



## Thermal and mechanical properties of bio-nanocomposites reinforced by *Luffa cylindrica* cellulose nanocrystals

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### ARTICLE INFO

#### Article history:

Received 14 May 2012

Received in revised form 17 August 2012

Accepted 18 August 2012

Available online 24 August 2012

#### Keywords:

Cellulose nanocrystals

*Luffa cylindrica*

Nanocomposites

Surface chemical grafting

Mechanical properties

### ABSTRACT

Cellulose nanocrystals have been prepared by acid hydrolysis of *Luffa cylindrica* fibers. The acid-resistant residue consisted of rod-like nanoparticles with an average length and diameter around 242 and 5.2 nm, respectively (aspect ratio around 46). These cellulose nanocrystals have been used as a reinforcing phase for the processing of bio-nanocomposites using polycaprolactone (PCL) as matrix. To promote interfacial filler/matrix interactions the surface of cellulose nanocrystals was chemically modified with n-octadecyl isocyanate (C<sub>18</sub>H<sub>37</sub>NCO). Evidence of the grafting was supported by infrared spectroscopy and elemental analysis. X-ray diffraction analysis was used to confirm the integrity of cellulose nanocrystals after chemical modification. Both unmodified and chemically modified nanocrystals were used to prepare nanocomposites. The thermal properties of these materials were determined from differential scanning calorimetry and their mechanical behavior was evaluated in both the linear and non-linear range.

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### 1. Introduction

Materials, together with energy and information, are regarded as the pillar industries in the world economy of twenty-first century. An increasing demand emerges for biodegradable materials and products made from renewable resources. Moreover, replacement of traditional microcomposites by nanocomposite materials has grown rapidly during the last two decades to overcome the limitations of the micrometer-scale, designing new materials and structures with unprecedented flexibility, improved physical properties and significant industrial impact.

All these requirements are fulfilled by nano-scaled cellulose. It is the most abundant polymer on earth, it is biodegradable and its structural hierarchy can be used to prepare high strength nanoparticles. An abundant and exponentially increasing literature is devoted to cellulose nanoparticles obtained either (i) by a disintegration shearing action to obtain microfibrillated cellulose (Siró and Plackett, 2010) or (ii) by a chemical acid hydrolysis treatment to obtain cellulose nanocrystals or whiskers (Azizi Samir, Alloin, & Dufresne, 2005; Habibi, Lucia, & Rojas, 2010; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Several sources of cellulose have been used to prepare such cellulosic nanoparticles. Generally, the elongated

rod-like cellulose nanocrystals consist of high-purity single cellulose nanocrystals formed from a variety of cellulose fiber sources under controlled conditions whose dimensions depend on the nature of cellulose source as well as the hydrolysis conditions. Their diameter and length typically range from 5 to 10 nm and from 100 to 500 nm, respectively.

Fibers extracted from a tropical plant named *Luffa cylindrica*, belonging to the family of *Cucurbitaceae*, has been recently studied as a new potential source of microfibrillated cellulose and cellulose nanocrystals (Siqueira, Bras, & Dufresne, 2010a) able to impact the properties of bio-nanocomposites. In fact, the *L. cylindrica* cellulose has been investigated in the field of polymer composites owing to its high cellulose content and its density around 0.82 and 0.92 g cm<sup>-3</sup> (Satyanarayana, Guilmaraes, & Wypych, 2007) lower than the one of some common natural fibers such as sisal (1.26 g cm<sup>-3</sup>), hemp (1.48 g cm<sup>-3</sup>) or ramie (1.5 g cm<sup>-3</sup>) and cotton (1.51 g cm<sup>-3</sup>) (Siqueira et al., 2010a). However, to be efficiently used as a reinforcing phase in a polymeric matrix material, the surface of the cellulosic filler usually needs to be compatibilized to reduce its inherent hydrophilic character and improve its dispersability in the continuous phase which is generally hydrophobic. Several possibilities have already been described and the positive impact of such surface treatment has been confirmed with PCL-nanocellulose composites (Siqueira, Bras, & Dufresne, 2009). In this case, sisal based nanocellulose were used. Up to our knowledge, the influence of source of whiskers on PCL

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nanocomposites thermal and mechanical properties has never been proposed.

Such nanocomposite materials can also have an interest regarding transport properties as very recently published on similar PCL-*L. cylindrica* whiskers composites (Follain et al., submitted for publication). In the present study, cellulose nanocrystals extracted from *L. cylindrica* fibers have been used to prepare fully biodegradable bio-nanocomposites with a polycaprolactone matrix and their thermal and mechanical properties have been analyzed and compared with other sources.

## 2. Experimental

### 2.1. Materials and processing

Native *L. cylindrica* fibers were purchased in Belo Horizonte (Minas Gerais, Brazil). Poly(caprolactone) (PCL) ( $M_n = 42,500 \text{ g mol}^{-1}$ ,  $M_w = 65,000 \text{ g mol}^{-1}$ ), sulfuric acid ( $\geq 95 \text{ wt\%}$ ), and *N*-octadecyl isocyanate were obtained from Aldrich. Ethanol, acetone, chloroform, toluene, and dichloromethane were purchased from Chimie-Plus and used as delivered.

#### 2.1.1. Cellulose nanocrystals

Cellulose nanocrystals were prepared from *L. cylindrica* fibers as described elsewhere (Siqueira et al., 2010a). Briefly, fibers were treated three times with 4 wt% NaOH solution at 80 °C for 2 h under mechanical stirring and bleached with a solution made by equal parts of acetate buffer, aqueous chlorite (1.7 wt% in water) and distilled water. The bleaching treatment was performed 4 times at 80 °C, under mechanical stirring, during 2 h each one. Acid hydrolysis was achieved at 50 °C with 65 wt% sulfuric acid (pre-heated), for 40 min, using mechanical stirring. Successive centrifugations were performed at 10,000 rpm and 10 °C for 10 min each step and the suspensions was dialyzed against distilled water. Homogenization was carried out using an Ultra Turax T25 homogenizer for 5 min and the suspensions was filtered in glass filter no. 1. Some drops of chloroform were added to the nanocrystal suspension that was stored at 4 °C.

#### 2.1.2. Surface chemical modification

The surface chemical modification of *L. cylindrica* nanocrystals was performed in toluene as described elsewhere for sisal nanocrystals (Siqueira, Bras, & Dufresne, 2010b). To avoid drying of the nanocrystals that undoubtedly should lead to a strong aggregation process we used never dried cellulose. A solvent exchange procedure from water to toluene was used. For that, an aqueous suspension with the desired amount of cellulose nanocrystals (1 wt%) was solvent exchanged to acetone and then to dry toluene by several successive centrifugation and redispersion operations. Sonication was performed after each solvent exchange step to avoid aggregation.

In a three-necked round-bottomed flask, equipped with a reflux condenser, 3 g of cellulose nanocrystals in toluene and 100 mL of toluene were added. The system was kept in a nitrogen atmosphere. An excess of *n*-octadecyl isocyanate (16.9 g) was added drop by drop when the temperature of the system reached 90 °C. The temperature was then increased up to 110 °C and it was kept in this condition for 30 min. The modified nanocrystals were filtered and washed with ethanol to remove amines formed during the reaction and the isocyanate that did not react. Afterward, the modified materials were washed with ethanol and centrifuged four times at 10,000 rpm and 10 °C for 15 min each step. The final step consisted in changing the solvent of the modified nanocrystals from ethanol to dichloromethane, which was the solvent used for the film preparation.

### 2.1.3. Preparation of nanocomposite films

Polycaprolactone (PCL,  $M_n = 42,500 \text{ g mol}^{-1}$ ) was first dissolved in dichloromethane at room temperature for 20 h ( $0.036 \text{ g L}^{-1}$ ). Different amounts of *L. cylindrica* nanocrystals (3, 6, 9 and 12 wt% calculated on the dry basis) were used to prepare nanocomposites. The corresponding nanocrystal content in dichloromethane suspensions was magnetically stirred for 6 h with the PCL solution. The suspensions were sonicated for 2 min before casting in Teflon molds and solvent evaporation was performed at room temperature. The thickness of nanocomposites was approximately  $350 \pm 50 \mu\text{m}$  from the average value of 13 measurements per film.

The designation of nanocomposites is reported as follows: PCL/X wt% ULW nanocomposite and PCL/X wt% MLW nanocomposite, with X being the weight content of nanocrystals within the nanocomposite film, ULW and MLW designing unmodified and modified *L. cylindrica* nanocrystals, respectively.

### 2.2. Characterizations

#### 2.2.1. Morphological analyses

Transmission electron microscopy (TEM) observations were performed with a Philips CM200 transmission electron microscope using an acceleration voltage of 80 kV. A drop of diluted suspension of *L. cylindrica* nanocrystals was deposited on a carbon-coated grid. The samples were stained with a 2 wt% solution of uranyl acetate.

Elemental analysis was carried out at the Laboratoire Central d'Analyses de Vernaison, France (CNRS). The carbon, oxygen, hydrogen and nitrogen contents for unmodified and modified *L. cylindrica* nanoparticles were measured independently. The results from elemental analysis were used to determine the degree of substitution (DS, number of grafted hydroxyl function per anhydroglucose unit (AGU)) according to Eq. (1):

$$DS = \frac{72.07 - C \times 162.14}{281.48 \times C - 216.20} \quad (1)$$

where *C* is the relative carbon content in the sample and 72.07, 162.14, 281.48, 216.20 correspond to the molecular weight of the anhydroglucose unit, mass of anhydroglucose unit, mass of *n*-octadecyl isocyanate residue and carbon mass of the *n*-octadecyl isocyanate residue, respectively.

The obtained values were averaged over two measurements and the standard deviation ranged between 0.10 and 0.30. The precision of the measurement was considered to be 0.3% for C and H atoms, and 0.5% for O atoms. They have been corrected assuming unmodified samples as pure cellulose and samples made during the same analysis series.

Infrared spectroscopy (FTIR) was used to evidence the chemical grafting of cellulose nanocrystals. FTIR spectrograms were recorded by directly depositing the dried powder of nanoparticles on the surface of the crystal. FTIR analysis was performed with a Mattson 5000 spectrometer, equipped with single reflection HATR and a ZnSe crystal using a resolution of  $4 \text{ cm}^{-1}$  and with a total of 64 scans.

X-ray diffraction analysis were recorded with a Panalytical X'Pert Pro MPD-Ray diffractometer with Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) generated at a voltage of 45 kV and current of 40 mA. The  $2\theta$  diffraction diagrams were determined between 5° and 60°. The crystallinity index was calculated using the Buschle-Diller and Zeronian equation (Eq. (2)) (Buschle-Diller & Zeronian, 1992):

$$I_c = \frac{1 - I_1}{I_2} \quad (2)$$

where  $I_1$  is the intensity at the minimum ( $2\theta = 18^\circ$ ) and  $I_2$  is the intensity associated with the crystalline region of cellulose ( $2\theta = 22.5^\circ$ ).

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