

## Nanostructured Films Produced from the Bleached *Pinus* sp. Kraft Pulp

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### ABSTRACT

This study investigates the physical and mechanical properties of nanostructured films produced from *Pinus* sp. kraft pulp. To obtain the nanocellulose, the bleached kraft pulp was submitted to six different grinding regimes: two, five, ten, 20, 30, and 40 passes through the grinder. The influence of the number of passes was evaluated through the films' physical and mechanical properties. The results show that the nanofibers reduced the thickness and considerably increased the density values of the fabricated films. The tensile strength increased more than 300% and the burst index was ten times higher in relation to normal papers. The more compact structure and lower porosity caused by the larger contact surface between nanofibers in the nanostructured films resulted in higher values of density, tensile strength, and burst resistance.

**Keywords:** nanocellulose, grinder, mechanical properties, density, crystallinity index.

### Filmes Nanoestruturados Produzidos a partir de Polpa Kraft Branqueada de *Pinus* sp.

### RESUMO

Este trabalho investiga as propriedades físicas e mecânicas de filmes nanoestruturados produzidos a partir da polpa kraft branqueada de *Pinus* sp. Para obter a nanocelulose, a polpa kraft branqueada foi submetida a seis diferentes intensidades de desfibrilação pelo moinho: dois, cinco, dez, 20, 30 e 40 passes. A influência do número de passes foi avaliada por meio das propriedades físicas e mecânicas dos filmes. Os resultados indicam que a presença de nanofibrilas reduziu a espessura e aumentou consideravelmente os valores de densidade dos filmes fabricados. Observou-se aumento da resistência à tração de 300% e o índice de ruptura foi dez vezes maior em relação aos papéis normais. A estrutura mais compacta e a menor porosidade causada pela maior superfície de contato entre as nanofibrilas nos filmes resultaram em maiores valores de densidade, resistência à tração e resistência à ruptura.

**Palavras-chave:** nanocelulose, moinho, propriedades mecânicas, densidade, índice de cristalinidade.

## 1. INTRODUCTION AND OBJECTIVES

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The growing search for products that cause less impact on the environment has motivated the study and application of biodegradable and renewable raw materials. Among these natural resources, cellulose stands out as a renewable, biodegradable and inexpensive material, also presenting excellent physical and mechanical properties.

In nanotechnology, attainment and use of the cellulose's nanofibers and its applications in composite materials have attracted attention of researchers due to its high resistance and rigidity and low weight (Julkapli & Bagheri, 2017). Besides those desirable mechanical properties, cellulose nanofibers present other interesting features for reinforcing nanocomposites, enabling optically transparent films with a very low thermal expansion coefficient that are still easily foldable (Fall et al., 2014; Kargazadeh et al., 2017; Shimizu et al., 2016; Toivonen et al., 2015).

Wood has been the main source of cellulose used for the production of nanofibrils (Berglund & Burgert, 2018; Chinga-Carrasco, 2011). Vegetable fibers, especially from wood, are important sources of reinforcement material for the substitution of conventional fibers in composites for semi-structured and structured applications. The high percentage of cellulose in wood, which in terms of mass is the most important component of the cell wall (occupying about 45%), along with the fact that as a renewable material it has less impact on the environment, encourages research to produce nanofibers from this resource.

The wall of wood cells is composed of layers of microfibril aggregates combined with hemicellulose and lignin (Sjöström, 1993). The obtainment and separation of nanofibers from the cell wall requires some form of chemical and/or mechanical treatment. According to existing works, cellulose nanofibers can be obtained from the disintegration of cellulose submitted to a mechanical homogenization process in which it is degraded, exposing and opening the surfaces previously situated inside the fibers, fibrils and microfibrils (Brodin & Gregersen, 2014; Suopajarvi et al., 2017; Turbak et al., 1983). This process causes a significant decrease in fibers' size and consequently an increase of specific areas, promoting better connection between the microfibrils (Jonoobi et al., 2012).

Cellulose nanofibers are hydrophilic, with high capacity to form strong interfibrillar hydrogen bonds that produce a material with high density and resistance properties. They can be used in nanocellulosic films for coating or as reinforcement for many products in the paper industry (Balea et al., 2018; Campano et al., 2018; He et al., 2016; Josset et al., 2014). Due to their larger specific surface area, nanofibers also have increased accessibility, solubility, and reactivity (Ioelovich & Larina, 1999).

Recent research shows that in relation to conventional material, the paper or film produced from nanocellulose presents higher density, flexibility, and mechanical resistance, as well as lower porosity (Balea et al., 2016; Bharimalla et al., 2015; González et al., 2014). Cellulosic nanofiber films have properties considered satisfactory for application in packages, a fact that explains the food industry's increasing interest in replacing packaging made of petroleum-based polymers with biodegradable materials such as paper coated with cellulosic nanofilms (Aulin & Ström, 2013; Herrera et al., 2016; Vandermoere et al., 2011).

The isolation of cellulosic nanofibers from wood sawdust and cellulosic pulp has been reported through the mechanical process of grinding or defibrillation, by using a grinder that allows obtaining nanofibers with average width around 15 nm and length measured in micrometers (Abe et al., 2007; Abe & Yano, 2010; Ifuku et al., 2010; Panthapulakkal & Sain, 2012; Vartiainen et al., 2011; Wang et al., 2013; Wang et al., 2015).

In this context, this article aims at investigating the physical and mechanical properties and characteristics of nanostructured films from bleached *Pinus* sp. kraft pulp, obtained through different numbers of passes through the defibrillator grinder.

## 2. MATERIALS AND METHODS

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### 2.1. Material

An unbleached *Pinus* sp. kraft pulp obtained from pulp and paper industry was used. It went through a mechanical process of tracheids disintegration, after which it was washed to remove excess cooking liquor and then submitted to centrifugation and bleaching.

The bleaching process was adapted from Wise et al. (1946). For each 10 g of dried pulp, 1.5 g of 80% sodium chlorite ( $\text{NaClO}_2$ ) and 10 drops of glacial acetic acid in 160 mL of distilled water were added. The material was maintained in a water bath at 80 °C for one hour. Three bleaching steps were performed, and in each interval the pulp was abundantly washed to remove possible residues of  $\text{NaClO}_2$ .

The kappa number (Tappi, 1999b) used to measure the quantity of residual lignin in the pulp was determined before and after the bleaching. The values found were 51.7 and 3.6, respectively.

## 2.2. *Obtainment of cellulose nanofibers*

The concentration of the bleached kraft pulp in suspension was adjusted to 1 wt% by adding water

(Iwamoto et al., 2008), followed by mechanical defibrillation in a Masuko Sangyo Super Masscolloider grinder (MKCA6-3; Masuko Sangyo Co., Ltd.) (Figure 1) at a frequency of 1,500 rpm. Six different numbers of passes through the grinder were evaluated: two, five, ten, 20, 30, and 40, as well as treatment without any mechanical processing, thus totaling seven treatments. These treatments were called T02, T05, T10, T20, T30, T40, and T00, respectively.

After a few passes through the grinder, the cellulosic suspension is transformed into a stable suspension, acquiring a gel-like aspect, as observed by Besbes et al. (2011), called a nanocellulosic suspension. Part of the obtained nanocellulosic suspension was used to determine the viscosity of treatments and to observe nanofibers through transmission electron microscopy (TEM).



**Figure 1.** Masuko Sangyo Super Masscolloider grinder.

### 2.3. Preparation of nanostructured cellulosic films

Nanostructured films were produced through deposition of the nanocellulosic suspension on a whole filter paper placed under a nylon screen (opening: 5  $\mu\text{m}$ ) and then filtered in a vacuum. After being filtered, the films were taken for pre-drying at 60 °C in an oven for 10 minutes and then dried in the paper forming machine at a temperature of around 70 °C and constant pressure of 80 KPa. The desirable grammage of 60  $\text{g}\cdot\text{m}^{-2}$  was established.

The paper samples were made with a Rapid-Köethen apparatus, with drying temperature of  $90 \pm 2$  °C and pressure of 80 Kpa, according to the ISO 5269-2 (ISO, 1980) and Tappi T 205 sp-02 (Tappi, 2004a) standards. Each treatment was repeated five times, for a total of 30 nanostructured films and 5 papers.

The nanostructured films and papers were stored in an acclimatized room with temperature of  $23 \pm 2$  °C and relative humidity of  $50 \pm 2\%$  for further preparation of the sample and measurement of physical parameters (thickness, density, and absorption) and mechanical testing (tensile strength and burst resistance), as well as to determine the crystallinity index.

### 2.4. Electron microscopy

To visualize the structures and dimensions of the cellulose nanofibers, a Jeol JEM 1200EXII transmission electron microscope (600,000  $\times$ ) was used. The nanocellulosic suspensions were diluted in distilled water, which was then replaced by t-butyl alcohol (Iwamoto et al., 2008). The suspension diluted in alcohol was dripped on the surface of the mesh intended for observation under the microscope. The samples were left at room temperature for solvent evaporation and drying, forming nanocellulosic films.

Scanning electron microscopy (SEM) was used to visualize the dimensions of the tracheids before they were submitted to defibrillation. The papers were previously submitted to metallization and observed in an operating range of 0.5 – 30 k to obtain the SEM images.

### 2.5. Viscosity and crystallinity index

Two samples from each treatment were submitted to viscosity and crystallinity index tests. The viscosity

was determined in a cupriethylenediamine (CED) solution using a capillary viscometer according to the Tappi T 230 om-94 standard (Tappi, 1999a).

To determine the crystallinity structure of the cellulose in the papers and films, a Shimadzu XRD-7000 x-ray diffractometer was used along with the XRD-6100/7000 v. 5.0 software. The selected velocity for scanning was 1 °/min, varying between 3 ° and 45 °, using Cu-K $\alpha$  radiation with wavelength of 0.15418 nm and voltage of 40 kV with current of 20 mA. The crystallinity index was determined by the method suggested by Segal et al. (1959). Using the Origin Pro 8.5 software, the data received smoothing treatment by Fourier Transform with 15% of the points cut to obtain the crystalline and amorphous intensity peaks.

### 2.6. Physical and mechanical tests

For each physical test, five samples were evaluated per treatment. The thickness of the films, expressed in micrometers ( $\mu\text{m}$ ), was determined following the Tappi T 411 om-97 standard (Tappi, 2004b). The density of the films, expressed in  $\text{g}\cdot\text{cm}^{-3}$ , was calculated as the ratio between the weight and the thickness of the paper. The films presented moisture of 9%. Water absorbance was obtained through the Cobb method (expressed as  $\text{g}\cdot\text{m}^{-2}$ ), according to which the water mass absorbed by one square meter of film or paper in a determined interval of time (in this case, 60 seconds) is measured. This method was adapted from the Tappi T 441 om-98 standard (Tappi, 2004c).

The tensile test was performed using a horizontal digital dynamometer with distance between clamps adjusted to 100 mm and a test velocity of 10  $\text{mm}\cdot\text{min}^{-1}$ . The tensile strength was presented through tensile index, which corresponds to the ratio between the resistance and weight of the sample, expressed in  $\text{N}\cdot\text{m}\cdot\text{g}^{-1}$ . The burst index, calculated through the ratio between burst resistance and weight of a sample, is expressed in  $\text{KPam}^2\cdot\text{g}^{-1}$ .

To evaluate the effect of the number of passes through the grinder, density properties, water absorbance, tensile strength, and the burst resistance of nanostructured films, the values were submitted to variance analysis, compared through the Tukey's test at 5% probability. The Bartlett's test was previously performed to test homogeneity of variance.

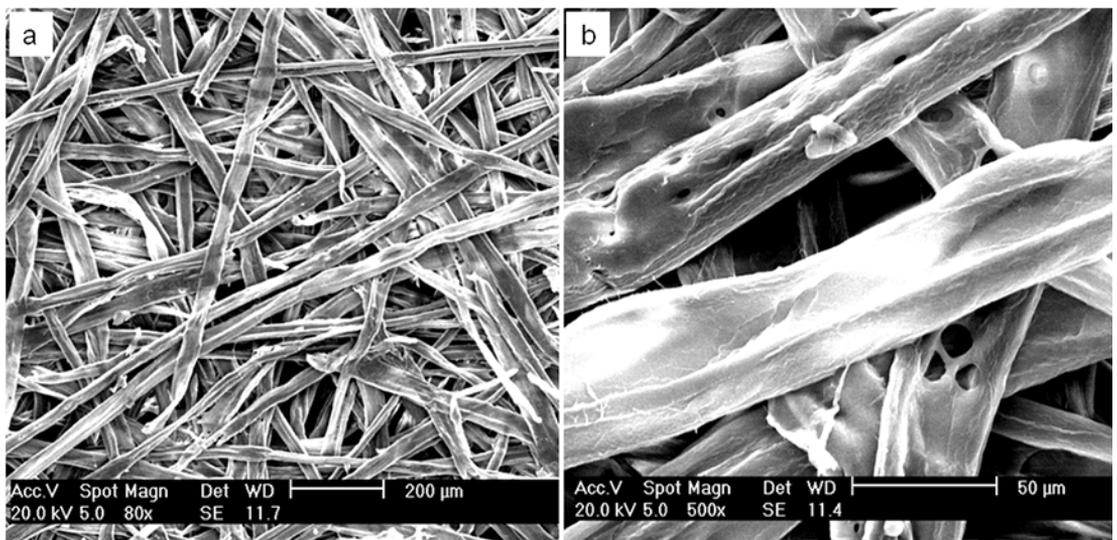
### 3. RESULTS AND DISCUSSION

#### 3.1. Electron microscopy

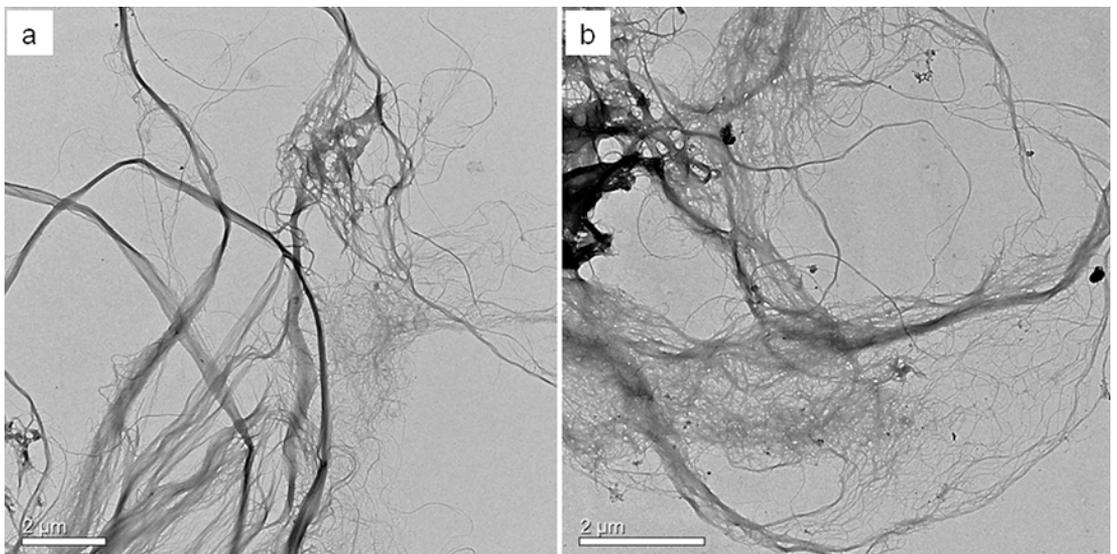
Figures 2a and 2b, obtained through SEM, present characteristics of the *Pinus*' tracheids before they were submitted to the defibrillation process.

The images acquired through TEM related to the fibers from the cellulosic pulp after mechanical defibrillation with two and 40 passes are presented in Figures 3a and

3b, respectively. It can be observed that the grinding process with two passes resulted in the fibrillation of the fiber's cell wall (tracheid) and in its reduction to nanofibers. Defibrillation promotes the exposure of surfaces previously situated in the interior of the fiber, the microfibrils, through the action of shear force. As a result, internal fibrillation occurs, which consists of the rupture of hydrogen bonds between the molecules of cellulose and hemicellulose inside the fiber, along with external fibrillation on the outside surface of the cellulose fibers.



**Figure 2.** SEM images of kraft pulp tracheids from *Pinus* before the mechanical defibrillation process a) at 80 × magnification; b) at 500 × magnification.



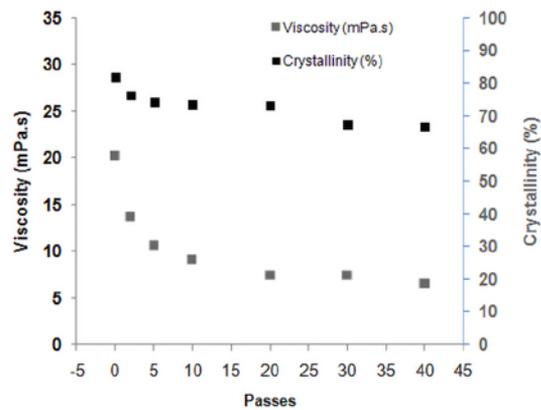
**Figure 3.** TEM images of cellulose nanofibers obtained with a) two passes; b) 40 passes.

The *Pinus* wood's tracheids, which present an average diameter of around 40  $\mu\text{m}$ , were completely defibrillated after the process, decreasing the fiber's width from dozens of micrometers to dozens of nanometers.

### 3.2. Viscosity and crystallinity index

To analyze the possible degradation experienced by the cellulose in the fiber, resulting from the mechanical process of defibrillation in the grinder, the viscosity and crystallinity of the papers and nanostructured films were measured after the different treatments. The results can be observed in Figure 4. Viscosity was used to indirectly evaluate the average degree of polymerization of the cellulose chains and detect cellulose degradation. A large decrease in viscosity can be observed in the T00 samples (20.13 mPa.s) in relation to the T02 treatment (13.72 mPa.s). The viscosity loss was significant, varying from 13.72 mPa.s for the nanocellulosic suspension obtained with two passes to 6.63 mPa.s for the nanofibers generated through 40 passes (Figure 4). The nanocellulosic suspension's viscosity decreased due to the increase in the number of passes through the grinder, suggesting higher carbohydrate depolymerization with the defibrillation process, as reported by other authors (Abe et al., 2009; Syverud et al., 2011).

The crystallinity index refers to the relative quantity of cellulose in the crystalline region (intercept), where the fiber presents higher resistance to tensile force, stretching, and solvation (Fengel & Wegener, 1984). According to the adopted method, the crystalline cellulose percentage is calculated by the difference between the highest intensity peak (crystalline peak) and the lowest peak (amorphous peak). The highest crystallinity index obtained in this study was 81.8%, for the treatment where the fibers were not submitted to mechanical processing (T00), and the lowest was 66.4%, corresponding to the treatment with the highest number of passes (T40). Based on these results, the crystallinity and viscosity indices also decreased with an increase in the number of passes through the grinder, indicating that the crystalline structure was slightly degraded through the mechanical defibrillation, which causes the nanofibrillation of fibers, but at the same time promotes the degradation of cellulose, as seen by the decrease in the crystallinity index values and polymerization as the number of passes increases (Iwamoto et al., 2008; Kalia et al., 2014).



**Figure 4.** Crystallinity and viscosity of the papers and nanostructured films according to the number of passes through the grinder.

### 3.3. Physical and mechanical tests

Table 1 presents the physical properties of the papers and films (thickness, density, and Cobb<sub>60</sub> absorption) in relation to the number of passes through the grinder. The average thickness of the papers when fibers without mechanical treatment (T00) were used was 167  $\mu\text{m}$ , while for the nanostructured films with different numbers of passes through the grinder the values varied from 56  $\mu\text{m}$  for the treatments with ten and 30 passes to 64  $\mu\text{m}$  for the treatment with two passes. The thickness of the films formed by nanofibers of cellulose presented the same tendency for all treatments, with threefold reduced thickness when compared to the papers with T00 treatment. The decrease in fibers' dimension after the defibrillation process in the grinder allowed a stronger connection and better arrangement of the nanofibers, allowing a more uniform and compact structure and decreasing the thickness of the films.

As a consequence of the reduced thickness, an increase in density can be observed in the same proportion for the nanostructured films. The density values varied from 0.33  $\text{g}\cdot\text{cm}^{-3}$  for T00 to 1.16  $\text{g}\cdot\text{cm}^{-3}$  for T30. The values found for the nanostructured films are close to those reported by other authors (Henriksson et al., 2008; Spence et al., 2010; Stelte & Sanadi, 2009). The density has a strong and positive influence on the mechanical properties of paper and films. At the same time, it depends on the fibers' dimension: the smaller the fibers, the better the adaptation, thus producing denser films.

The nanostructured films presented  $Cobb_{60}$  absorption values around three times smaller compared to those formed by fibers without mechanical treatment (T00) (Table 1). These papers presented the highest values, with average of 231.64  $g \cdot m^{-2}$ , and the group formed by treatments T02 and T05 presented the lowest values of water absorption, near 76.00  $g \cdot m^{-2}$ . According to Dufresne (2012), this behavior can be explained by the very compact structure and low porosity of nanostructured films, which decreases water penetration. The porosity, surface rugosity, moisture content, and hydrophobicity of the papers can influence the resistance to liquid penetration, as observed by Sjöström & Alén (1999).

The enlargement of the fibers' specific surface with the defibrillation process favors a higher number of interfiber bonds due to the increased availability of OH groups (Carrasco et al., 1996; González et al., 2012). A denser nanostructured films structure indicates an increase in the Schopper-Riegler degree. The Schopper-Riegler degree indicates the difficulty of water draining and expresses the resistance to drainage that has a layer of fibers. This increased retention can result in difficulties in draining water, causing operability problems during the formation of paper.

The mechanical property values of the nanostructured films can be observed in Table 2. The tensile strength (tensile index) showed an increase of approximately 300% with the presence of nanofibers in the films. The tensile index values varied from 26.24  $Nm \cdot g^{-1}$  for the T00 treatment to 114.60  $Nm \cdot g^{-1}$  for the T02 treatment.

The T02 treatment stood out with the highest resistance values. The burst index increased around ten times for

treatments T02, T05, and T10 in comparison with the treatment that did not go through the defibrillation process (T00). Treatments with two, five, and ten passes were statistically identical. Therefore, two passes through the grinder are enough to produce nanostructured films with higher tensile strength and burst resistance. From an economic standpoint, this is attractive because it requires less energy.

The significant increase in mechanical properties can be explained by the density increase, the denser network of hydrogen bonds created, and the bigger surface area produced by the defibrillation process (Spence et al., 2010).

Among the nanostructured films (Table 2), the treatment with 40 passes had the lowest mechanical resistance (Tensile Index = 66.56  $Nm \cdot g^{-1}$  and Burst Index = 3.33  $KPa \cdot m^2 \cdot g^{-1}$ ), coinciding with the lowest crystallinity and molecular weight of the cellulose. As can be seen in Figure 4, the viscosity of treatment T02 was 13.72 mPa.s, dropping to 6.63 mPa.s for treatment T40. The crystallinity index went from 76.1% (T02) to 66.4% (T40). With the sharp reduction of viscosity and the partial degradation of the cellulose chains, caused by increased intensity of the defibrillation, a decrease of the tensile and burst indices was also observed.

Despite the relationship between molecular weight and resistance properties of the cellulose fiber, these aspects should not be analyzed in isolation, since other factors also contribute to this, such as crystallinity, the fibers' anatomy, density and capacity of forming bonds, the films manufacturing process, and others. According to Gomide et al. (2005), higher viscosity is usually associated with better physical properties of

**Table 1.** Average values of thickness, density, and  $Cobb_{60}$  absorption properties of papers and nanostructured films.

Treatments <sup>a</sup>	Thickness ( $\mu m$ )		Density ( $g \cdot cm^{-3}$ )		$Cobb_{60}$ ( $g \cdot m^{-2}$ )	
	Average	SD <sup>b</sup>	Average	SD	Average	SD
T00	167	2.59	0.33 (c)	0.01	231.64 (a)	8.12
T02	64	1.40	1.03 (b)	0.09	75.66 (d)	3.54
T05	59	1.88	1.09 (ab)	0.03	75.86 (d)	1.67
T10	56	2.42	1.04 (b)	0.01	84.60 (bcd)	3.19
T20	57	1.31	1.13 (a)	0.03	85.70 (bc)	2.91
T30	56	1.78	1.16 (a)	0.05	76.99 (cd)	2.85
T40	63	0.73	1.15 (a)	0.02	87.64 (b)	6.08

<sup>a</sup>T: treatments, with the numbers after T relating to the number of passes through the grinder; <sup>b</sup>SD: standard deviation. Averages followed by the same lower-case letter are not different by the Tukey's test, with significance of 5%.

**Table 2.** Average values of tensile and burst indices of papers and nanostructured films.

Treatments <sup>a</sup>	Tensile Index (Nm.g <sup>-1</sup> )		Burst Index (KPam <sup>2</sup> .g <sup>-1</sup> )	
	Average	SD <sup>b</sup>	Average	SD
T00	26.24 (d)	0.82	0.85 (d)	0.06
T02	114.60 (a)	8.56	8.38 (a)	0.53
T05	75.38 (bc)	4.07	8.71 (a)	0.71
T10	72.32 (bc)	3.82	8.45 (a)	0.50
T20	80.23 (b)	10.50	4.76 (b)	0.18
T30	80.06 (b)	3.98	5.50 (b)	0.35
T40	66.56 (c)	1.21	3.33 (c)	0.25

<sup>a</sup>T: treatments, with the numbers after T relating to the number of passes through the grinder; <sup>b</sup>SD: standard deviation. Averages followed by the same lower-case letter are not different by the Tukey's test, with significance of 5%.

the pulp, but it does not necessarily guarantee papers with higher mechanical resistance.

Physical and mechanical properties depend on the degree of the bond between fibers, in which smaller and/or fibrillated fibers provide a larger specific area and more contact points, increasing the number of bonds. More bonds promote higher density, tensile strength, and burst resistance. However, extensive defibrillation can negatively affect the mechanical properties of the nanostructured films by shortening the fibers, decreasing the polymerization degree of the cellulose chains, and causing a loss of crystallinity (Iwamoto et al., 2008; Sixta, 2006).

#### 4. CONCLUSIONS

The results presented in this article allow the conclusion that the films constituted of nanofibers from mechanical defibrillation in a grinder display significant improvement in their physical and mechanical properties when compared to traditional papers (T00).

The average density value of the nanostructured films increased more than 200% in comparison with the papers formed by fibers that did not undergo mechanical treatment. Nanostructured films presented lower water absorption. Regarding mechanical properties, the presence of nanofibers in the films provided a 300% gain of tensile strength, and burst resistance was around ten times higher in the films when compared to the papers without mechanical processing.

The increase in the number of passes also causes a reduction of the crystallinity index and depolymerization of the cellulose. This reduction, from a certain number

of passes, can entail a significant reduction of the mechanical properties of the nanostructured films.

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