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Extraction and characterization of cellulose whiskers from commercial cotton fibers

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Abstract During the past few years, there has been a growing interest in incorporating cellulose whiskers from different sources as nanoreinforcement in polymer matrixes. The purpose of this study is to evaluate the performance of the cellulose whiskers obtained from Brazilian commercial cotton. In this sense, cellulose whiskers were prepared by acid hydrolysis which was carried out with a sulfuric acid solution 6.5 M at 45 and 60 °C for 75 and 20 min, respectively, and dried using different methods—an oven, a freeze dryer, and an air circulation oven. Cellulose whiskers were investigated in respect of crystallinity, thermal stability, and morphologically by scanning transmission electron microscopy. Cellulose cotton whiskers, independently of extraction conditions, provided an average length and a diameter of 150 ± 50 nm and of 14 ± 5 nm, respectively, and showed a rod-like shape. Whiskers extracted at 45 °C for 75 min have shown similar crystallinity and better thermal stability in oxidizing atmosphere. The use of the freezing dry process resulted in whiskers with better thermal stability and similar crystallinity than those obtained when dried in the air circulation oven process.

Introduction

Nowadays, biodegradable materials from renewable resources have attracted great attention for a sustainable development and environmental conservation. Utilization of natural fillers from renewable resources not only contributes to a healthy ecosystem, but also makes them economically interesting for industrial applications due to the high performance of the resulting composite [1–3].

Cellulose is the most abundant and renewable biopolymer provided by nature. Its low crystalline region can be dissolved away by controlled acid hydrolysis, while the water-insoluble, highly crystalline region can be converted into a stable suspension by mechanical shearing. The crystalline parts are the cellulose whiskers, whose main characteristics are a high aspect ratio and a large interface area. Cellulose whiskers had attracted significant attention during the last decade, and have now been successfully used as a new kind of filler, as reinforcing phases in both synthetic polymeric matrices and natural ones. This interest is due to their renewable nature, abundance, good mechanical properties, good biocompatibility, and large specific surface area. These nanoscale fibers have shown great potential in applications including tissue engineering, and nanodevices [1, 4]. More recently, there has been an increased use of whiskers as reinforcement in nanocomposites. The reason why the cellulose whiskers can be used as a reinforcing phase in nanocomposite because, besides having a high aspect ratio, they

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also have a high bending strength [3–11]. The use of natural sources, such as kraft bagasse [3], cotton [12], sisal [13], mulberry [14], and cassava bagasse [15], to produce cellulose whiskers has been increasing.

Cotton (*Gossypium hirsutum* L.) fiber is one of the most important raw materials for the textile industry. For this reason, cotton plants are widely grown in many areas throughout the world. The producers as per order of importance are China, the United States, India, Pakistan, Uzbekistan, Brazil, and Turkey, which account for 77%, in average, of the global volume [16]. In Brazil, researchers have been using genetic breeding of cotton plant to enhance the production and quality of cotton fibers [17]. Cotton fibers are the seed hairs of the plant *Gossypium*. It is typically composed of 88-96% cellulose, the remainder being protein, i.e., pectin materials and wax. Cotton must be scoured and usually bleached before use, where its cellulose content is increased to about 99% [18]. Several studies have shown that cotton cellulose whisker can be obtained from cotton slivers [12], waste cotton fabric [19], filter paper Whatman [11, 20–22], and cotton linter [23]. One of the aims in our laboratory is to evaluate the use of different sources of cellulose to produce cellulose whiskers. The aims of this present study were to produce cellulose whisker from Brazilian commercial cotton fiber through different hydrolysis procedures and to perform the characterization of the cellulose whiskers obtained.

Experimental part

Materials

Commercial cotton fibers (Johnson & Johnson cotton balls) were purchased from the local market. Analytic-grade sodium hydroxide, NaOH (from Qhemis); sulfuric acid, H_2SO_4 (from Synth); glacial acetic acid (from Synth); and sodium chlorite ($NaClO_2$, from J. T. Baker) reagents were used. All the reagents were used as received.

Methods

For the chemical composition determination, the commercial cotton fibers were chopped using a sieve of 10 mesh. The lignin content of the fibers was determined by a reaction with sulfuric acid according to standard methods of TAPPI- T222 om-88. The holocellulose (cellulose + hemicelluose) content was determined according to TAPPI T19 m-54. The α-cellulose was removed from holocelluose by alkali extraction [24]. The hemicellulose content was obtained by subtracting the α-cellulose part from the holocellulose content. Analyses were performed in triplicate.

In order to prepare cellulose whiskers, about 5 g of fibers was dispersed in 100 mL of 6.5 M sulfuric acid at 45 and at 60 °C under vigorous stirring for 75 and 20 min, respectively. After that, 500 mL of cold distilled water was used to complete the reaction. The sulfuric acid was partially removed from the suspension by centrifugation at 10,000 rpm for 10 min. The suspension was submitted to dialysis under tap water using a cellulose membrane up to pH 6–7. The resulting suspension was re-submitted to stirring at 5,000 rpm for 60 min, to ultrasonic treatment for 5 min, and stored in a refrigerator after an addition of drops of chloroform. For the dry process, the suspension of cotton whiskers was dried using an oven (temperature 50 °C), an air circulation oven (temperature 50 °C for 12 h), and a freeze dryer EZ-DRY FTS System. The determination of cellulose whiskers' yield was achieved by weighing 10 mL of the suspension after drying overnight.

Scanning electron microscopy (SEM) of cotton fiber was performed using a Zeiss DSM 960 microscope instrument. A drop of water-dispersed solution was coated with a thin layer (ca. 15 nm) of sputter-coated gold.

Scanning transmission electron microscopy (STEM) samples were examined in a TECNAI G^2 microscope. A droplet of diluted cellulose whiskers' suspension was deposited on a carbon microgrid (400 mesh) and dried at room temperature. Next, the samples were stained with a 1.5 wt% solution of uranyl acetate for 2 min.

The X-ray diffraction (XRD) patterns were measured for cottons fibers and for the cellulose whiskers using an X-ray diffractometer (VEB CARL ZEISS-JENA URD-6 Universal Diffractometer), CuKα radiation ($\lambda = 1.5406$ Å) at 40 kV and 20 mA. Scattered radiation was detected in the range of $2\theta = 5$–$40°$, at a speed of 2°/min. The extent of the crystallinity index (I_c) was estimated by means of Eq. 1 using the height of 200 peak (I_{200}, $2\theta = 22.6°$) and the minimum between 200 and 110 peaks (I_{am}, $2\theta = 18°$). I_{200} represents both the crystalline and the amorphous material, while I_{am} represents amorphous material.

$$I_c(\%) = (I_{200} - I_{am}/I_{200}) \times 100 \tag{1}$$

Thermogravimetric analysis was obtained in a TA Instrument model Q500, in the temperature ranging from 25 to 800 °C, at a heating rate of 10 °/min in inert (nitrogen) and oxidative (synthetic air) atmospheres, with a flow rate of 60 mL min^{-1}. Approximately 10 mg was used for each sample preparation.

Results and discussion

The morphological characterization of Brazilian commercial cotton fibers by SEM analysis under two magnifications is shown in Fig. 1. Figure 1a shows the cylindrical

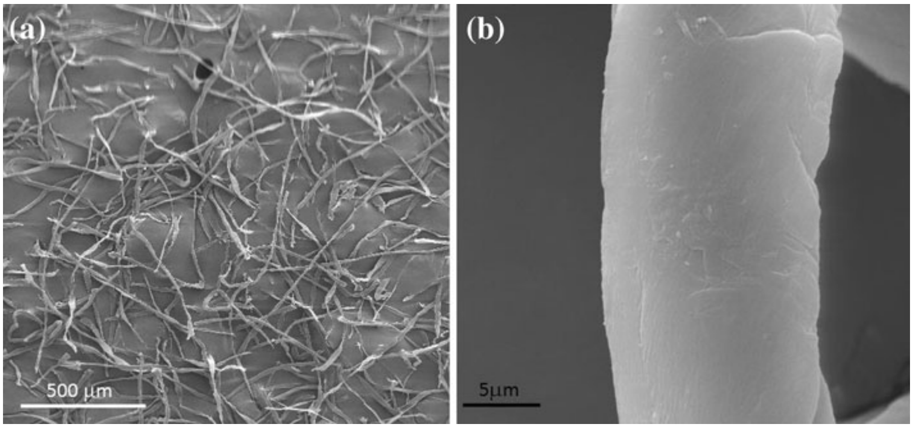

Fig. 1 Scanning electron microscopy (SEM) of the cotton fibers **a** ×50 and **b** ×3,000

shape and size distribution of fibers' bundles in commercial cotton. These well-separated bundle fibers have lengths of around 500–1,000 µm and diameters of 25–27 µm. The SEM image (Fig. 1b) of one individual fiber at large magnification shows that the surface of commercial fibers of cotton has a smooth and uniform surface and shows no sign of external fibrillation or formation of fibrils.

The chemical composition shows that commercial cotton fibers have 97.2% ± 2.2 of cellulose, 0.5% ± 0.4 of hemicellulose and 0.4% ± 0.1 of lignin. Rowell and Han [25] reported on the chemical analysis of the major components of some plant fibers. For cotton fibers, they found that the cellulose content ranges from 85 to 90 (% of total) and the lignin from 0.7 to 1.6 (% of total). In Brazil, cotton fibers cultured by Embrapa have been studied by Corradini et al. [17]. They found that the chemical composition of white cotton is 88.3% ± 0.3, hemicellulose 8.0% ± 0.3 and lignin 4.8% ± 0.5. The literature has reported that boiled and bleached flax and degummed ramie might contain over 95% cellulose [26]. Cotton raw fibers consist of cellulose basically. The major portion of the noncellulosic compounds is located primarily in the cuticle and in the primary cell wall, and it contains wax, pectin substances, organic acids, sugar, and ash-producing organic salts. After cotton fibers are chemically processed (by scouring and bleaching), these noncellulosic materials are removed, and the cellulose content of the cotton fibers can be over 99% [27]. In our study, the high cellulose content obtained for the Brazilian commercial cotton, about 97%, must be because of the industrial processing of the fibers.

Figure 2 shows TG/DTG curves of cotton fibers in inert (nitrogen) and oxidative (air) atmospheres. Cellulose can be considered as a polymer of moderate thermal stability. Studies with TGA have shown that different steps are involved in the degradation of cellulose. The complexity of this degradation results from a large number of steps of the parallel and consecutive reactions, which can be affected by the structure of the cellulose sample, and by the ambient atmosphere involved [17, 27]. The DTG and TG curves of cotton fibers (Fig. 1) show an initial peak between 50 and 100 °C, which corresponds to the vaporization of water in all samples. After this peak, in inert atmosphere, the TG curve has only one large plateau, and the DTG curve has one degradation peak, indicating that the thermal degradation of

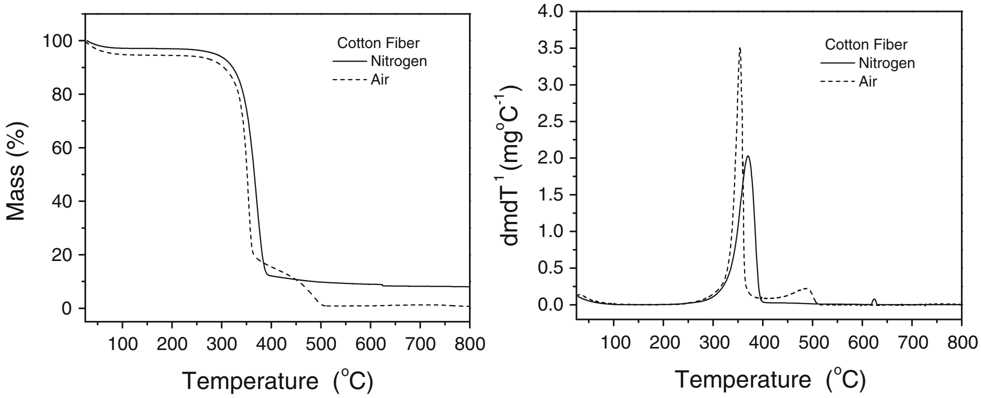

Fig. 2 TG/DTG curves of the cotton fibers in inert and oxidative atmospheres, 10 °C/min

fibers is a one-stage process. This peak at about 370 °C is attributed to the thermal depolymerization of hemicellulose, lignin, and α-cellulose decomposition (wt loss 60%). It was proposed that this stage consists of random scission in the low-order regions of the cellulose followed by reaction of broken chains and dehydration, decarboxylation, or decarbonylation of anhydroglucose units [27]. The temperature of the maximum mass loss rate or the peak temperature of the DTG curve is around 370 °C in inert atmosphere, and 350 °C in oxidative one. According to Shafizadeh et al. [28], the activation energy values necessary to promote bond scission of cellulose molecules are 27 and 21 kcal mol^{-1}, respectively, in nitrogen and air atmospheres. This can be explained because in atmospheric air the maximum rate of weight loss for cellulose degradation occurs at lower temperatures compared to that in nitrogen atmosphere, which is a consequence of the thermooxidative events occurring during the decomposition of the sample. At 600 °C, the content of residues was about 10% in inert atmosphere, and about 1% in oxidative one. The Brazilian commercial cotton fibers showed higher thermal stability in inert atmosphere than in oxidative one.

Figure 3 shows typical STEM micrographs cellulose whiskers obtained, which revealed that the whiskers generated were in a nanometer range. It showed the presence of few aggregates and individual nanofibers. The size of cellulose whiskers is mainly dependent on the source and on the acid hydrolysis conditions [1]. However, the average length (L) and diameter (D) of commercial cotton cellulose whiskers were of 150 ± 50 nm and of 14 ± 5 nm, respectively, independent of the extraction conditions studied, which are close to the values for cellulose whiskers already reported [22, 29]. Therefore, the average aspect ratio, L/D, was 10.7. This value was in agreement to the values of the average aspect ratio reported for cotton whisker in the literature [20, 30]. These values were calculated from the ImageJ software from about 120 counts. The cotton whiskers obtained showed a rod-like shape, and a tendency for aggregation could be observed.

The X-ray diffractograms of cotton fibers and cellulose whiskers obtained at different acid hydrolysis conditions are shown in Fig. 4. Three peaks were observed for all samples at $2\theta = 16$; 22.6, and 34.7°. These peaks are characteristic of the crystal polymorph I of cellulose, since there is no doublet in the main peak at $2\theta = 22.6°$ [14, 31]. According to the literature, for fibers with higher cellulose content, like cotton or flax, two peaks around 16° were observed. It is also reported that the presence of noncellulosic substances, such as hemicellulose and lignin causes the merging of these two distinct peaks into a single one [32]. All the samples investigated showed two peaks at 16°, which is in agreement with the higher cellulose content of the cotton fibers obtained by chemical compositions. The peak at $2\theta = 16°$ corresponds to (101) crystallographic plane, the peak at $2\theta = 22.6°$ correspond to (002), and the peak at $2\theta = 34.7°$ corresponds to (023) and (040) planes [33, 34]. From the cotton whiskers to the original cellulose fibers, the diffraction peak at $2\theta = 22.6°$ became sharper

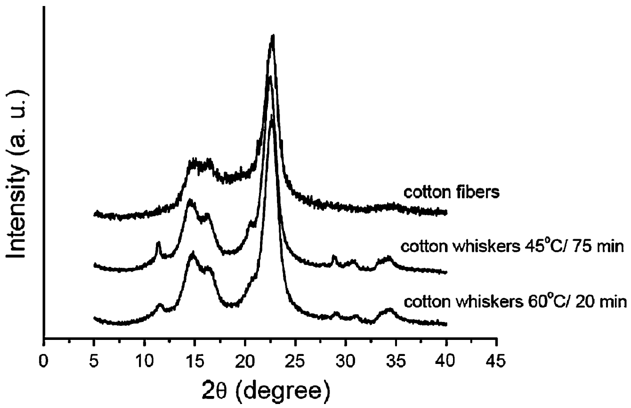

Fig. 4 XRD patterns for cotton fibers and cotton whiskers obtained at different acid hydrolysis conditions

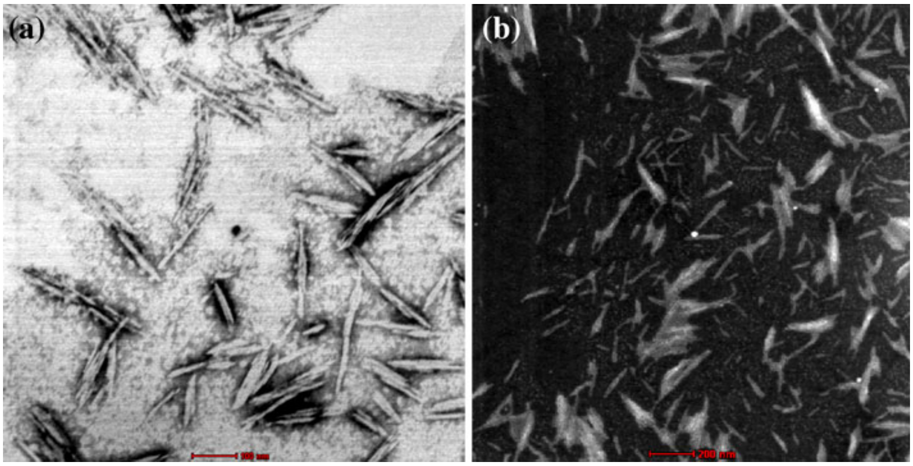

Fig. 3 Transmission electron microscopy (TEM) of the cellulose whiskers obtained at **a** 45 °C (*scale* 100 nm) and **b** 60 °C (*scale* 200 nm)

Table 1 Crystallinity index (I_C) and initial temperature of thermal degradation (T_{id}) of cotton fibers and cotton whiskers extracted at different conditions

Samples	I_C (%)	T_{id} (°C)
Cotton fiber	77	300
Cotton whiskers (45 °C, 75 min)	91	255
Cotton whiskers (60 °C, 20 min)	90	200

indicating an increase of crystallinity after the hydrolysis due to the removal of the amorphous phase by an acid attack. The values of the crystallinity index are shown in Table 1. As observed, the crystallinity of the whiskers was similar regardless of the hydrolysis conditions.

The effect of different hydrolysis conditions on the thermal behavior of cotton whiskers in an oxidizing atmosphere (whiskers freeze-drying) is shown in Fig. 5, and their initial temperature of thermal degradation is shown in Table 1. The TG/DTG curves and date of cotton fibers were put together to make the observations easier. Cellulose cotton whiskers obtained have less thermostability when compared to cotton fibers, independent of the hydrolysis conditions. This occurs because the sulfate groups introduced on cellulose chains catalyze the thermal degradation of cellulose. According to Roman et al. [35], this catalysis could proceed either directly through the acid molecules or indirectly by promoting dehydration reactions. The broad DTG peak centered at 50 °C, corresponding to a weight loss of 1% for the cotton whiskers obtained at 60 °C and 4% for the cotton whiskers obtained at 45 °C, was due to the evaporation of adsorbed water. The DTG peak above 425 °C was attributed to the oxidation and breakdown of the charred residue. Residue mass at 700 °C is close to 1% for cotton fibers and to 4% for cotton whiskers. Through the DTG curves, it can be verified that, between 180 and 250 °C, there is a small peak for all whiskers, and between 250 and 400 °C, a double peak for those obtained at 60 °C, 20 min. According to Wang et al. [36], this occurs because of different levels of sulfonation of the cellulose chains. Chains with a higher sulfate group present degradation at a lower temperature and have shown separated pyrolysis processes in the DTG curves. The whiskers obtained at 60 °C, 20 min had higher sulfonation and, therefore, less thermal stability than those obtained at 45 °C, 75 min.

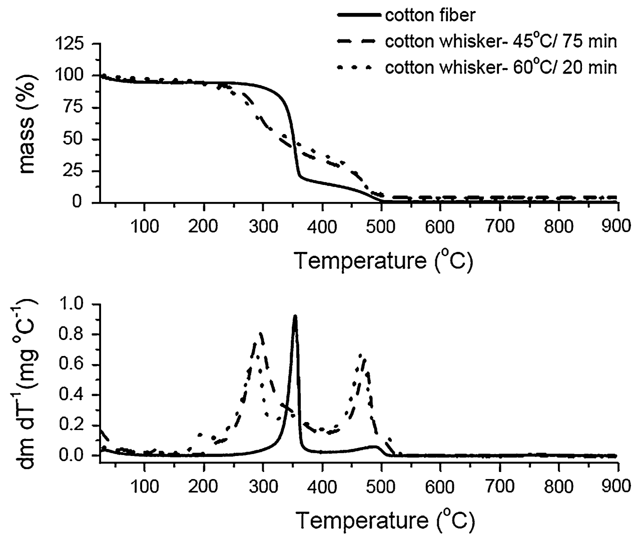

Fig. 5 TG-DTG curves of the cellulose whiskers obtained at 45 and 60 °C in oxidative atmosphere 10 °C/min (freeze-drying)

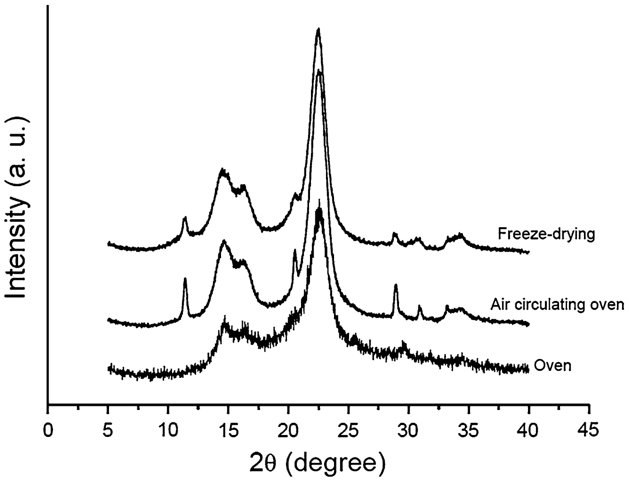

Fig. 6 XRD patterns for cotton whiskers obtained at different drying methods (hydrolysis at 45 °C, 75 min)

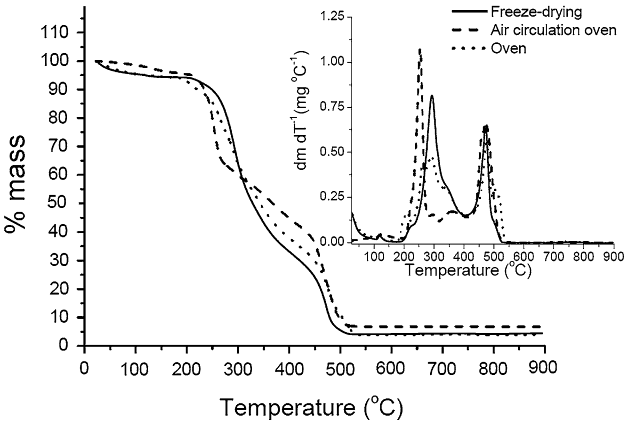

Fig. 7 TG/DTG curves of the cellulose cotton whiskers obtained through different drying methods, in oxidative atmosphere, 10 °C/min (hydrolysis at 45 °C, 75 min)

The influence of different dry methods on the crystallinity and on the thermal stability of cotton whiskers were investigated (Figs. 6, 7; Table 2). During the drying process, the cellulose whiskers can be aggregated by hydrogen bonds and covalent crosslinking. Crosslinking in cellulose

Table 2 Crystallinity index (I_C) and initial temperature of thermal degradation (T_{id}) of cotton whiskers obtained through different drying methods (hydrolysis at 45°C, 75 min)

Samples	I_C (%)	T_{id} (°C)
Cotton whiskers (freeze-drying)	91	255
Cotton whiskers (air circulation oven)	91	230
Cotton whiskers (oven)	80	200

can take two forms: a more organized structure, or a structure with a lot of chain scissions. Chain scissions lead to a decrease in the degree of polymerization, which could induce changes in crystallinity [37]. Figure 6 shows the diffractograms of XRD of cotton whiskers dried under different methods and their respective crystallinity indexes are shown on Table 2.

It can be observed (Fig. 6; Table 2) that cotton whiskers obtained by freeze-drying and by air-circulating-drying methods had the same crystallinity index, while for those that were obtained through the oven-drying method there was a decrease of the crystallinity. Therefore, the last method induces the cellulose chain scission which should be avoided. Analyzing the thermal stability of these samples (Fig. 7; Table 2), the freeze-dried samples have shown a better thermal stability than the other samples. Cellulose whiskers obtained using the air-circulating method had similar crystallinity to that of those obtained by the freeze-drying method. However, the results of thermogravimetric analysis suggest that some thermal degradation occurred in the whiskers dried through this method. The samples dried in an oven showed less thermal stability probably due to the thermal degradation of the cellulose chains as verified by XRD analysis. Hence, the freeze-drying method is mostly indicated for drying whiskers, even though it requires higher processing time.

Conclusions

Cellulose whiskers could be successfully obtained directly by commercial cotton without any pretreatment of the fibers. Cellulose cotton whiskers (independently of extraction procedure) provided an average length and diameter of 150 ± 50 and of 14 ± 5 nm, respectively, rod-like shape, and higher crystallinity structures (90–91%). Higher extraction temperature makes cotton whiskers less thermally stable probably because of the greater number of sulfate groups introduced on the cellulose surfaces. The freeze-drying method used for whiskers can prevent the thermal degradation of cellulose chains. The results of this study demonstrate that the use of these whiskers offers promising potential for applications in nanomaterials.

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