Effect of the hemicellulose in the properties of nanopaper

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Abstract

The foldable, low thermal expansion, and optically transparent are main properties of paper produced with cellulose nanofibers (nanopaper), being able to be used in the development of flexible circuit technologies. In this context, this work evaluates the importance of hemicellulose in the properties of nanofiber paper (NFP). The hemicellulose extraction from *Pinus* sp bleached cellulose pulp was performed with NaOH 17.5% for 1.5 h. Thereafter, the pulp was washed with 8.3% NaOH, then was add 10% acetic acid until neutralization, and washed with water. The nanofibrils were obtained by mechanical defibrillation in a Super Masscoloider Masuko Sangyo mill. The NFP with the grammage of 40 and 50 g/m² were produced by filtration and drying under pressure. The extraction process reduced 80% of xylose, 40% of mannose and 40% of galactose compared of the bleached cellulosic pulp. The NFPs with around 15% of hemicellulose are homogeneous and transparent, the interstices between the fibers, observed by scanning electron microscopy, are small enough to avoid light scattering, making the cellulosic material transparent. The NFP of 40 and 50 g/m² had a thickness of 45 µm, water absorption of 63 and 34 g/m², respectively. They did not present air permeability. NFP of 40 and 50 g/m² without hemicellulose had a thickness of 76 and 87 µm, water absorption of 128 g/m² and air permeability of 202 and 384 s/100 cm³, respectively. The spaces created by the coalescence of the cellulose nanofibrils after the extraction of the hemicellulose result in the dispersion of the light and consequently in the opacity of the NFP. Extraction of hemicellulose reduced the tensile and bursting strength by 80%. Therefore, hemicellulose acts as an inhibitor of the coalescence of microfibrils, providing adhesion and increase of the mechanical properties.

Keywords: nanofibers, bleached pulp, hemicellulose, tensile strength, air permeability.

Introduction

The term hemicellulose is used to denominate distinct groups of polysaccharides of branched chain and low molecular weight, constituted by sugars pentoses and / or hexoses, uronic acids and acetyl groups [1]. The hemicelluloses are deposited between the microfibrils by binding to cellulose through hydrogen bonds, acting as a binding agent between cellulose and lignin, forming a solid structure that composes the primary plant cell wall [2]. Alkaline solutions hydrolyze the ester bonds by releasing the hemicellulose in aqueous medium [3]. Hemicelluloses serve as inhibitors of the coalescence of microfibrils during drying, that is, the cellulose microfibrils are tightly bound through multiple hydrogen bonds filling the space between the microfibrils and acting as a physical barrier inhibiting nanofibers aggregation and facilitating the nanofibrillation. Furthermore, they provide adhesion to the nanofibers contributing to the reduction of the thermal expansion and increase of the mechanical properties [4,5].

Low thermal expansion and optical transparency are the main properties of the paper produced with cellulose nanofibers, which can be used in the development of flexible circuit technologies. In this context, this paper evaluates the influence of hemicellulose on the properties of nanofiber paper (NFP).

Experimental

Extraction of hemicellulose

For 60 g of cellulosic pulp were added 300 ml of sodium hydroxide (NaOH) 17.5%. A further 3 additions of 150 mL of NaOH were added every 5 minutes, leaving a pulp to stand for 30 min. Under stirring was added 990 mL of distilled water, letting it stand for 1 h. The mixture was filtered and washed with 3 L of 8.3% NaOH and hot distilled water. The material was immersed in 450 mL of 10% acetic acid for 3 min. Then washed with distilled water until pH neutral. It was then dried in a 60 ° C oven for 24 h.

Suspension of cellulose nanofibrils

The nanofibrillated cellulose was obtained from the bleached pulp cellulose pulp, which was dispersed in distilled water and homogenized in a laboratory blender. Then, this mixture, at a concentration of 3%, was inserted into the Super Masscoloider Masuko Sangyo mill, with rotation of 1500 rpm and 20 passes through the mill. The mill is composed of a rotating silicon carbide ceramic disc and a static ceramic disc with an adjustable aperture between the discs. Through the mechanical compression process and shearing forces when the pulp is forced through the opening between the discs the mechanical defibrillation process occurs.

Sugar content

The carbohydrate content of the cellulose nanofibrils suspensions were quantified by ion exchange chromatography. The separation was done on CarboPac PA 20 column (4 mm x 250 mm, 5 µL looping, flow rate 0.5 mL min-1 and temperature 30 °C). The quantification of sugars was performed by an external calibration curve. Sample preparation was performed by total acid hydrolysis (H_2SO_4 12M) of the previously dried nanocellulose suspensions in stoves at 60 °C.

Production of nanofiber papers

The NFP with the grammage of 40 and 50 g/m were produced by filtration with 22 µm aperture nylon membranes. The masses of the suspension required to obtain the NFP were diluted in distilled water to a concentration of 3×10^{-3} $g.mL^{-1}$, the mixtures were stirred for 1 min until complete homogenization. After they were filtered on 22 µm nylon membrane supported in 60 mesh sieves. The suspensions were pressed with glass plate to remove excess water, then the sieve assembly, material and glass plate were placed in an oven at 60 °C for 24 h drying.

Characterization of NFPs

The nanopapers were characterized by: Water absorption; Permeability of the passage of air; Traction test; Burst test. The tests were carried out in the Pulp and Paper Laboratory of the Federal University of Paraná in a controlled environment (temperature of 23 ± 2 ºC and relative humidity of 50 ± 2%).

Results and Discussion

Sugar content

The sugar content of the suspensions submitted to the acid hydrolysis (Table 1) showed a great reduction of the xylose and mannose content in the pulp that underwent the basic treatment, evidencing that the hemicellulose was extracted from the pulp.

Table 1 - Content of sugars in nanofibrils suspensions.

Suspension	Xylose (mg/g)	Mannose (mg/g)	Glucose (mg/g)	Galactose (mg/g)
With hemicellulose	74,5 ± 1,2 a	45 ± 1 a	(79 ±1).10 a	5,2 ± 0,2 a
Without hemicellulose	15,0 ± 0,8 b	26,8 ± 0,8 b	(89 ± 6).10 b	3,1 ± 0,3 b

Characterization of NFPs

The NFP with hemicellulose is homogeneous and translucent, as mentioned by other authors [6,7]. The difference with the common paper is in the width of the forming fibers and in the size of the interstitial cavities. If the cellulose nanofibrils are densely close and the interstices between the fibers are small enough to avoid scattering of light, the cellulosic material becomes translucent (Figure 1B) [8,9]. This is evidenced in Scanning Electron Microscopy (SEM) micrographs (Figure 2), which shows the surface of the uniform, non-porous and compact NFP without individual fibers.

After treatment of the cellulosic pulp for the extraction of the hemicellulose in basic medium, papers of cellulose nanofibrils were obtained. The obtained NFPs were visibly non-uniform and less resistant compared to the films obtained from the crude pulp. Micrographs of the NFP without hemicellulose (Figure 3) show the non-uniform and highly porous surface. The hemicellulose acts as inhibitor of the coalescence of the microfibrils, providing adhesion and increase of the mechanical properties [4,5].

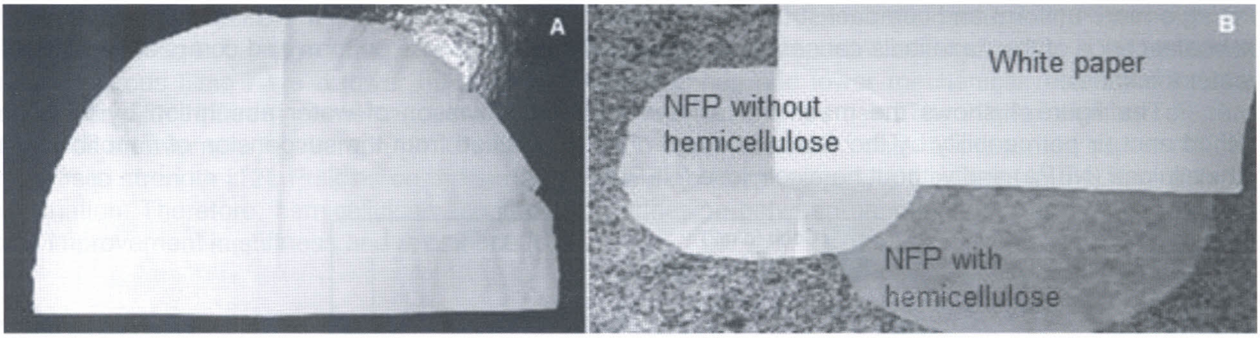

Figure 1 - A) NFP without hemicellulose B) NFP without hemicellulose, white paper, NFP with hemicellulose.

Therefore, the extraction of the hemicellulose from the cellulosic pulp caused the NFP to become non-uniform due to the coalescence of the nanofibrils. The space created by the coalescence of the cellulose nanofibrils after the extraction of the poliosis results in light scattering and consequently the film opacity (Figure 1A) [8].

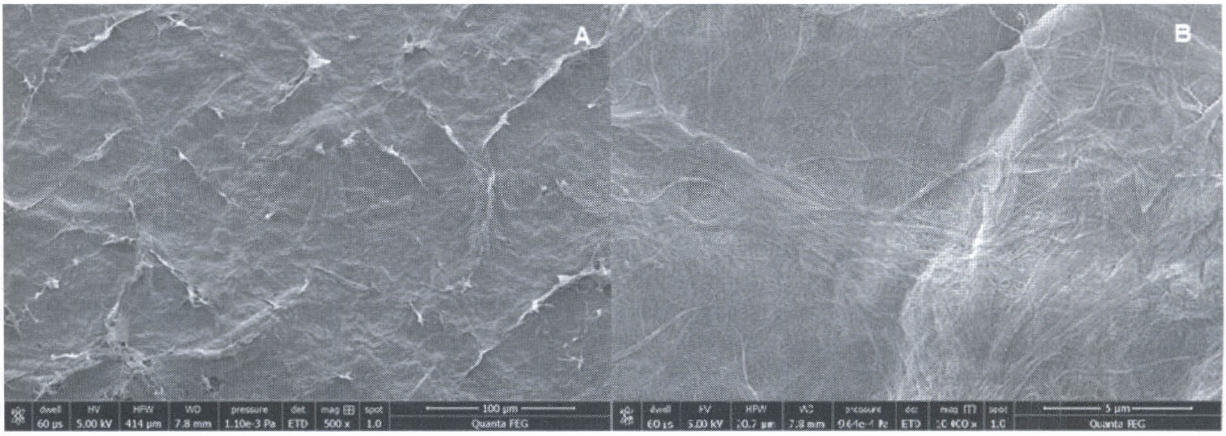

Figure 2 –Micrographs of the NFP with hemicellulose magnification A) 500X B) 10KX

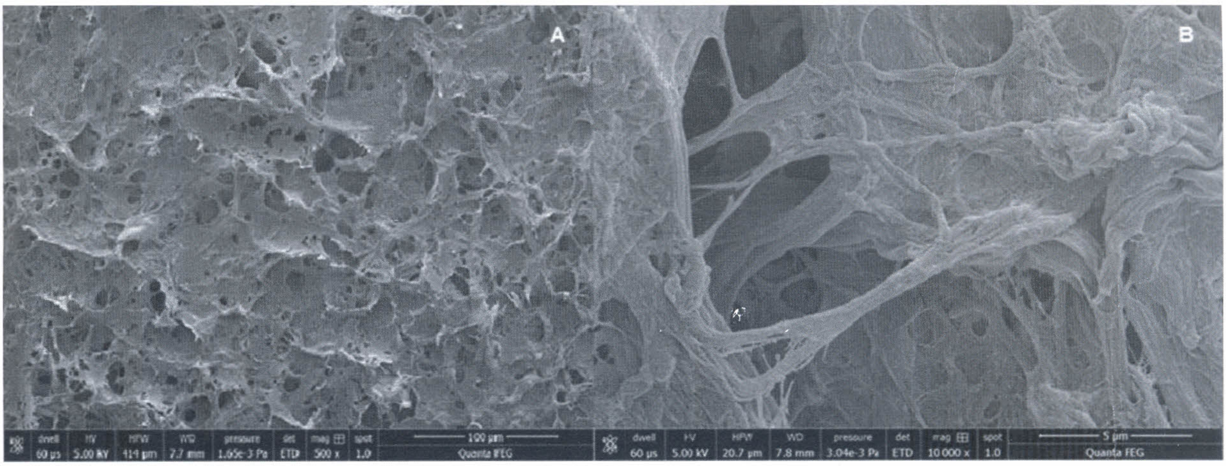

Figure 3 – Micrographs of the NFP without hemicellulose magnification A) 500X B) 10KX

The thickness of the papers formed by the nanofibrils with hemicellulose (45 µm) was considerably smaller than the papers without hemicellulose (76 to 87 µm). The presence of hemicellulose in the mechanical defibrillation process allowed a better bonding and better rearrangement of the nanofibrils, forming a more uniform and compact structure, reducing the thickness of the film. In films of the treated pulp the coalescence of the nanofibrils causes the surface of the film not to be uniform and compact presenting a greater thickness.

The figure 4 shows the mean values and standard deviation of water absorption by the Cobb method and air permeability by the Gurley method of NFP obtained from the suspension of nanofibrils with hemicellulose (NFPa) and without hemicellulose (NFPb).

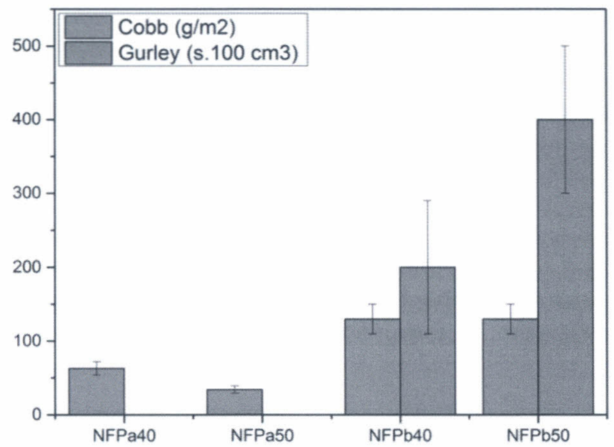

Figure 4 - Water absorption (Cobb) and air permeability (Gurley) of the NFP.

The water absorption determined by the Cobb method of the NFPa presented different values for the weights of 40 g / m^2 and 50 g / m^2. The compact and low porous structure reduces the penetration capacity of water [10]. A higher number of fibrils due to a larger weight, 50 g / m^2, produces more compact films, with lower porosity due to the greater contact area of the fibrils and greater interaction between them, which leads to a lower capacity of water penetration and lower absorption of water in relation to the lesser weight film of 40 g / m^2. The NFPb have high porosity which allows greater penetration and retention of the water and, consequently, greater water absorption determined by the Cobb method.

The NFPa exceeded the maximum time determined by Norm T460-om02 for the air permeability, therefore they were considered as non-permeable air passage. The compact, very dense and low porous morphology creates a resistance to air passage; however, the absence of hemicellulose generates large cavities in the morphology of NFPb that allow the passage of air after a certain time. Films of cellulose nanofibrils are known for their great barrier properties, acting as an excellent barrier to oxygen gas [11].

The NFPa presented statistically higher tensile strengths than the NFPb, in addition to the increase in the weight to generate greater tensile strength in these films. The NFBbs with weights of 40 and 50 g / m^2 showed similar tensile strength (Figure 5).

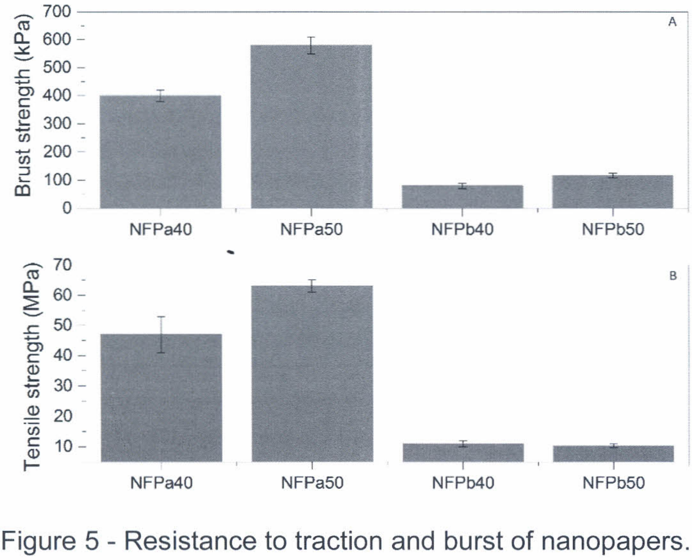

Figure 5 - Resistance to traction and burst of nanopapers.

The same occurs for resistance to bursting, the presence of hemicellulose in the NFPa results in a higher resistance to bursting compared to NFPb. The mechanical properties depend on the interfiber bonds, and the porous films have a lower number of interfiber bonds and lower mechanical resistance indexes. nanopaper with different porosities have different mechanical properties. The higher number of pores generates a lower tensile strength [9]. Sheets with higher hemicellulose contents presented higher stiffness and tensile strength [12]. Poliosis on the surface of the pulp fibers adhere to the fibers in the film, inhibiting deformation. Therefore, hemicelluloses contribute to adhesion between nanofibrils in the dry state, leading to an improvement in stiffness and resistance [5].

Conclusions

The hemicellulose has great importance in the characteristics of the NFP, its removal causes loss of translucency as well as drastic reduction of the mechanical properties. Therefore, hemicellulose acts as an inhibitor of the coalescence of microfibrils, providing adhesion and improvement of the mechanical properties.

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Acknowledgements

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