis (DMA)

The tensile strength and elongation at break of the films were measured in a Dynamic Mechanical Analyzer 2980 (TA Instruments) at 25 °C. Sample sizes were 40 mm × 6.2 mm × 0.05 mm (length × width × thickness). A force of 0.01 N was used as preload and a ramp-force of 8 N min^{-1}, until the fracture of the sample. The device was previously calibrated and was made a total of five measurements for each sample to ensure reproducibility of results.

Results and Discussion

Cellulose nanocrystals, also known as whiskers, are crystalline domains of cellulose fibers isolated mainly by acid hydrolysis, and are so called because of their physical rigidity, thickness and length. Hydrolysis with sulfuric acid involves the introduction of sulfate groups on the surface of the CNC, and these groups carry the surface of CNC negatively, provoking anionic stabilization by repulsive forces, thus leading to the achievement of stable aqueous dispersions.[2] As can be seen in Figure 1a, the hydrolysis conditions used led to obtaining a homogeneous and stable aqueous suspension.

The incorporation of CNC in the matrix of CMC did not affect the transparency or homogeneity of the polymer, as can be seen in the pictures in Figure 1b, 1c and 1d. There are not aggregates in the films produced, and it was concluded that there was an uniform dispersion of CNC in the polymer matrix.

The characterization by AFM supports the evidence for the development of cellulose in nanometric scale. The AFM image (Figure 2) also shows that the nanoparticles have the shape of needles. The size determination was challenging due to agglomeration, but from several images the length and the diameter could be measured. The length and diameter values of the CNC produced ranged from 100 to 300 nm and 5 to 10 nm, respectively. This

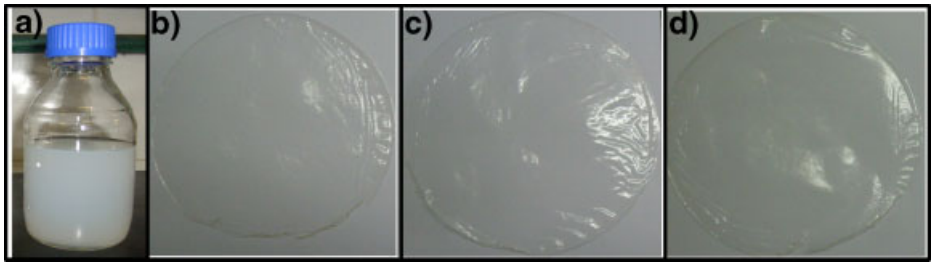

Figure 1.
a) Aqueous suspension obtained after isolation of the CNC; b) Picture of pure CMC film; c) Picture of CMC film with 6% CNC; d) Picture of CMC film with 15% of CNC.

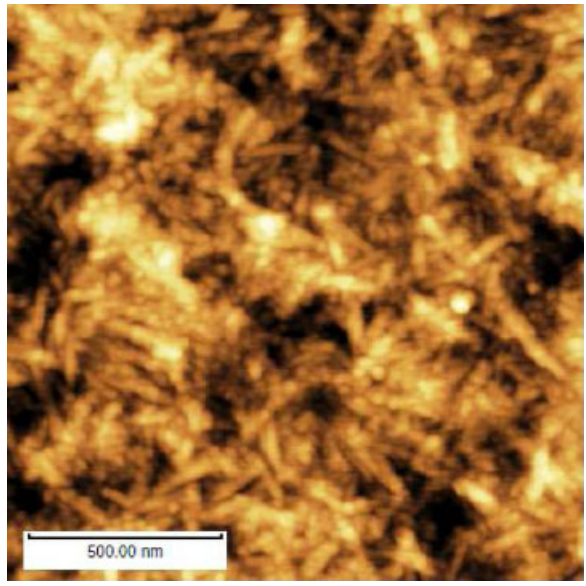

Figure 2.
AFM image of cellulose whiskers extracted from Kraft pulp of *Eucalyptus urograndis*.

agrees with earlier AFM analyses on cellulose whiskers from wood sources.[10] As the AFM analysis overestimates the diameter of the nanocellulose due to the tip-broadening effects, the diameter of nanoparticles was measured from the height of the nanowhiskers.[11]

By X-ray diffractograms of the Kraft pulp and CNC (Figure 3), there is a predominance of type I cellulose, verified by the presence of peaks at $2\theta = 15^\circ$ (plane 101), 17° (plan 10i), 21° (plane 021) and 23° (plane 002), though there are traces of cellulose type II in the diffraction patterns

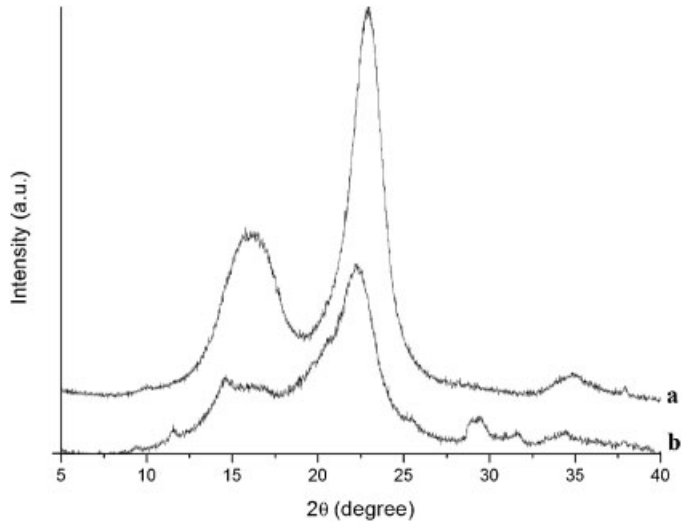

Figure 3.
X-ray diffraction patterns of a) Kraft pulp of *Eucalyptus urograndis*; b) cellulose nanocrystals.

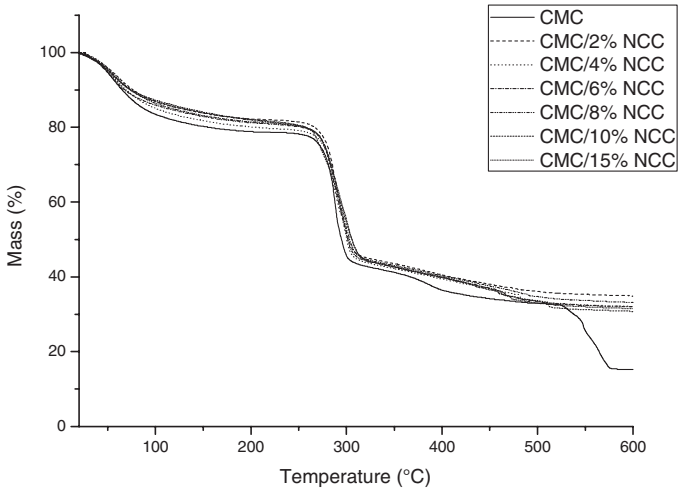

Figure 4.
TGA curves for the nanocomposites.

of CNC, observed by peaks at $2\theta = 12^{\circ}$ (plane 101), 20° (plan 10i) and 22° (plane 002).[12] Possibly the presence of traces of cellulose type II is associated to recrystallization of cellulose after hydrolysis, since 64% sulfuric acid solution can be a solvent for cellulose.[13] The crystallinity index (CI) of the CNC and the original Kraft pulp were estimated and found that there was a significant decrease in the original Kraft pulp CI (CI = 86%) compared to CNC obtained (CI = 71%), and this behavior can be attributed to partial dissolution of the cellulose sample during hydrolysis and may have been re-precipitated.[13]

Figure 4 shows TGA curves and shows the mass loss of composites when they are heated. The mass loss profiles are similar and feature two main events: the evaporation of water in the range 70-100 °C and thermal degradation of carboxymethyl cellulose at approximately 280–300 °C.

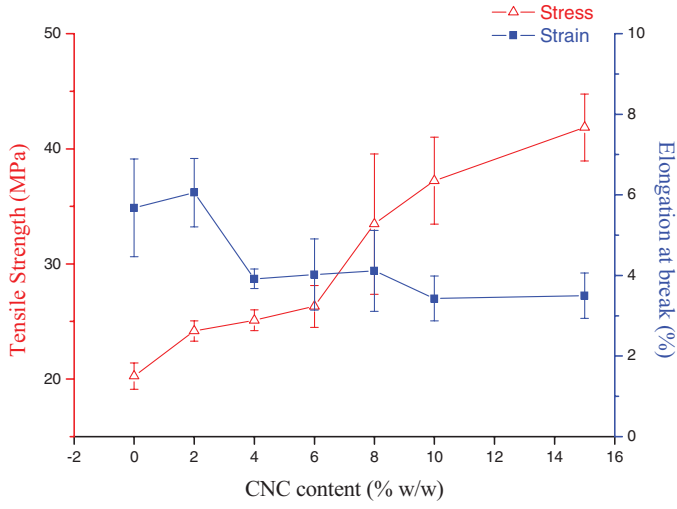

Figure 5.
Tension and elongation at break of the films as a function of CNC content.

There was a subtle improvement in thermal stability of nanocomposites compared to pure CMC film, and this improvement can be attributed to the presence of cellulose nanocrystals.

The Figure 5 presents the results of dynamic-mechanical tests, and shows the effect of CNC contents on the tensile strength and the elongation at break of the films produced. It can be seen that there was an increase in tensile strength of the polymer up to 107% and a decrease in the same stretch up to 48% as a result of incorporation of the CNC. Evidently the increased load increased the rigidity of the polymer due to the homogeneous distribution of the crystalline reinforcement within the matrix and the possibility strong interactions of the CNC with the polymer matrix, and therefore the mobility of polymer segments was reduced thus increasing the tensile strength and decreasing the elongation at break.

Conclusion

CMC composites were successfully prepared by casting with the reinforcement of cellulose nanocrystals manufactured from Kraft pulp of *Eucalyptus urograndis* using sulfuric acid hydrolysis. Even with high content of CNC the CMC/CNC nanocomposites were transparent. The CNC are satisfactory reinforcement agents for the CMC, since the data showed a marked increase in thermo-mechanical properties of CMC film. These improvements in thermo-mechanical properties suggest a close association between filler and matrix. The utilization of CNC as reinforcing agent is an alternative that would expand the commercial use of CMC films.

Acknowledgements: The authors thank CAPES/PROAP, CNPq and FAPEMIG for financial support.

[1] A. K. Mohanty, L. T. Drzal, M. Misra, *Polym. Mater Sci. Eng.* **2003**, *88*, 60.
[2] D. J. Silva, M. L. O. D'Almeida, *O Papel* **2009**, *70*, 34.
[3] A. Dufresne, *J. Nanosci. Nanotechnol.* **2006**, *3*, 322.
[4] H. M. C. Azeredo, L. H. C. Mattoso, D. Wood, T. G. Williams, R. J. Avena-Bustillos, T. H. McHugh, *Jounal of food science* **2009**, *74*, N31.
[5] N. Wang, E. Ding, R. Cheng, *Polym.* **2007**, *48*, 3486.
[6] E. M. Teixeira, C. R. Oliveira, L. H. Mattoso, *Polímeros* **2010**, *20*, 264.
[7] T. Heinze, K. Pfeiffer, *Angew. Makromol. Chem.* **1999**, *37*, 266.
[8] R. A. Khan, S. Salmieri, D. Dussault, J. Uribe-Calderon, M. R. Kamal, A. Safrany, M. Lacroix, *J. Agric. Food Chem.* **2010**, *58*, 7878.
[9] L. Segal, *Text. Res. J.* **1959**, *29*, 786.
[10] S. Beck-Candanedo, M. Roman, D. Gray, *Biomacromolecules* **2005**, *6*, 1048.
[11] R. Rusli, K. Shanmuganathan, S. J. Rowan, C. Weder, S. J. Eichhorn, *Biomacromolecules* **2011**, *12*, 1363.
[12] S. Borysiak, J. Garbarczyk, *Fibres Text East Eur.* **2003**, *11*, 104.
[13] G. Jayme, F. Lang, in Methods in Carbohydrate Chemistry, R. L. Whistler, Ed.; Academic Press. New York: **1963**, Vol. **3,** 75–83.

