CHEMICAL ENGINEERING TRANSACTIONS
VOL. 50, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Katharina Kohse-Höinghaus, Eliseo Ranzi
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ISBN 978-88-95608-41-9; **ISSN** 2283-9216
DOI: 10.3303/CET1650068

Achievement and Characterization of Cellulose Nanowhiskers of Palm (*Elaeis Guineensis)* and Bromelia Fibers (*Neoglaziovia Variegate)*

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The cellulose nanocrystals, also known as nanowhiskers, are particles extracted from crystalline regions of cellulose in which one of its dimensions is on the nanometric scale. They have the following advantages: low density, renewable character, good mechanical properties, availability, biodegradability and can be obtained from various vegetable fibers, whom originated from biomass residues, through different methods. For example, the acid hydrolysis in controlled conditions destroys the amorphous regions between the cellulose microfibrils. Brazil has a high lignocellulosic biomass availability deriving from waste produced in different industrial sectors. This, combined with the necessity to employ renewable resources for production of new materials, inspires a great opportunity for technological advancements, adding value to agribusiness products. The fibers of a kind of palm *(Elaeis guineensis)* and of bromelia *(Bromeliaceae)* are highlighted in this work as a source for obtaining cellulose nanowhiskers.This study aimed to obtain and characterize through TG, DSC, FTIR, XRD and TEM two different cellulose nanowhiskers *and* from two studied fibers, as well as to compare them as raw materials for future use as reinforcement in polymers composites. From the results of the TEM, it could be inferred that the acid hydrolysis allowed the attainment of nanowhiskers with a needle format. Based on the results of XRD and TG, the bromelia fibers had higher thermal stability and higher crystallinity index when compared to the palm fibers.

1. Introduction

Currently a concern with the environment have required from the industrial sector the development of biodegradable materials, the use of renewable sources of energy and reutilization of wastes deriving mainly from agribusiness. In this context, discussions and incentives to researches that enables the use of renewable resources - such as biomass - are a challenge to be overcome, since those resources can work as new power supplies that minimize or even replace processes and products derived from the oil. The use of local natural resources stands out as a viable alternative, because besides the incentive and added value to local products, there is also an impact of lower energy expenditure due to lower need for distribution and consumption of goods transport (Basile *et al*., 2015; Mezule *et al*., 2015). Brazil`s fertile soil conditions and climate favour an abundance in natural resource which translates into a wide variety of biomass. Most vegetable fibers are obtained from agricultural waste and they arouse interest into the development of new materials, as they present features such as: low cost, low density, high elastic modulus, in addition to define the destination for the waste and its appreciation as raw material (Miranda *et al.,* 2015).

The major components of biomass are cellulose, hemicellulose and lignin. The former, a polysaccharide composed of crystalline and amorphous regions, is considered the most important and abundant (Gorsek *et al.*, 2015; Portela *et al.,* 2015).

Please cite this article as: Goncalves A.P., Cruz A., Sales J., Souza M., Silva F., Guimaraes D., Mattedi S., Jose N., 2016, Achivement and characterization of cellulose nanowhiskers of palm (elaeis guineensis) and bromelia fibers (neoglaziovia variegate), Chemical Engineering Transactions, 50, 403-408 DOI: 10.3303/CET1650068

The bromelia fibers are a native plant typically from northeastern Brazil. Its scientific name is Neoglaziovia variegata and it belongs to the bromeliad family. Its fibers are extracted from the leaves. They have high resistance and are shiny. Because of these characteristics, they are used extensively to manufacture ropes, nets, bags and strings (Nóbrega, 2007).

The palm fibers represent the crop with the highest productivity per acreage in the world (Carvalho, 2006).

The fibers of palm are obtained after pressing the mesocarp to extract the oil that is used as raw material in the manufacture of food products, cosmetics and presents potential for the development of biodegradable materials (Vasconcelos, 2010). The studied materials correspond to the development of cellulose nanoparticles, also called cellulose nanowhiskers, which were extracted from palm and bromelia fibers by acid hydrolysis. The cellulose nanowhiskers are extracted from the crystalline regions of the cellulose under controlled conditions. They exhibit at least one of their dimensions in the nanometric scale and have highly ordered structures, which can provide characteristics such as: high mechanical strength; optical, electrical and dielectric properties; and are extracted from different plant sources (Silva *et al.;* 2009). Therefore, the study aims at the development and evaluation of thermal, structural and morphological properties of cellulose nanowhiskers from these two sources through acid hydrolysis.

2. Materials and Methods

2.1 Materials

The palm oil and bromelia fibers were obtained from the municipalities of Taperoá and Araci, respectively, both municipalities of Bahia - Brazil .

2.2 Methods

In order to obtain cellulose nanoparticles, two steps were previously carried out that correspond to the removal of the lignin and the bleaching of the fiber (Miranda *et al.;* 2015).

2.2.1 Preparation of *cellulose nanowhiskers*

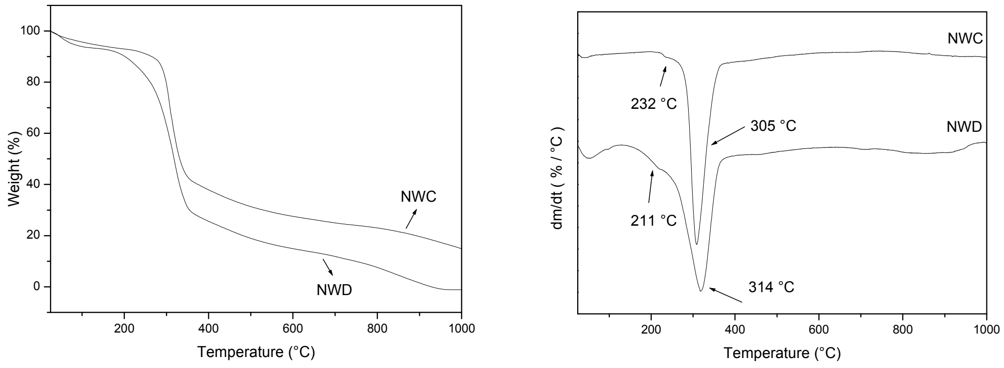
20.0 g of fiber were used in 300 mL of 5 % solution (w/v) sodium hydroxide in a system with mechanical stirring for 2 h at 80 °C. Then, the material was vacuum filtered, washed with distilled water and dried in an oven at 70 °C for 24 h. Subsequently, 5.0 g of the treated fiber were subjected to a 200 mL sodium hypochlorite 2 % (v/v) solution and a 1: 1 (5 % acetic acid (v/v) and sodium hydroxide 5 % (w /v) buffer solution with constant mechanical stirring for 2 h at 80 °C. After this step, the fibers were vacuum filtered, washed with distilled water and dried in an oven at 70 °C. The bleached fiber was subjected to acid hydrolysis with 100 mL solution of 55 % (v/v) sulfuric acid under mechanical agitation at constant temperature of 50 °C for 2 h. Then the suspension was centrifuged at 4,400 rpm for 10 min until the absence of supernatant. It was subsequently subjected to dialysis to reach pH between 6 and 7. From this methodology, cellulose nanowhiskers were extracted from two different sources. Samples labelled NWD and NWC refer to nanoparticles extracted from palm and bromelia fibers, respectively.

2.2.2 Characterization of cellulose nanoparticles

The cellulose nanoparticles were characterized by Thermogravimetric Analysis (TG), Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffratometry (XRD) and Transmission Electron Microscopy (TEM). The TG analysis was performed on a Seiko 6000 thermal-balance, model TG/DTA 6200, between 25 and 1000 °C at a heating rate of 10 °C/min under nitrogen flow. For DSC analysis it was used a Seiko equipment, model Exstar DSC-6220, where the samples were analyzed from 25 to 600 °C with a heating rate of 10 °C/min. FTIR spectra was obtained in a Bomem spectrometer, model ABB Bomem MB Series in wavelength of 4000-800 cm^{-1}. The crystallinity was analyzed on a Shimadzu XRD-6000 diffractometer, with angles 2θ between 5 and 80°. The TEM micrographies was recorded in a JEOL (JEM-1230) microscope.

3. Results and discussion

Figure 1a shows the thermogravimetric analysis of the cellulose nanowhiskers of palm and bromelia fibers. The degradation of NWD sample started at 211 °C with weight loss of 95 %. For sample NWC this event occurred at 232 °C with weight loss of 97 %. Comparing the heat stability of the samples, it was found that the nanoparticles extracted from the bromelia fibers cellulose were more thermally stable. The DTG curves represented by Figure 1b show the thermal events for both sources of cellulose nanoparticles. Four events were observed for NWD sample: the first one at 108 °C, associated with humidity; the second one at 211 °C, attributed to degradation of the most accessible regions of sulfation during the acid hydrolysis - the residual amorphous regions in the nanoparticle cellulose; the third one observed at 314 °C, which is superimposed on the second, corresponds to decomposition of the less accessible regions of nanoparticle that have probably suffered a lesser degree of sulfation; and the fourth event occurred at the maximum degradation temperature, that ranges from 400-800 °C, was attributed to oxide formation (Miranda, 2015; Roman *et al.,* 2004). Regarding the NWC sample, these first three reported events occurred at 55, 232 and 305 °C respectively.



(a) (b)

Figure 1: (a) TG; (b) DTG curves of nanowhiskers of palm and bromelia fibers.

The DSC data of the samples are illustrated in Figure 2. The first event attributed to the removal of humidity at the temperature of 67- 90 °C. The second endothermic event occurred at 142 to 150 °C for both samples. This event can be assigned to the merging of the degraded sugars remaining in the solution after hydrolysis or even generated during this step (Oliveira, 2015). The third exothermic event is related to the degradation of cellulose, which for all samples occurred in the range between 255 and 315 ºC.

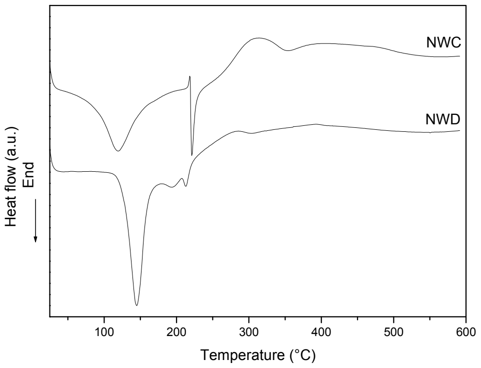


Figure 2: DSC curves of nanowhiskers of palm and bromelia fibers.

The crystalline structure of cellulose nanowhiskers were investigated by XRD analysis. The results showed peaks corresponding to reflections of the (110), (200) and (040) planes of the type I cellulose for both samples (Taipina *et al.,* 2012). The crystallinity index (Ic) of the samples were calculated by Equation (1) and the results are shown in Table 1.

$$Ic = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100 \qquad (1)$$

Table 1: Crystallinity index of cellulose nanowhiskers

Sample	I_c (%)
NWD	56
NWC	76

From these values it can be seen that the NWC sample was more crystalline when compared with the extracted cellulose nanoparticles of palm fiber and this result is consistent with the illustrated diffraction (Figure 3).

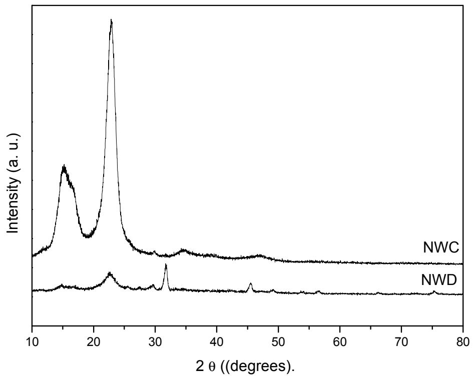


Figure 3: X-ray diffraction patterns of nanowhiskers palm and bromelia fibers.

The FTIR spectra of nanowhiskers of palm and bromelia fibers are shown in Figure 4. The tested samples showed bands at 3450 cm^{-1}, approximately, indicating the free OH group referring to the cellulose molecule (Miranda, 2015). In 1620 cm^{-1} it is verified the band associated with the adsorbed water, confirming the hydrophilic nature of the cellulose nanoparticles (Pereira, 2013). That behaviour is more noticeable for NWD sample. The band observed at 1638 cm^{-1} can be attributed to the deformation of OH bonds and the band at 1375 cm^{-1} corresponds to the symmetrical angular deformation of the CH bond (Moran, 2008). The vibration regarding the S = O group is associated with the esterification of cellulose and it was observed around 1211 cm^{-1} (Neto, 2012). Based on these results, it can be inferred that the procedure for obtaining the cellulose nanoparticles was efficient, since bands were observed relating to functional groups present in the cellulose.

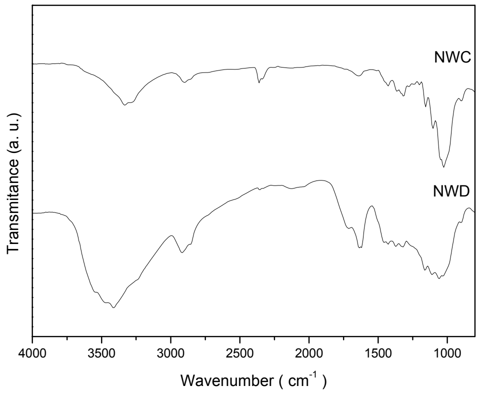
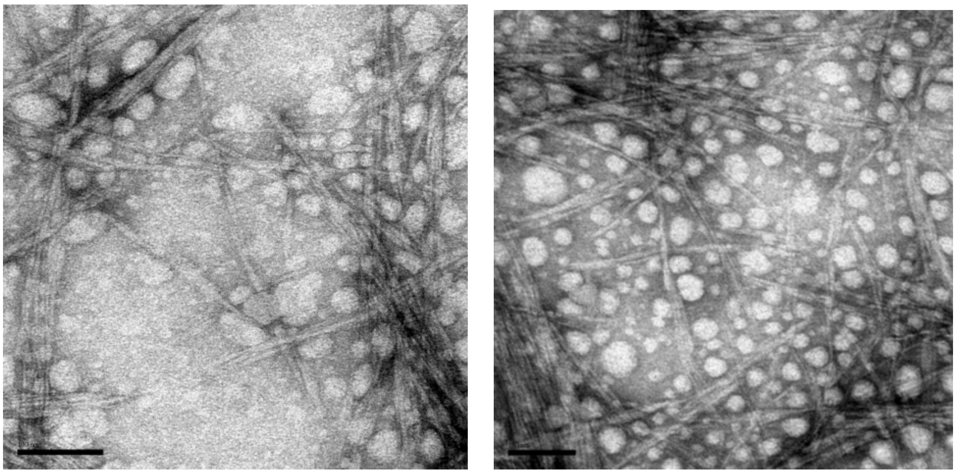


Figure 4: FTIR spectra of nanowhiskers palm and bromelia fibers.

The morphology of the cellulose nanowhiskers of NWD and NWC samples (Figure 5) obtained from acid hydrolysis was evaluated by TEM. The images show structures with needle format in the nanoscale obtained after acid hydrolysis (Oliveira, 2015).The structures are elongated and scattered, though prone to agglomeration. These results are consistent with the XRD analysis in which samples with high crystallinity index values were observed, suggesting that the H_2SO_4 was effective in promoting the hydrolysis of the amorphous regions of cellulose.



(a) (b)

Figure 5: Transmission electron micrograph of nanowhiskers (a) of palm fibers (Scale bars: 100 nm); (b) bromelia fibers (Scale bars: 100 nm).

4. Conclusions

Based on the results of TEM, it can be seen that was possible to obtain cellulose nanowhiskers extracted of palm and bromelia fibers by acid hydrolysis. This was confirmed through the FTIR and XRD analysis, which showed bands and peaks present in the cellulose. The diffraction profile and the crystallinity index showed that the sample NWC was more crystalline when compared to NWD. The results of thermogravimetric analysis showed different behavior regarding the thermal stability of the samples, indicating that the extracted nanoparticle from bromelia fibers was thermally more resistant. The same methodology for the extraction of cellulose nanoparticles used in different raw materials resulted in materials with distinct thermal, morphological and structural characteristics. Therefore, the obtained cellulose nanowhiskers are promising materials, since they showed relevant performance and a significant potential for application as reinforcement in polymer, in addition to allocate value to regional biomass waste used as sources of raw materials.

Acknowledgements

The authors thank PPEQ - UFBA, FAPESB and Fiocruz.

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