



Thermal characterization of cellulose nanocrystals isolated from sisal fibers using acid hydrolysis



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ABSTRACT

Besides interesting properties and potential applications, cellulose nanocrystals (CNCs) present some limitations which remain a challenge in many application fields. These nanomaterials are sensitive to thermal degradation due to their natural source and surface characteristics, limiting their processing at high temperature. In this study, pristine sisal fibers were bleached using different acid (ABF) and basic (BBF) techniques prior to sulfuric acid hydrolysis under the same conditions. This procedure provided two CNCs with different characteristics (ACNC and BCNC). The compositions of the bleached cellulosic pulps were characterized and was found that ABF and BBF presented different cellulose contents of 61.5 and 72.4% respectively. It clearly impacts the thermal behavior of the obtained nanomaterials, leading BCNC to present a maximum degradation temperature of approximately 100 °C higher than ACNC. Other CNC characteristics, such as surface charge, crystallinity and aspect ratio also seem to play an important role in relation to the thermal behavior. A decrease in the stability and the modification of the volatile content and composition were observed during the thermal degradation.

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1. Introduction

Since the first publications on cellulose nanomaterials in the mid-1990s, the interest in these materials has grown exponentially. Many studies have been carried out to develop techniques for the obtainment and application of these nanostructures due to their unique characteristics of mechanical resistance, optical properties, biodegradability and abundance in nature. The obtained nanostructured cellulosic materials have shown potential in the fields of electronics (Juntaro et al., 2012; Muller et al., 2013), optics (Cranston and Gray, 2008), 3D printing (Shao et al., 2015) and biomedicine (Kuzmenko et al., 2013; Sanna et al., 2013).

However, the wider potential of these materials has not been fully explored due to some intrinsic limitations. World-scale production remains a challenge, despite optimistic predictions for production growth and the appearance of some pilot industrial plants in recent years. During the last decade, many authors have developed methods to isolate nanomaterials from biomass residues (Alemdar and Sain, 2008; Kvien et al., 2005; Li et al., 2009; Oksman et al., 2011), to provide better compatibility with a hydropho-

bic/thermoplastic matrix (Lin and Dufresne, 2013; Ly et al., 2010; Martínez-Sanz et al., 2013) and to improve the resistance to thermal degradation through chemical modification or using alternative production methodologies (Filpponen and Argyropoulos, 2010; Kalashnikova et al., 2012; Novo et al., 2015; Siqueira et al., 2013).

These new methodologies expand the possibilities for the application of these materials. Initially, the cellulose nanomaterials, in particular cellulose nanocrystals, were used only in aqueous suspension to form composites with hydrophilic polymers (Cheung et al., 1993; Angle and Dufresne, 2001; Roohani et al., 2008). However, due to the development of surface modifications, these materials can now be used with thermoplastic and hydrophobic matrixes (Hassan et al., 2012; Khoshkava and Kamal, 2013; Potthast et al., 2006) creating new possibilities for their application in nanocomposites based on commercial polymers prepared using large-scale processing techniques, such as extrusion and injection molding. Recently, good results have been reported for the use of cellulose nanocrystals to develop new materials prepared at high temperatures with improved properties (Lemahieu et al., 2011; Lin and Dufresne, 2013). The application of these composites in the industrial sector requires solid knowledge regarding the thermal properties, especially when the surface is modified during the acid hydrolysis process.

Sisal (*Agave Sisalana*) fiber is one of the most widely used natural fibers and is an excellent source of nanocrystals. Sisal fibers gen-

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erally contain 60–80% cellulose, 5–20% lignin and 5–20% moisture content in their composition, being obtained from the residues of the plant processing (Martin et al., 2010).

In this study, cellulose nanocrystals were extracted from sisal fiber by chemical methods. The pristine fiber was milled and bleached with two different techniques: an acid-based and a basic-based methodology. The resultant bleached fibers were neutralized and different techniques were employed to characterize them. The thermal behavior of these cellulosic nanomaterials was determined and compared to that of the pristine cellulose present in the sisal fiber.

2. Material and methods

2.1. Materials

The sisal fiber was provided by Fios Naturais Ltda. Sulfuric acid (H_2SO_4 , 98%) and sodium hydroxide (NaOH) were purchased from Lafan Química Fina, hydrogen peroxide (H_2O_2) from Nuclear and the celluloses membrane D9402-100FT (76 mm) from Sigma-Aldrich.

2.2. Preparation of cellulose nanocrystals

2.2.1. Fiber bleaching and nanocrystal preparation

With the objective of comparing nanocrystals with different characteristics (such as the dimensions and surface charge), applying the same hydrolysis process, the bleaching of sisal fiber (FB) was carried out by two different methodologies.

2.2.1.1. Basic bleaching (BBF). The basic bleaching process was carried out with 2.5 g of sisal fibers (milled and selected using a size 20 mesh). These fibers were suspended in a NaOH (10% w/v) aqueous solution under strong stirring for 4 h at 60 °C and then washed until neutral pH. In the second stage, the fibers were re-suspended in an aqueous solution of NaOH (5% w/v) and $\text{Ca}(\text{OCl})_2$ (2.5% w/v) for 4 h at 45 °C, washed until neutral pH and dried.

2.2.1.2. Acid bleaching (ABF). In the acid-based bleaching process 2.5 g of sisal fibers (milled and selected using a size 20 mesh) were suspended under vigorous stirring in a peracetic acid (PAA) solution for 6 h at 60 °C. After the reaction the fibers were washed until neutral pH and dried. The PAA was prepared through the simple mixing of water (15% v/v), hydrogen peroxide (40% v/v) and acetic acid (45% v/v) in the reaction medium. To ensure a chemical shift in the direction of the products, 0.3 mol/L of H_2SO_4 was used as a catalyst (Xue-bing et al., 2008; Zhao et al., 2008).

2.2.2. Isolation of cellulose nanocrystals (CNCs)

The same hydrolysis process was used for the fibers bleached using the two different techniques. In a round bottom flask, 1 g of the bleached fibers (milled and selected using a size 20 mesh) was suspended in 20 mL of an H_2SO_4 solution (60% w/w) and kept under strong stirring for 30 min at 55 °C. The suspension was diluted with the addition of 20 mL of cold water to stop the reaction and centrifuged applying cycles of 20 min under a force of 1373.6g. After each cycle the supernatant was discarded and the volume completed with water. This processes was repeated until there was no sign of complete precipitation after the cycle. This suspension was dialyzed with a cellulose membrane until reaching neutral pH.

The optimal conditions for the isolation of cellulose nanocrystals (or whiskers) previously described by Teodoro (Teodoro et al., 2011) were used in this study.

2.3. Determination of fiber components

The amount of holocellulose in the fibers corresponds to the sum of all the polysaccharides present in the sample. It can be obtained from the total mass of the fiber subtracting the values of lignin and humidity. The hemicellulose content is the difference between the holocellulose and the α -cellulose fractions. These values were obtained by gravimetric methods, as described below.

2.3.1. Lignin content

The method for the lignin determination was based on TAPPI T222 om-88. In a beaker, 15 mL of H_2SO_4 (72% w/w) was added to a sample (1 g) of the sisal fiber (*in natura* and bleached) at 10–15 °C and left to stand for 2 h. This material was then transferred to an Erlenmeyer flask and diluted with 560 mL of water to give an acid concentration of 3%. The suspension was then boiled for 4 h. The lignin was decanted for 12 h and filtered through a glass filter n°2 and washed with hot water. The sample was dried for 4 h at 105 °C and the lignin quantity was determined using Eq. (1).

$$\% \text{de Lignin} = \frac{\text{lignin mass}}{\text{initial sample mass}} \times 100 \quad (1)$$

2.3.2. α -Cellulose content

The α -cellulose is the fraction of the holocellulose which is insoluble in a 17.5% (w/w) NaOH solution under certain conditions. Here, an amount of 0.5 g of sisal (*in natura* and bleached) fibers was placed into a beaker in which 6 mL of a 17.5% NaOH solution was slowly added (over approximately 10 min). The sample was macerated and left to stand for 3 min. A further 5 mL of the same NaOH solution was then added and the suspension was stirred for 30 min. Water (15 mL) was added and the solution was stirred for a further 30 min for homogenization. This suspension was filtered through a n°2 glass filter and washed with a 8.5% NaOH solution and a diluted solution of acetic acid. The filter was dried for 4 h at 105 °C and the amount of α -cellulose was determined by gravimetric analysis (Eq. (2)).

$$\% \text{of } \alpha \text{ cellulose} = \frac{\alpha - \text{cellulose mass}}{\text{initial sample mass}} \times 100 \quad (2)$$

2.4. Characterizations and measurements

2.4.1. Zeta potential

The zeta potential (ξ) of the suspensions was obtained in a Zeta sizer Nano Z (Malvern) analyzer. The diluted suspensions (1.5 mg mL^{-1}) were analyzed over a period of 60 days. To determine the stability of the suspensions over time, no ultrasound was applied to disperse the nanocrystals before the analysis and only gentle magnetic stirring was carried out to homogenize the dispersion.

2.4.2. Thermal analysis

The thermogravimetric analysis (TGA) was conducted on a thermal analyzer, model STA 449 F1 Jupiter (Netzsch) attached to a Bruker Tensor 27 FT-IR spectrometer. Approximately 5 mg of each sample was heated from 25 and 600 °C at a heating rate of $10^\circ\text{C min}^{-1}$ with a nitrogen flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The TGA and the FT-IR spectroscopy allow qualitative analysis of the volatiles. The experimental data were also used to provide thermal parameters, such as the activation energy (E_a). The Coats-Redfern equations were used to obtain the values in the principal degradation stage of each sample.

2.4.3. Microscopy analysis

The morphology of the fibers was analyzed by a JSM-6340 and JSM-6390LV scanning electron microscopes (SEM – JEOL), while the

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