

Comparison between Cellulose Nanocrystals Extracted From Different Agro-Industrial Residues Using the Same Obtaining Methodology

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Abstract

The development of CNC obtaining methodology will be the focus of this study, which will seek to get particles in nanoscale dimension. The banana leaf and corn stover residues were used as raw materials for this study. Initially, the waste was subjected to chemical treatment (cleaning, bleaching and hydrolysis). After all treatment processes to which it was submitted, the crystals were characterized by the Fourier Transform Infrared Spectroscopy Analysis (FTIR), Thermogravimetric Analysis and its derived (TGA e DTG), X-ray diffraction (XRD), determining of cellulose, hemicellulose, and lignin percentage, Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS) and Atomic Force Microscopy (AFM), seeking to verify their compositions, crystallinity index, morphology and size of the particles obtained. It was observed that the hemicellulose and lignin extraction was effective as well as the reduction of the particle scale, that raised the sample's surface area, what improved the treatment efficiency. The obtained cellulose crystals had particles in a nano-scale size, although the method has proved impracticable for use in banana leaves, since there is the need for further processing steps, generating a lot of waste process.

Keywords: *nanocrystals, cellulose, thermoplastic reinforcement, banana waste, corn stover.*

1. Introduction

The agro-industrial sector benefits with natural products several areas such as the food industry and the generation of energy from renewable sources. However, the growing of this industry raised the amount of waste thrown in the environment. This huge volume of waste attracts the attention of researchers, aiming at the reuse of these resources, which one use would be the reinforcement of polymeric materials. The lignocellulosic fibers are excellent for use as a material reinforcement, deserving more attention from the scientific community for the intense use of it to the development of polymers and composites, which take full advantage of its unique characteristics from every one of the great variety of lignocellulosic matrices, as is the case of the cellulose nanocrystals, particles with nanometric dimensions, that are one of the trend topics arising on academy.¹ Cellulose

nanocrystals are the nanoparticles extracted from the cellulose fibers, i.e., they are the crystalline domains of the cellulosic fibers obtained through treatment processes such as acid hydrolysis. This denomination is due to its physical characteristics of rigidity, thickness, length and because they are structures that have dimensions in nanoscale.^{2,3} In order to obtain the cellulose nanocrystals it is necessary the treatment on natural fibers to extract the hemicellulose, lignin and other components present in lesser quantity, remaining only the cellulose. It is also needed that the cellulose obtained be reduced in size, reaching a nanoscale dimension, which is also possible through the treatments. Pretreatments are used to clean and modify surfaces of natural fibers, reducing surface tension, which may improve adhesion between the fiber and the polymer matrix. The pretreatment of fibers can be done in more than one step. Initially, a treatment can be carried out for the removal of organic substances of lower molar mass, commonly present in the plant structures, being this the first stage called cleaning. The second step is the bleaching, which is widely used by the paper industry, whose main objective is to remove lignin and hemicellulose from the fiber, as well as to remove the characteristic color of the biomass, leaving it white. To obtain a good bleaching result, in some cases it is necessary to repeat this step for a few times.⁴⁻⁶ The alkaline treatment is considered as a pretreatment for further use of an acid treatment. This treatment is a very important stage for the preparation of the fibers to subsequent obtaining of nanocrystals.^{2,4,6-8} Acid hydrolysis is the method with the greatest knowledge and use for the extraction of cellulose nanocrystals, and can be carried out with the sulfuric acids (H₂SO₄) or chloridric acids (HCl) uses. This method is based on the fact that the crystalline regions are insoluble in acid under the conditions used for the extraction.⁹ The extraction process and the source of cellulose are extremely influential in the morphology and other properties of nanocrystals. The use of acid hydrolysis treatment for the cellulose nanocrystals extraction causes the digestion of the amorphous regions of the pretreated fiber structure, obtaining crystalline nanoparticles.^{10,11} Based on this, the objective of this study is the use of a single methodology of cellulose nanocrystals extraction

using chemical pretreatments and acid, on two agricultural residues, corn straw and banana leaf, comparing the thermal behavior, morphological and structural compositions of each one at each treatment step.

2. Materials

Were used residues of corn straw (CS), parts that involved the cobs, obtained at a fair in the city of Santa Cruz do Rio Pardo/SP. Residues of banana leaf (BL) were obtained in a plantation in the city of Apiaí/SP. The residues were exposed to the sun for about 3 days, completing the drying in a circulatory oven for 24 hours/60°C, after being ground in a knife mill and sieved in an electromagnetic sieve, with Mesh 20 sieve, being this corn straw residue named as CS-V and the banana leaf as BL-V.

3. Methods

3.1 Cleaning

The amount of 5 g of the residue was treated with 150 mL of distilled water solution containing 1.5 g of calcium hypochlorite (Ca (ClO)₂) and 10 drops of glacial acetic acid (AcOH), being stirred continuously under 70°C/1h, followed by washing with distilled water, filtering and drying in an oven at 100°C/1:30 h. The sample obtained in this were named CS-C and BL-C.

3.2 Bleaching

The cleaned sample was submitted to 100 mL of a solution composed of 24% (v/v) hydrogen peroxide (H₂O₂) and 4% (w/v) sodium hydroxide (NaOH) in a ratio of 1:1 under continuous agitation at 50°C/2h. After that, it was washed with distilled water, filtered and oven dried at 100°C/1:30h. It was necessary to repeat this step many times to make the fibers white. The sample obtained after the bleaching were named CS-B and BL-B.

3.3 Acid hydrolysis

After the samples had been bleaching, they were subjected to acid hydrolysis with 30% (v/v) sulfuric acid under continuous stirring at 45°C/2h. After this time, the stirring was stopped and ice water distilled in a ratio of 1:5 was added. The sample was centrifuged for 10 minutes at 8000 rpm, and this procedure was repeated three times, always performing the water exchange of the Falcon tubes. Then, the samples underwent ultrasonification for 8 minutes and placed on cellulose membranes for dialysis achieving stabilization at pH 5. The sample obtained in this step was named CS-H and BL-H.

4. Characterization

4.1 Fourier transformation infrared spectroscopy (FTIR)

FTIR measurements were performed on the Perkin Elmer Spectrum FTIR equipment; model VARIAN 660, with a scan of 400 to 4000 cm⁻¹, averaging 10 scans.

4.2 Thermogravimetric analysis (TGA)

TGA measurements were performed on the Perkin-Elmer equipment, model STA 6000, with nitrogen atmosphere (N₂), under a flow rate of 50 ml.min⁻¹, the constant heating rate of 10 °C/min, and range temperature of 30-600°C.

4.3 X-ray diffraction (XRD)

X-ray powder diffraction data were collected on a Stoe® STADI-P diffractometer, operating in transmission mode, using CuK_{α1} (λ = 1.54056 Å) radiation, in the range of 10-60°, with step sizes of 0.015° and a counting time of 100 s at each 1.05°.

4.4 Determining of cellulose, hemicellulose and lignin percentage

The samples were characterized in fiber-determining Tecnal equipment, model TE-159. The first step of analysis determines the acid detergent fibers, which are the remaining residues from the digestion with H₂SO₄ and CTAB. The second step determines the neutral detergent fibers, which are the remaining residues from the digestion in a detergent solution. The methodology used was adapted from the methodology of Van Soest.¹²

4.4 Scanning Electron Microscopy (SEM)

The samples were analyzed by scanning microscope model JSM 6010 LA from Jeol. Sample preparation was done by deposition of a small amount of dry sample on carbon tape and subsequent metallization by deposition of gold.

4.5 Dynamic light scattering (DLS)

We used the ALV CGS-3 equipment, with polarized HeNe laser (22 mW), wavelength λ = 633 nm, digital correlator ALV 7004 and pair of APD detectors operating in pseudo-correlation mode. Scanning was performed between 70-130°. The data were analyzed using ALV 7004 software. Sample preparation was done by diluting 2 μl of the colloidal solution in 98 μL of distilled water, undergoing ultrasonication for 280 s.

4.6 Atomic force microscopy (AFM)

The AFM / SPM Series 5500, Agilent, was used with 670 nm laser multifunction scanning stage. Sample preparation was done by diluting 2 μL of colloidal solution in 98 μL of distilled water, undergoing ultrasonication for 280 s. After ultrasonication, the solution was placed on a silicon plate and analyzed after drying in a desiccator.

5. Results and Discussions

5.1 Fourier transformation infrared spectroscopy (FTIR)

The FTIR curves of the CS and BL samples are shown in Fig. 1a) and 1b). It is verified for CS-V and BL-V, curves containing the same characteristic peaks of lignocellulosic material. There is little change in the curves of CS-C and BL-C, but it is noticed the peaks intensification when comparing to the virgin residue. The peak in the 3330 cm^{-1} band is present in all CS and BL samples, as observed in Fig. 1a), and is related to O-H stretching (hydroxyl groups), related to carbohydrate (cellulose and hemicellulose) vibrations and lignin. The narrowing and deepening behavior in the region related to O-H vibrations is due to the increase in bond strength of hydrogen caused by the amorphous components removal and the subsequent crystallinity increase.^{5,13,14} In the Fig. 1a), for CS-B, BL-B, CS-H and BL-H, occurred the intensity decreasing and subsequent disappearance of the vibrations in 2920 cm^{-1} range, indicating the total removal of lignin, considering that this peak is characteristic of this component. In the range of 2885 cm^{-1} , the vibration intensity relative to cellulose occurs.¹³ The characteristic peak of lignin and hemicellulose presence, associated with the carboxylic acid and aliphatic ketone groups, located at 1726 cm^{-1} disappears for CS-B, BL-B, CS-H and BL-H, indicating these substances removal, as is shown in Fig. 1b). The absence of this peak indicates these substances removal due to the alkaline bleaching treatment.¹⁵⁻¹⁷ In $1645\text{-}1632\text{ cm}^{-1}$ range, the peaks show the existence of group C=C of the aromatic rings indicating the lignin presence. A intensity decrease is observed as there is the lignin removal after bleaching and acid hydrolysis treatments.^{17,18}

For C-H cellulose and lignin vibrations, the peak between $1465\text{-}1421\text{ cm}^{-1}$ is maintained in all samples, as well as the C-O-H vibrations related to cellulose, in $1319\text{-}1314\text{ cm}^{-1}$ range, always showing intensity decreasing after bleaching and acid hydrolysis. Also in Fig. 1b), it is possible to verify that the peak between $1249\text{-}1199\text{ cm}^{-1}$ is relative to the hemicellulose and lignin elongation present in the samples. The vibrations on $1113\text{-}1101\text{ cm}^{-1}$ of C-O cellulose bonds are also present in all samples, indicating that lignin and hemicellulose have been removed. For CS-

B, BL-B, CS-H and BL-H, is noted the presence of a peak between $1060\text{-}1052\text{ cm}^{-1}$, representing the C-H cellulose stretching. The prominent peak at $1036\text{-}1022\text{ cm}^{-1}$ found in all samples represents the C-O vibration of the cellulose and lignin pyranose ring, indicating xylans presence and is associated with hemicellulose, confirming that xyloglucans are strongly bound to cellulose nanofibers. Also the intense band in this waves number proves higher cellulose content in chemically treated cellulose nanocrystals, as can be observed in the CS-H and BL-H spectra.^{2,19,20} The peak at $893\text{-}900\text{ cm}^{-1}$, related to cellulose C-O stretches, is well defined for both samples.^{14,16}

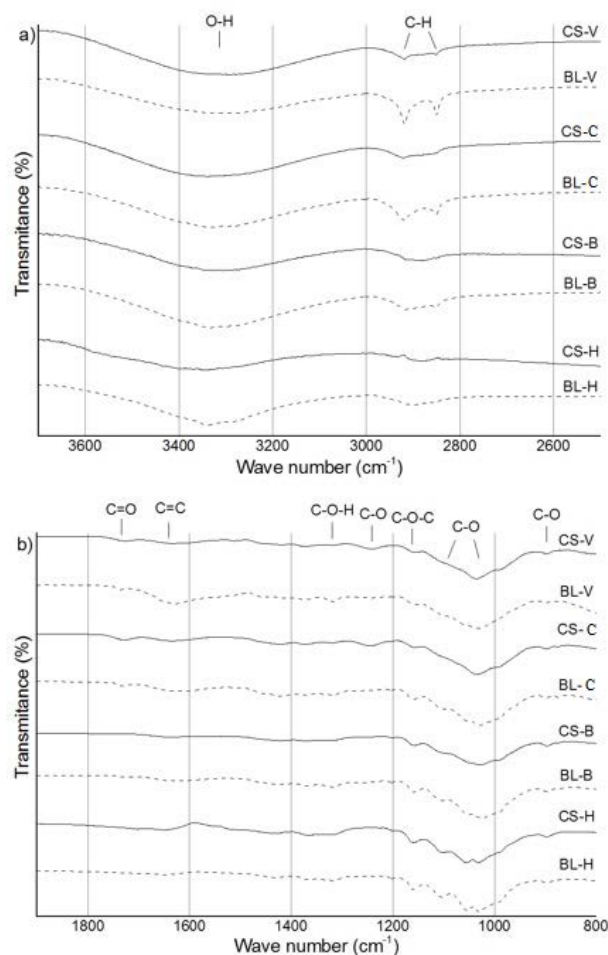


Fig. 1: a) FTIR $3700\text{-}2500\text{ cm}^{-1}$ wavenumber. b) FTIR $1900\text{-}800\text{ cm}^{-1}$ wavenumber.

5.2 Thermogravimetric analysis (TGA)

It can be seen from the curves shown in Fig. 2 that all samples present an initial event between $30\text{-}170\text{ }^{\circ}\text{C}$, indicating the water loss contained in the samples, which shows that it is hydrophilic materials.^{4,17} Two

interconnected and large exothermic peaks are observed at 280 °C and 350 °C in Fig. 2b) and 2f), occurring in a temperature range between 210-370 °C, a range related to the hemicellulose, cellulose and part of the lignin degradation events. It is verified that the mass loss occurred in the first event decays gradually after the treatments, indicating that hemicellulose, substance with lower thermal stability, was eliminated during these treatments.²¹ The mass loss occurring between 250-325 °C is caused by simultaneously occurring different processes of cellulose degradation, such as depolymerization, dehydration, decomposition and glycosidic units, followed by a carbonized residue formation.^{22,23} This lignin decomposition large peak at 350 °C is due to the several functional groups of oxygen present in this structure, with differences in thermal stability and the cleavage occurrence at different temperatures.²⁴

d)) presented lower thermal stability than the samples from the previous treatment steps, with 267 °C maximum degradation temperature. This decrease in outcome may have been caused by excess of exposure to NaOH, followed by acid action.^{15,25} Despite the thermal stability presented by the bleached sample, after BL-H undergoes the acid hydrolysis process, there is a loss of stability, causing an anticipated degradation. The initial degradation temperature drops to 120 °C, having its 173 °C maximum temperature, then initiating a new thermal event, with a second maximum degradation temperature at 220 °C. These thermal behavior changes in hydrolyzed samples can be justified by the sulfate groups presence, and it is possible that part of the sample is dissolved during the hydrolysis.²³

5.3 X-ray diffraction (XRD)

It can be observed in Fig. 3a) that the crystallinity degree remains after the cleaning treatment, with a low value, indicating that much of the material is in the amorphous phase. After the bleaching treatment the crystallinity of the samples started to increase, the crystallinity of CS-V was 22.2% and after bleaching, the crystallinity of CS-B increased to 45.1%. After the acid hydrolysis, there was an increase in crystallinity, which increased to 49.9%, a considerable increase in crystallinity when compared to the virgin sample. This CS result obtained corroborates the results in the literature presented, where the corn straw crystallinity increased from 24.3% to 44.8% after acid hydrolysis, indicating the lignin and hemicellulose removal.²⁶ The crystallinity degree results of the BL samples are shown in Figure 3b) and the values obtained are contained in Table 1.

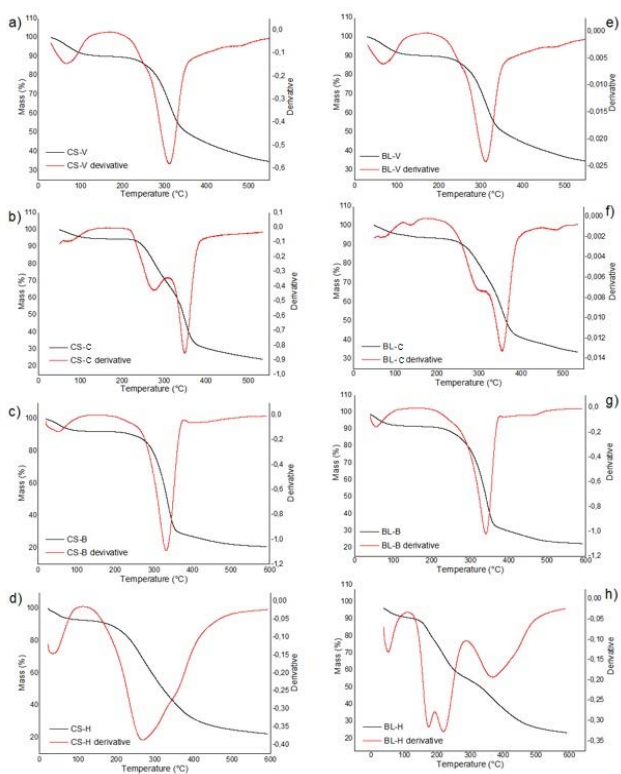


Fig. 2: Thermal curves obtained by TGA and respective DTG of the samples: a) CS-V. b) CS-C. c) CS-B. d) CS-H. e) BL-V. f) BL-C. g) BL-B. h) BL-H.

For CS-B and BL-B (Fig. c) and g)), the main event occurs at 330 °C and 340 °C respectively, representing cellulose degradation. There is no occurrence of a previous event interconnected to this, as occurred for the other samples treated by alkaline means, indicating that the hemicellulose and lignin were removed. The CS-H (Fig.

Sample	Xc
CS-V	22.2%
CS-C	21.9%
CS-B	45.1%
CS-H	49.9%
BL-V	41.1%
BL-C	25.8%
BL-B	49.4%
BL-H	52.6%

The crystallinity presented by BL-V is 41.1%, consistent with the literature results, ranging from 35-39%.^{27,28} After the cleaning step BL-C presented crystallinity degree of 25.8%. Upon cleaning treatment subjected, the cellulose residue is penetrated by the alkali, which causes a

crystalline packaging rearrangement of the native cellulose chains, with chains aligned in parallel to the cellulose II, where the chains are antiparallel.^{29,30} Cellulose I (native) has three equatorial arcs assigned to planes (1-10), (110) and (200), as well as a characteristic southern arc corresponding to plane (004). Cellulose II has three equatorial arcs assigned to the planes (1-10), (110) and (020).³¹ It is an irreversible change and accompanied by a decrease in the material crystallinity degree. After the bleaching treatment, the crystallinity increase starts, being 49.4% for the BL-B sample. The BL-H sample presented 52.6% crystallinity.

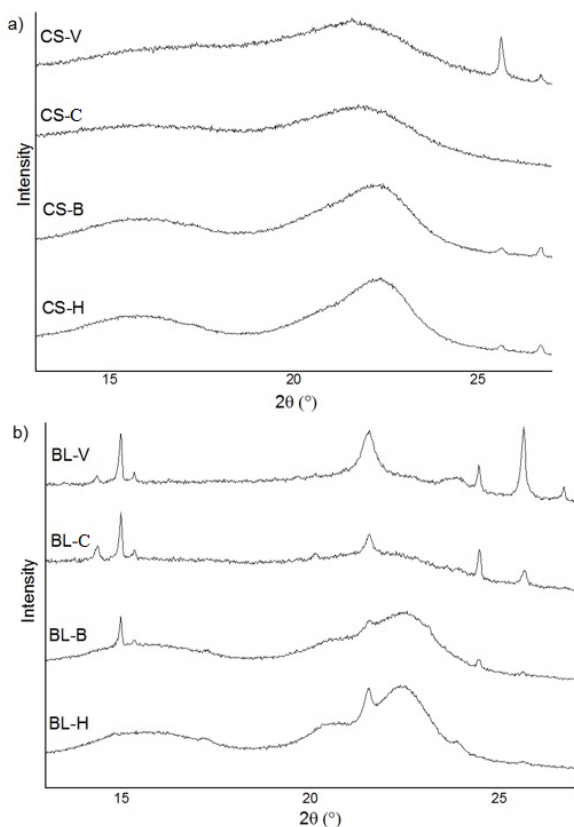


Fig. 3: Sample XRD Curves: a) CS. b) BL.

5.4 Determining of cellulose, hemicellulose and lignin percentage

Table 2 shows the results obtained from the CS and BL samples, where it is verified that there is a progressive increase in the cellulose amount as the samples pass through alkaline and acid treatments. CS-B presented $83.0 \pm 4.0\%$ cellulose in its structure, while CS-V presented $32.1 \pm 0.3\%$, indicating an increase of 158.6%. Although there is such a progressive increase between alkaline treated samples, when CS-B is compared with CS-H, there is a small reduction in the percentage of cellulose, which is $77.9 \pm 0.6\%$ for the hydrolyzed sample, a reduction of

5.9 %. This reduction corroborates with the TGA result, where there is a reduction in the thermal stability of the material, indicating that there was part of the material oxidation due to chemical treatments excessive exposure.^{15,25} In contrast to this cellulose percentage increase in the structure of CS samples, there is a reduction in the hemicellulose and lignin percentage. For CS-H, the value for lignin was not quantified, but presented a residual percentage of $6.6 \pm 0.6\%$, referring to the material oxidized. The hemicellulose present in the structures of the samples is a water-soluble polysaccharide, which is extracted more easily, since lignin is a complex organic compound of an alkaline soluble nature, therefore decrease after bleaching.³²

Table 2: Hemicellulose, cellulose and lignin percentages in the samples.

Sample	Hemicel. (%)	Cellulose (%)	Lignin (%)	Residue (%)
CS-V	35.4 ± 1.9	32.1 ± 0.3	3.2 ± 0.9	-
CS-C	35.2 ± 3.6	43.3 ± 0.1	1.0 ± 1.2	-
CS-B	12.4 ± 4.0	83.0 ± 4.0	1.1 ± 0.3	-
CS-H	9.5 ± 0.7	77.9 ± 0.6	-	6.6 ± 0.6
BL-V	21.0 ± 3.3	35.7 ± 3.2	16.7 ± 0.2	-
BL-C	20.9 ± 1.6	35.5 ± 2.9	11.7 ± 4.4	-
BL-B	5.8 ± 1.7	74.1 ± 4.7	7.5 ± 0.0	-
BL-H	2.6 ± 0.9	78.6 ± 0.7	6.7 ± 1.9	-

As for the CS samples, the increase in the percentage of cellulose for the BL samples is observed. When BL-V and BL-B were compared, there was an increase of 107.6%, as the cellulose values found for these samples were $35.7 \pm 3.2\%$ and $74.1 \pm 4.7\%$, respectively. When comparing the virgin residue with BL-H, which presents the amount of $78.6 \pm 0.7\%$ in its composition, the increase is 120.2%. The hemicellulose and lignin analysis corroborate with the result of cellulose increase since there is the continuous decrease of these two components in the BL samples structures as submitted to the treatments. These results show that there was efficiency in the hemicellulose and lignin extraction from the BL sample structures, although there is a lignin percentage in the BL-H structure, a 16.3% reduction can be considered significant. When obtaining cellulose nanocrystals still with lignin residue, there is the hybrid compound formation that can contribute to other characteristics of the composite in which it will be applied. A small lignin amount may be beneficial in achieving improved interfacial fiber-matrix resistance, which results in better composites, it can also act as a dispersant, improving the dispersion of cellulose crystals. Another advantage of maintaining part of the lignin is the increase in thermal stability.^{4,33}

5.5 Scanning Electron Microscopy (SEM)

The SEM CS and BL images are shown in Fig. 4. It is observed in Fig. 4b) and 4e) the formation of holes in the CS-C and BL-C surface, indicating the action of alkaline treatment, showing some substances removal already in this stage.¹³ The cleaning step may cause hemicellulose and lignin solubilization, in addition to causing changes in cellulose crystallinity.^{17,34} After bleaching, CS-B and BL-B (Fig. 4c) and 4f)) presented loose fibers as defibrillation occurred, indicating that most of the lignin matrix was removed, allowing fiber mobility. Fibers separation allows the contact surface to become larger, thus improving the acid treatment action that will be applied later. Also be observed size irregularity of the obtained fibers, besides being visible that CS-B and BL-B present fibers with diameters in millimeter scale.^{27,35} As the alkaline treatments were used, it was possible to verify the CS and BL structure disintegration, being easily observed that there was the components removal of its structure and individual cellulosic fibers permanence.^{5,36}

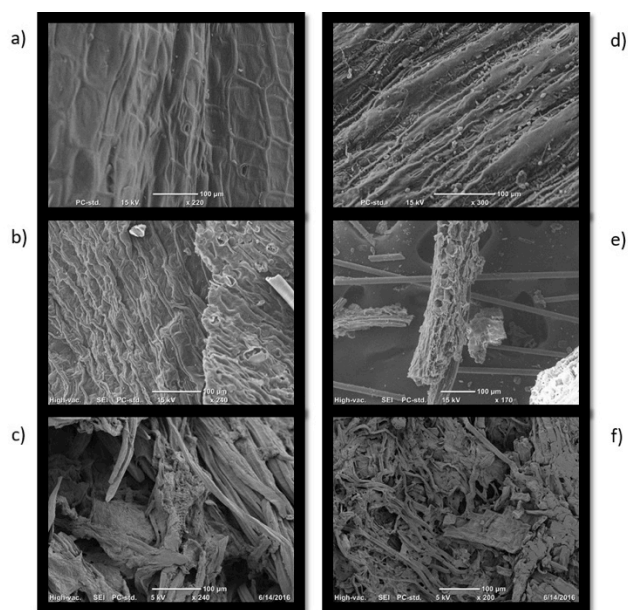


Fig. 4: Sample micrographs: a) CS-V. b) CS-C. c) CS-B. d) BL-V. e) BL-C. f) BL-B.

5.6 Dynamic light scattering (DLS)

Fig. 5a) illustrates the CS-H particle size distribution curves, where it is observed that there are four peaks, distributed between 10^{-1} and 10^6 nm, with 337 nm average size. The first peak shows a size distribution between 0.4-5 nm, with 1.37 nm mean radius size, representing the smallest particle sizes measured for CS-H, although this peak represents only 1.6% of the analyzed sample. The second peak, where the largest amount of analyzed

material is found with 85.9%, has a size distribution between 17-1242 nm, with 189 nm average size. This value is representative to prove the efficiency of nanometric particles obtaining, since there was size reduction at values close to the found in the literature, between 4-548 nm in diameter.³⁷⁻³⁹ Its third peak represents 9.3% of the sample and has $1.7 \cdot 10^4$ nm average size, with distribution between $6.1 \cdot 10^3$ - $4.6 \cdot 10^4$ nm, while its fourth peak represents 3.2% of the material in the size range of $1.4 \cdot 10^5$ - $6.9 \cdot 10^5$ nm.

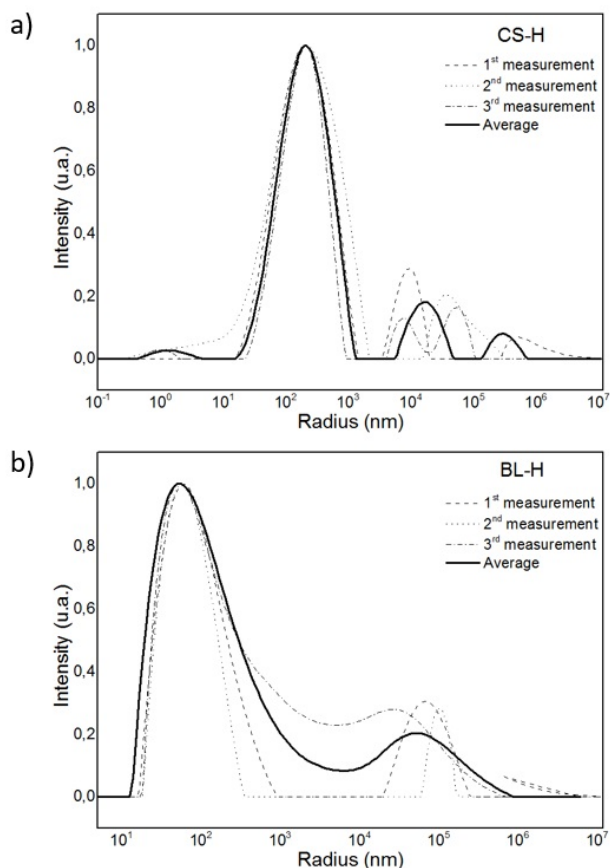


Fig. 5: Curves of the scattering intensity distribution as a function of the hydrodynamic radius: a) CS-H. b) BL-H.

When analyzing the data generated by this curve, it is noticed that there is a greater CS-H particles amount in nanometric size, although the PDI of this sample is 0.513, also indicating an average polydispersity. Fig. 5b) illustrates the BL-H particle size distribution curve, where a bimodal curve, distributed between 13 - $8.8 \cdot 10^5$ nm, with a mean particle size of 304 nm, representing 100% of the Material analyzed. The BL-H PDI is 0.473, also indicating median polydispersity. The DLS results provide an overview of the particle size distribution, although it is not the most efficient method for the exact particle size

determination, as the cellulose nanocrystals tend to clump together and the higher values read by the DLS may be from agglomerated particles.^{22,37,40} In order to confirm the particles size of CS-H and BL-H, the AFM technique was used, being possible to verify its morphology and also the measurement of its size.

5.7 Atomic force microscopy (AFM)

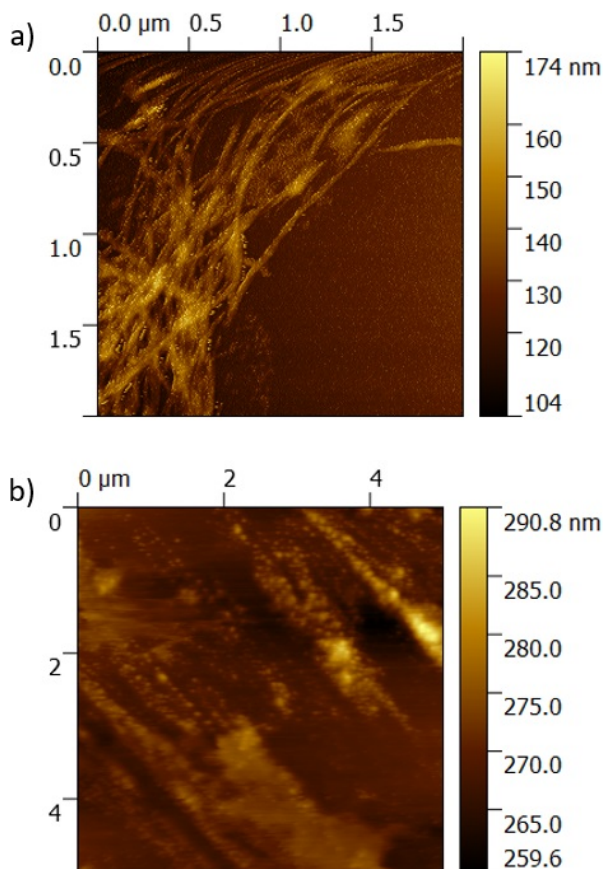


Fig. 6: Image obtained by AFM: a) CS-H. b) BL-H.

It is observed in Fig. 6a) that CS-H has nanofibers aspect, given the diameter size of the fibers, although the length cannot be measured. In the image, the fibers agglomeration tendency is observed, which corroborates with the assumption that the greatest measures obtained by DLS are those nanocrystals agglomerates. When measuring the diameter of the fibers, a value between 26-78 nm is obtained, an excellent result, with a value within the range found in the DLS analysis, 17-1242 nm. For BL-H, the tendency for particle agglomeration is also observed, as shown in Fig. 6b). The fibers diameter varies between 120-510 nm, which also corresponds to the mean size of 304 nm obtained by DLS.

4. Conclusions

The particle sizes obtained for CS-H and BL-H were at nano scale, indicating the formation of cellulose nanocrystals applicable as reinforcement in nanocomposites. Despite good results in sizing terms, particle morphology, decrease in the hemicellulose and lignin amount, generating samples with a higher percentage of cellulose in its composition, the CS-H and BL-H thermal stability was impaired due to treatments excess employed, thus reducing its processing temperature, preventing its use together with polymers that require high temperatures. The total lignin non-removal from the sample structure is not considered an undesired result since there is the hybrid cellulose nanocrystals formation, which can bring differentiated characteristics to the composite when these are incorporated into polymer matrices. It can be affirmed that the same treatment methodology can be used for more than one vegetable fiber type, obtaining good results and extending the application range of the obtaining crystals process.

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References

1. Silva, R., Haraguchi, S. K., Muniz, E. C. & Rubira, A. F. Aplicações de fibras lignocelulósicas na química de polímeros e em compósitos. *Quim. Nova* **32**, 661–671 (2009).
2. Ludueña, L. N., Vecchio, A., Stefani, P. M. & Alvarez, V. A. Extraction of cellulose nanowhiskers from natural fibers and agricultural byproducts. *Fibers Polym.* **14**, 1118–1127 (2013).
3. Nascimento, D. M. *et al.* A novel green approach for the preparation of cellulose nanowhiskers from white coir. *Carbohydr. Polym.* **110**, 456–63 (2014).
4. Rosa, M. F. *et al.* Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. *Carbohydr. Polym.* **81**, 83–92 (2010).
5. Mtibe, A. *et al.* A comparative study on properties of micro and nanopapers produced from cellulose and cellulose nanofibres. *Carbohydr. Polym.* **118**, 1–8 (2015).
6. Li, X., Tabil, L. G. & Panigrahi, S. Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review. *J. Polym. Environ.* **15**, 25–33 (2007).
7. Hajlane, A., Kaddami, H., Joffe, R. & Wallström, L. Design and characterization of cellulose fibers with hierarchical structure for polymer reinforcement. *Cellulose* **20**, 2765–2778 (2013).
8. Saheb, D. N. & Jog, J. P. Natural Fiber Polymer

- Composites : A Review. *Adv. Polym. Technol.* **18**, 351–363 (1999).
9. Martins, D. F. *et al.* The influence of the cellulose hydrolysis process on the structure of cellulose nanocrystals extracted from capim mombaça (*Panicum maximum*). *Ind. Crops Prod.* **65**, 496–505 (2014).
 10. Siqueira, G., Bras, J. & Dufresne, A. Cellulose Whiskers versus Microfibrils: Influence of the Nature of the Nanoparticle and its Surface Functionalization on the Thermal and Mechanical Properties of Nanocomposites. *Biomacromolecules* **10**, 425–432 (2009).
 11. de Souza Lima, M. M. & Borsali, R. Rodlike Cellulose Microcrystals: Structure, Properties, and Applications. *Macromol. Rapid Commun.* **25**, 771–787 (2004).
 12. P. J. Van Soest. in *Journal of Animal Science* (ed. Intergovernmental Panel on Climate Change) **26**, 119–128 (Cambridge University Press, 1967).
 13. Bilba, K., Arsene, M. & Ouensanga, A. Study of banana and coconut fibers Botanical composition, thermal degradation and textural observations. *Bioresour. Technol.* **98**, 58–68 (2007).
 14. Moriana, R., Vilaplana, F. & Ek, M. Cellulose Nanocrystals from Forest Residues as Reinforcing Agents for Composites: A Study from Macro- to Nano-Dimensions. *Carbohydr. Polym.* **139**, 139–149 (2016).
 15. Sathasivam, K. & Haris, M. R. H. M. Thermal properties of modified banana trunk fibers. *J. Therm. Anal. Calorim.* **108**, 9–17 (2012).
 16. Johari, A. P., Kurmvanshi, S. K., Mohanty, S. & Nayak, S. K. Influence of surface modified cellulose microfibrils on the improved mechanical properties of poly (lactic acid). *Int. J. Biol. Macromol.* **84**, 329–339 (2016).
 17. Pereira, A. L. S. *et al.* Improvement of polyvinyl alcohol properties by adding nanocrystalline cellulose isolated from banana pseudostems. *Carbohydr. Polym.* **112**, 165–172 (2014).
 18. Morelli, C. L., Marconcini, J. M., Pereira, F. V., Bretas, R. E. S. & Branciforti, M. C. Extraction and Characterization of Cellulose Nanowhiskers from Balsa Wood. *Macromol. Symp.* **319**, 191–195 (2012).
 19. Renard, C. M. G. C. & Jarvis, M. C. A cross-polarization, magic-angle-spinning, C-nuclear-magnetic-resonance study of polysaccharides in sugar beet cell walls. *Plant Physiol.* **119**, 1315–1322 (1999).
 20. Khawas, P. & Deka, S. C. Isolation and characterization of cellulose nanofibers from culinary banana peel using high-intensity ultrasonication combined with chemical treatment. *Carbohydr. Polym.* **137**, 608–616 (2016).
 21. Reddy, K. O., Maheswari, C. U., Reddy, D. J. P. & Rajulu, A. V. Thermal properties of Napier grass fibers. *Mater. Lett.* **63**, 2390–2392 (2009).
 22. Espino, E. *et al.* Isolation and characterization of cellulose nanocrystals from industrial by-products of Agave tequilana and barley. *Ind. Crops Prod.* **62**, 552–559 (2014).
 23. Roman, M. & Winter, W. T. Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. *Biomacromolecules* **5**, 1671–1677 (2004).
 24. C.S., J. C., George, N. & Narayanankutty, S. K. Isolation and Characterization of Cellulose Nanofibrils From Arecanut Husk Fibre. *Carbohydr. Polym.* **142**, 158–166 (2016).
 25. Álvarez, P., Blanco, C., Santamaría, R. & Granda, M. Improvement of the thermal stability of lignocellulosic materials by treatment with sulphuric acid and potassium hydroxide. *J. Anal. Appl. Pyrolysis* **72**, 131–139 (2004).
 26. Zhang, M. *et al.* Fractionating lignocellulose by formic acid: Characterization of major components. *Biomass and Bioenergy* **34**, 525–532 (2010).
 27. Cherian, B. M. *et al.* A novel method for the synthesis of cellulose nanofibril whiskers from banana fibers and characterization. *J. Agric. Food Chem.* **56**, 5617–5627 (2008).
 28. Guimarães, J. L., Wypych, F., Saul, C. K., Ramos, L. P. & Satyanarayana, K. G. Studies of the processing and characterization of corn starch and its composites with banana and sugarcane fibers from Brazil. *Carbohydr. Polym.* **80**, 130–138 (2010).
 29. Zugenmaier, P. Conformation and packing of various crystalline cellulose fibers. *Prog. Polym. Sci.* **26**, 1341–1417 (2001).
 30. Ass, B. A. P., Belgacem, M. N. & Frollini, E. Mercerized linters cellulose: characterization and acetylation in N,N-dimethylacetamide/lithium chloride. *Carbohydr. Polym.* **63**, 19–29 (2006).
 31. Flauzino Neto, W. P. *et al.* Comprehensive morphological and structural investigation of cellulose I and II nanocrystals prepared by sulphuric acid hydrolysis. *RSC Adv.* **6**, 76017–76027 (2016).
 32. Abraham, E. *et al.* Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach. *Carbohydr. Polym.* **86**, 1468–1475 (2011).
 33. Thielemans, W., Can, E., Morye, S. S. & Wool, R. P. Novel applications of lignin in composite materials. *J. Appl. Polym. Sci.* **83**, 323–331 (2002).
 34. Herrera, M. a., Mathew, A. P. & Oksman, K. Comparison of cellulose nanowhiskers extracted from industrial bio-residue and commercial microcrystalline cellulose. *Mater. Lett.* **71**, 28–31 (2012).
 35. Nasri-Nasrabadi, B., Behzad, T. & Bagheri, R. Preparation and characterization of cellulose nanofiber reinforced thermoplastic starch composites. *Fibers Polym.* **15**, 347–354 (2014).
 36. Mwaikambo, L. Y. & Ansell, M. P. Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization. *J. Appl. Polym. Sci.* **84**, 2222–2234 (2002).
 37. Shanmugarajah, B. *et al.* Isolation of NanoCrystalline Cellulose (NCC) from Palm Oil Empty Fruit Bunch (EFB): Preliminary Result on FTIR and DLS Analysis. *Chem. Eng. Trans.* **45**, 1705–1710 (2015).
 38. Dadkhah Tehrani, A. & Basiryani, A. Dendronization of cellulose nanowhisiker with cationic hyperbranched dendritic polyamidoamine. *Carbohydr. Polym.* **120**, 46–52 (2015).
 39. Kalita, E., Nath, B. K., Agan, F., More, V. & Deb, P. Isolation and characterization of crystalline, autofluorescent, cellulose nanocrystals from saw dust wastes. *Ind. Crops Prod.* **65**, 550–555 (2015).
 40. Brito, B. S. L., Pereira, F. V., Putaux, J. L. & Jean, B. Preparation, morphology and structure of cellulose nanocrystals from bamboo fibers. *Cellulose* **19**, 1527–1536 (2012).

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