

## ORIGINAL ARTICLE

# Production and characterization of nanofibrillated cellulose powder

## *Produção e caracterização de celulose nanofibrilada em pó*

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### Abstract

The objective of this work was the characterization of nanofibrillated cellulose powder (NFC) from *Pinus sp.* bleached kraft pulp. First, nanofibrillated cellulose was produced by the mechanical defibrillation process at the Super Masscolloider Masuko Sangyo mill using five passes. Subsequently, to obtain nanofibrillated cellulose in the form of a dry powder, the equipment called Spray Dryer was used. The characterization of CNF powder was performed by transmission and scanning electron microscopy. The techniques of X-ray diffraction, medium infrared spectroscopy and thermogravimetric analysis were also performed. Compared to the literature, the results show that the drying process of nanofibrillated cellulose changed its morphology when compared to a CNF still in its liquid state, but the CNF powder is very similar in its morphology compared to other works with CNF Dry Spray Dryer. In the X-ray diffraction analysis, characteristic cellulose peaks were observed, but the crystallinity index was relatively low compared to the literature, possibly due to the concentration at which CNF was prepared. Near infrared spectroscopy analysis showed the characteristic peaks of cellulose. Regarding the thermal analysis, it is found that the CNF has high stability, in accordance with the literature. These new features may be interesting for different industrial uses, such as thermoplastic production.

**Keywords:** nanocellulose, Spray dryer, cellulose pulp.

### Resumo

Este trabalho teve como objetivo a caracterização de celulose nanofibrilada em pó (CNF) a partir da polpa kraft de *Pinus sp.* branqueada. Primeiramente, a celulose nanofibrilada foi produzida pelo processo de desfibrilação mecânica no moinho Super Masscolloider Masuko Sangyo usando cinco passes. Posteriormente, para obter a celulose nanofibrilada na forma de um pó seco foi utilizado o equipamento denominado Spray Dryer. A caracterização da CNF em pó foi realizada por microscopia eletrônica de transmissão e de varredura. As técnicas de difração de raios-X, espectroscopia de infravermelho médio e análise termogravimétrica também foram realizadas. Em comparação com a literatura, os resultados mostram que o processo de secagem da celulose nanofibrilada alterou a sua morfologia quando comparadas à uma CNF ainda em seu estado líquido, porém a CNF em pó mostra-se muito similar na sua morfologia em comparação a outros trabalhos com CNF seca em Spray Dryer. Na análise de difração de raios-X foram observados picos característicos de celulose, porém o índice de cristalinidade mostrou-se relativamente baixo em comparação à literatura, possivelmente, devido à concentração em que a CNF foi preparada. A análise de espectroscopia de infravermelho próximo apresentou os picos característicos de celulose. Com relação à análise térmica, tem-se que a CNF possui alta estabilidade, estando de acordo com a literatura. Estas novas características podem ser interessantes para diferentes usos industriais, como na produção de termoplásticos.

**Palavras-chave:** nanocelulose, Spray dryer, polpa de celulose.

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## INTRODUCTION

Cellulose is a renewable resource that has been widely studied because it is found abundantly in nature, is of low cost, is biodegradable and has application potential in several areas. One of the products obtained from cellulose by different methods is the nanocellulose, which presents potential for reinforcement and development of new products, since it has the capacity to form a greater amount of hydrogen bonds, besides having low weight and high resistance and rigidity, when compared to cellulose (Yano & Nakahara, 2004; Hubbe et al., 2008; Nakagaito et al., 2009; Frone et al., 2011; González et al., 2014).

There are several methods for obtaining nanocellulose, such as the chemical method, mechanical method and the combination of the chemical with the mechanic one. Depending on the process used, nanocellulose is obtained with differentiated structures for unique applications. In other words, depending on the raw materials used and the techniques employed, there is a change in the nanocellulose obtained with respect to size, morphology and other characteristics (Wang et al., 2007).

The mechanical method, suggested in recent studies, is mechanical defibrillation when using a grinder (Abe & Yano, 2010; Panthapulakkal & Sain, 2012; Wang et al., 2013). The mill consists of a rotating disc and a fixed disc with an adjustable aperture between them so that by mechanical contact the cellulose fibers are defibrillated by shear forces generated by the defibrillation stones (Potulski et al., 2016). In this process, cellulose is reduced to very small diameters, reaching from 25 to 100 nm, called microfibrillated cellulose. Diameters from 5 to 30 nm are considered nanofibrillated cellulose (Sehaqui et al., 2011).

Therefore, nanofibrillated cellulose (NFC) is a type of nanocellulose obtained from the mechanical defibrillation of cellulosic pulp or wood fibers with or without the application of pre-treatments (Nakagaito & Yano, 2004).

In the forestry sector, NFC becomes an attractive material for use in the pulp and paper industry, because it has unmatched physical and mechanical properties along with its low density. These properties make the NFC an excellent material for applications such as coatings, in the production of films and special papers and as additives in paper production (Wang et al., 2007).

NFC can be used in many other ways, such as reinforcement in composites, pharmaceuticals and cosmetics, construction products, food and packaging components, electronic and electrical industry, textiles and biomedicine (Ioelovich, 2008).

The abundance of applications and possible variations in the properties of the materials in which nanofibrillated cellulose is applied justifies the increasing interest in it. Studies about it can provide the knowledge of the main properties and characteristics of this type of nanocellulose (Potulski et al., 2016).

There are studies that characterize the nanocellulose, produced through the mechanical process, in gel form. Other characterizations are performed on nano films, produced from nanocellulose (Potulski et al., 2014). However, there are few studies characterizing the nanocellulose that underwent a spray-drying process, presenting itself in the powder conformation.

The characterization of nanocellulose in this format is important due to the demands of certain industries, such as food and chemical, that can use the drying of their raw materials in Spray Dryer within the production line.

In this context, the objective of this work was to characterize nanofibrillated cellulose - dried in Spray Dryer - from bleached *Pinus sp.* kraft pulp, obtained by the process of mechanical defibrillation.

## MATERIALS AND METHODS

### Producing the material

To produce nanofibrillated cellulose, bleached industrial kraft cellulose pulp of *Pinus sp.* (Kappa 0.8) was used. Masscolloider Masuko Sangyo grinder defibrillator (MKCA6-3; Masuko

Sangyo Co., Ltd.), using five passes and a constant frequency of 1500rpm. After the five passes through the defibrillator mill, the material obtained was destined for drying in the Spray Dryer. The parameters used in the Spray Dryer were flow rate of 500 ml/min at an average temperature of 200 °C. The material obtained is a fine white powder, and subsequently, the characterization of its properties was carried out.

### Characterization of material

A JEOL JEM 1200EX-II Electronic Transmission Electron Microscope was used for the characterization of nanofibrillated cellulose via transmission electron microscopy (TEM), with a resolution of 0.5 nm. The material used in the analysis was prepared from the dilution of a small amount of the powdered NFC in distilled water. A single drop of this suspended material was deposited on the sample holder and then dried at room temperature.

The NFC was also characterized by the Scanning Electron Microscopy (SEM) technique using the FEI Quanta 450 FEG Scanning Microscope, with a resolution of 1 nm. The material used in the analysis was prepared by depositing a quantity of powdered nanofibrillated cellulose on a double-sided copper tape adhered to the sample holder.

To determine the crystallinity of the nanofibrillated cellulose produced, the equipment used was a Bruker diffractometer, model D8 Advance. One reading per sample and per interval was made. The diffraction angle ( $2\theta$ ) ranged from 5 to 65° and the range used was 0.02°. In addition, the equipment was operated at 40 kV and 20 mA current. This equipment allows the sample to rotate around its axis while the readings are performed, which provides us with more accurate data. In addition, important data such as the percentage of crystallinity of the material is calculated directly by the Difrac.eva program version 4.0 2014.

For the medium infrared spectroscopy, five spectra were obtained in the spectral region of 400 to 4000  $\text{cm}^{-1}$ . The equipment used was a Bruker Tensor 37 spectrophotometer with 64 scans and 2  $\text{cm}^{-1}$  resolution.

To perform the thermogravimetric analysis (TGA), a SETARYS SETSYS EVOLUTION TGA equipment was used and the crucible used was Alumina. The sample was heated from 29.43 to 653.77°C at a heating rate of 0.05°C/min in an argon flux of 20 mL/min.

## RESULTS AND DISCUSSION

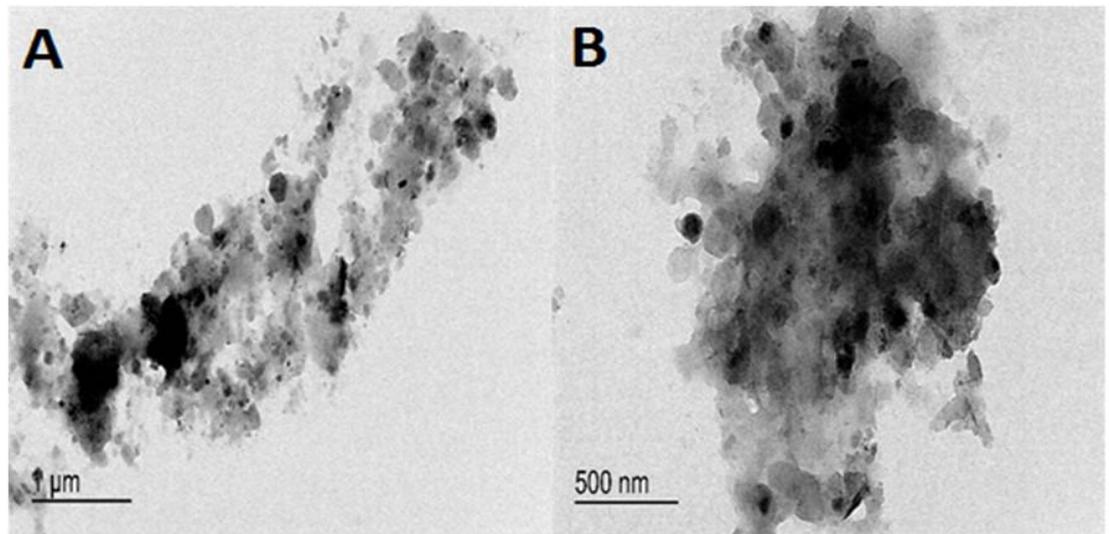
### Microscopic Characterization

TEM analysis showed that powdered NFC is formed in crowded structures of indefinite shapes. According to Gardner et al. (2008), due to its hydrophilic nature and propensity to form agglomerates, spray drying CNF liquid is a major challenge, as hydroxyl groups available to interact with water cause agglomeration during the removal of a high amount of system water.

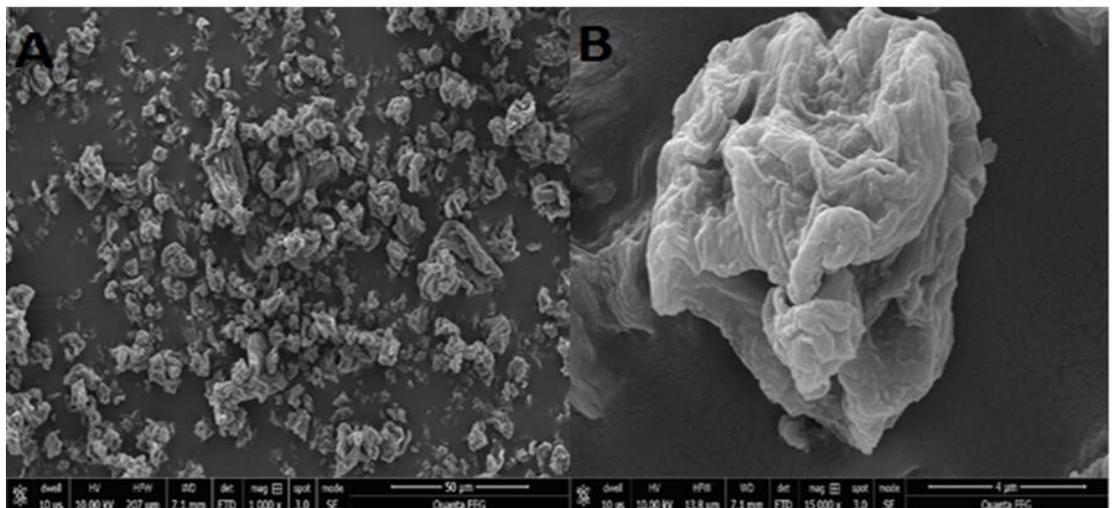
Therefore, the structures obtained are related to spray drying in the Spray Dryer (Figure 1) as reported in the literature. Nevertheless, it is possible to observe elements that have at least one of their dimensions smaller than 100 nm.

The mechanical defibrillation process resulted in the fibrillation of the cell wall of the fibers (tracheoids) producing nanofibrils. Therefore, it is possible to affirm that when using the Spray Dryer in the drying of NFC, this causes structural change of the material.

The Scanning Electron Microscopy analysis scans the surface of the material to be studied. The SEM has a great depth of focus, where the morphology is evident. The morphological changes that occurred after the mechanical defibrillation process and the passage of the material through the Spray Dryer are illustrated in Figure 2.



**Figure 1.** TEM (Transmission Electron Microscopy) of powdered NFC. A) 5000x increase; B) 10000x increase.



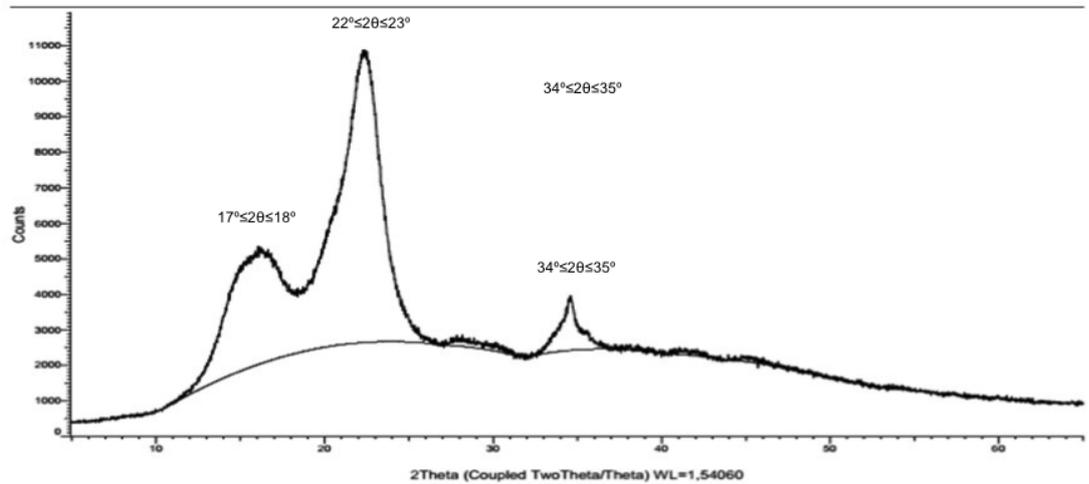
**Figure 2.** SEM (Scanning Electron Microscopy) of powdered NFC. A) 1000x increase; B) 15000x increase.

This analysis reinforces the fact that after drying in the Spray Dryer the material acquired an irregular morphology of compact aggregates and without defined format. Peng et al. (2012), in their work with NFC, using Spray Dryer, observed that this type of drying results in agglomerated NFC particles.

#### Characterization by X-ray Diffraction

Most of the cellulosic materials are constituted by crystalline and amorphous regions, in varying proportions, depending on the origin and sample of the material. The crystallinity index is related to the amount of crystalline regions of the cellulose, and these regions present greater resistance to traction and elongation. The ratio between crystalline and amorphous regions determines the crystallinity index (CI) of cellulose (Smook & Kocurek, 1989).

The intensities of the crystalline peaks located between the angles of  $22^\circ \leq 2\theta \leq 23^\circ$  and the amorphous halos ( $17^\circ \leq 2\theta \leq 18^\circ$  and  $34^\circ \leq 2\theta \leq 35^\circ$ ) for the powdered NFC are shown in Figure 3.



**Figure 3.** X-ray diffraction of powdered NFC.

The peak of higher intensity represents the crystalline portion, that is, the cellulose is more crystalline the larger the peak positioned in the 22° region is. The characteristic peaks of this diffractogram coincide with the literature. Potulski et al. (2016) in his work with *Pinus* NFC, found similar results.

Peng et al. (2013) in their work observed peaks at = 16.4° and 34.5° to NFC, corresponding to amorphous halos, that are mainly caused by the diffraction of the crystal.

The average crystallinity index obtained was 39.6%. This value was lower than those found in the literature. Peng et al. (2013) found a crystallinity index for NFC of 82,1% in their work, with Spray Dryer drying.

Potulski et al. (2016) obtained values of CI of 69.8; 72.1 and 72.2% for the nanofibrillated celluloses obtained from the consistencies of 1.0; 0.5 and 1.5%, resulting from 20 passes in the defibrillator mill.

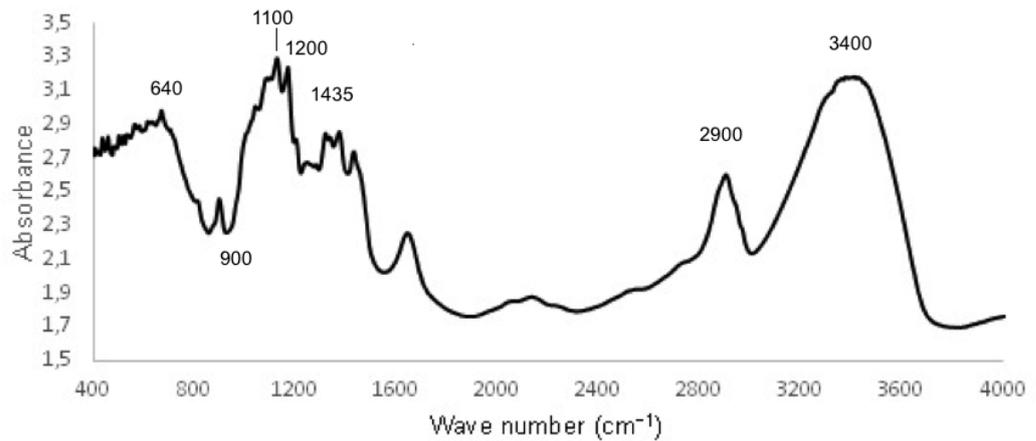
Spence et al. (2010) producing nanostructured cellulose films by mechanical processes of refining and homogenization, found indexes of crystallinity between 53 and 59% for long-fiber woods, using X-ray diffraction and the method proposed by Segal et al. (1959).

Depending on their intensity, the mechanical defibrillation process may cause degradation of the crystalline regions and exposure of OH groups which make the material more susceptible to formation of new chemical bonds. Thus, the determination of the crystallinity index allows to analyze the possible degradation suffered in the fiber.

Five passes were performed through the defibrillator, which is not considered a large number of passes. When observing the CIs found in the literature, we found that in this work the value was well low, which may be related to the concentration of the material at the time of spray drying. Peng et al. (2013) affirm that the agglomeration of nanocellulose fibrils may provide an opportunity to increase the crystallinity index of spray-dried NFCs, where the hydrogen-bonding drives nanocellulose fibrils to approach each other closely and form tight aggregates resulting in more formation of crystalline structures.

### Characterization by Medium Infrared Spectroscopy

The most useful portion for the study of organic molecules is between 400 and 4000 cm<sup>-1</sup>, called the medium infrared. Figure 4 below shows the average spectrum obtained for powdered NFC.



**Figure 4.** FTIR spectrum of powdered NFC.

It is possible to check common absorption bands for cellulose. The absorption at 3400  $\text{cm}^{-1}$  for the hydroxyl groups (OH) characteristic of cellulose is shown. Pastore et al. (2008) and Rangan et al. (2017) in their works also observed this peak.

We can observe a characteristic peak of cellulose near 2900  $\text{cm}^{-1}$ . Youssef et al. (2015), when using nanocellulose from the grass *Stipa tenacissima* L. - which belongs to the family Poaceae, with the purpose of increasing the resistance of films - observed a dominant peak at 2900  $\text{cm}^{-1}$ , which was attributed to the CH stretch of cellulose present in its material.

At 1435  $\text{cm}^{-1}$  we observed the presence of a peak. According to Merkel et al. (2014), this peak is attributed to the CH bond characteristic of amorphous and crystalline cellulose.

Pastore et al. (2008), in his work found absorption peaks with mean values of 1100  $\text{cm}^{-1}$  referring to the symmetrical stretch of the C-O-C binding characteristic of cellulose. Rangan et al. (2017), attributes to the peak at approximately 1200  $\text{cm}^{-1}$  also the symmetrical stretch of the C-O-C bond. In this work it is possible to observe peaks in this region, which thus evidences the C-O-C bond of the material.

Additionally, we observed a peak at 908  $\text{cm}^{-1}$ . Pastore et al. (2008), in his work, found a peak at 900  $\text{cm}^{-1}$  attributed to the CH bond, which is characteristic of cellulose.

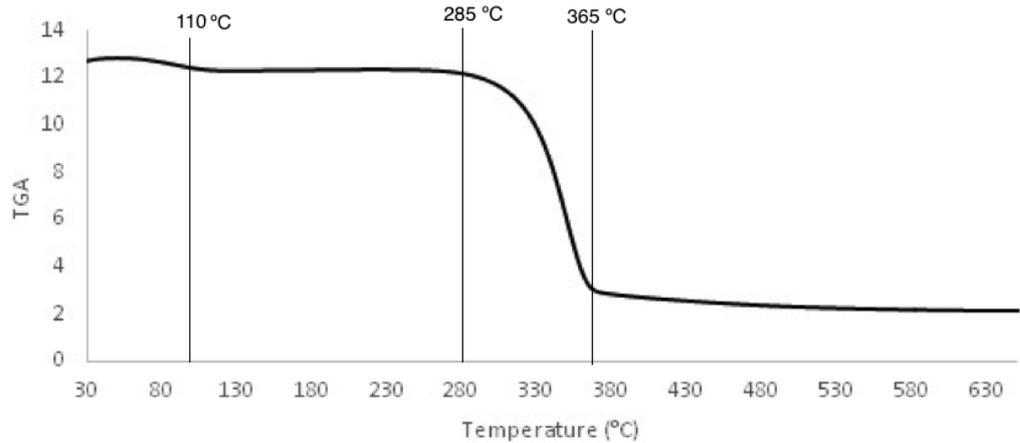
It is also worth noting the absorption peaks at approximately 640  $\text{cm}^{-1}$  and 1655  $\text{cm}^{-1}$  characteristic of the NH<sub>2</sub> bond. Rodrigues et al. (2016) in his work observed these characteristic peaks at 695  $\text{cm}^{-1}$  and 1620  $\text{cm}^{-1}$ .

### Characterization by Thermogravimetric Analysis

The thermogravimetric analysis is used to verify the thermal stability and degradation temperature. Through the curves of variation of mass as a function of temperature, it is possible to quantitatively determine the main components present in the samples. Figure 5 demonstrates the stages of thermal degradation of powdered NFC.

Initially, it is possible to observe that there was loss of initial mass at 110 °C that is attributed to the moisture loss of the sample. Merkel et al. (2014) in his work observed water loss between 25 and 150 °C. Although powdered NFC is still dry there is still a small loss of water-related mass, as observed in Figure 5.

The degradation interval of the powdered NFC occurred between 285 °C to 365 °C, with peak degradation at 350 °C. The obtained results show a high thermal stability, in agreement with the literature.



**Figure 5.** TGA of powdered NFC.

Youssef et al. (2015) observed that the degradation of nanocellulose started at 239 °C and stabilized at approximately 400 °C, with a peak degradation at 315 °C. Merkel et al. (2014) also observed a degradation period of cellulose between 250 and 350 °C, with degradation peak at 344 °C.

## CONCLUSIONS

The Spray Dryer drying process alters the NFC morphology, which then has irregular morphology, consisting of compact aggregates and no defined shape.

NFC presented a reduced crystallinity index compared to the literature. This interesting result may be related to the concentration of the material subjected to drying in the Spray Dryer.

Despite the low crystallinity index, NFC powder, if used in adequate quantities, can be considered as a possible additive in place of additives produced from non-renewable sources.

Regarding the analysis of mid infrared spectroscopy, results similar to the literature were found. Even after drying, it was possible to observe that the NFC presented the characteristic cellulose peaks.

Therefore, the produced NFC powder has different characteristics, which may be interesting for different industrial uses, especially the industries that use the drying of their raw materials during the process or in the application in non-polar thermoplastics, according to their higher thermal stability.

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