NANOFIBRILLATED CELLULOSE AS PAPER ADDITIVE IN EUCALYPTUS PULPS

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In this work, the physical and mechanical properties of bleached *Eucalyptus* pulp reinforced with nanofibrillated cellulose (NFC) are compared with those of traditional beaten pulp used in the making of writing/printing and offset printing papers. For this purpose, three different types of hardwood slurries were prepared: beaten pulps, unbeaten pulps reinforced with NFC, and slightly beaten pulps also reinforced with NFC. Physical and mechanical tests were performed on handsheets from these different slurries. The results showed that adding NFC to unbeaten pulps results in physical and mechanical properties similar to those in pulps used for printing/writing papers. Nevertheless, the best results were obtained in slurries previously beaten at slight conditions and subsequently reinforced with NFC. These results demonstrate that the addition of NFC allows a reduction in beating intensity without decreasing the desired mechanical properties for this specific purpose.

Keywords: Bleached Eucalyptus pulp; Nano- or microfibrillated cellulose; Beating; Physical and mechanical properties

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INTRODUCTION

Traditionally, printing/writing papers have been produced from bleached virgin pulp with about 16% mineral fillers. Hurter (2002) reports that paper for this purpose usually presents tensile index between 40 and 45 Nm/g, which corresponds to a breaking length of 4000 to 4500 m, though he does not specify whether or not these properties belong to paper filled with minerals. The fabrication process of paper is comprised of pulp beating as the main step. During beating, fibers are usually beaten by one or more passes between the rotor and stator of a typical beater (Hubbe *et al.* 2007). The outer layers of fibers are defibrillated, with some of them passing to a fibrous suspension in the form of fines. Defibrillating allows the swelling of fibers by hydration (Carrasco *et al.* 1996). In addition, beating also decreases the fiber’s length due to the cutting effect and superficial fibrillation. Beaten fibers exhibit more flexibility. Furthermore, the bonding ability between fibers is enhanced in the last stages of drainage when the distance between them becomes short enough to improve the paper sheet cohesion.

The basic structure of wood fibers is composed of a primary cell wall and secondary wall layers (S1, S2, S3), with lignin-filled intercellular spaces called middle lamella. Lignin acts as a cementing agent among cell walls (Côté 1967). The cell wall layers are composed of cellulose fibrils with diameters between 2 and 4 nm (Fengel and Weneger 1984). Fibrils are arranged into larger fibrillar structures called macrofibrils with diameters ranging from 8 to 60 nm (Daniel 2003). The orientation of macrofibrils within wall layers determines many of the mechanical properties in wood fibers (Molin and Daniel 2004). Thus, the S1 layer presents a disorganized network of macrofibrillar cellulose, while the S2 layer is the thickest layer and shows a more ordered structure of cellulose macrofibrils aligned parallel with respect to the fiber axis. This structure differs from the S1 and S3 layers, where fibrils are highly angled in relation to the fiber axis. Since the kraft process and beating aim to expose the outer layers of pulp fibers, orientation of fibrils is an important feature (Molin and Daniel 2004).

Bleached pulps require less beating than unbleached pulps when treated in a PFI mill. Unbleached pulps retain part of their primary and S1 layers after beating (Giertz 1958; Kibblewhite 1972). The S2 layer of kraft pulps shows significant damage after extensive PFI beating (Kibblewhite 1972). The effect of beating on the external layers of fibers has been extensively investigated by several authors. Light and scanning electron microscopy micrographs of beaten pulps show loosened parts of the fiber wall, but the wall is not completely removed (Teder 1964; Szwarcsztajn and Przybysz 1972; Kibblewhite 1972; Molin and Lennholm 2000). The increase in beating time or shear rate means also an increase in the amount of fines (Kibblewhite 1972; Page 1985), though such treatment may also lead to excessive shortening of fibers.

The term nano- or microfibrillated cellulose (NFC or MFC, respectively) is applied to those fibrils or cellulose aggregates that have a diameter between 5 and 60 nm and are several micrometers in length. NFC is typically obtained by delamination of wood fibers by mechanical pressure. This process is normally preceded by chemical or enzymatic treatment of fiber slurries (Klemm *et al.* 2011; Henriksson *et al.* 2007). NFC can be produced by high-pressure homogenization of a fiber suspension. This methodology consists of pumping a pretreated 1 to 2 wt% aqueous fiber suspension through a high-pressure homogenizer, where fibers are forced to collide against a valve and an impact ring (Nakagaito and Yano 2004). The shearing forces and drop in pressure delaminate the fiber, liberating the microfibrils from the cell wall layers. After several passes through the homogenizer, NFC presents gel-like characteristics when suspended in water in concentrations of about 1 wt%. In order to obtain a gel-like suspension, several passes are required (Besbes *et al.* 2011). Microfibrillation can be eased by TEMPO-mediated oxidation (Saito and Isogai 2004). This methodology has recently been widely used to facilitate the mechanical treatment of cellulose fibers (Besbes *et al.* 2011).

NFC has previously been used in the fabrication of films that proved to be stronger than paper (Taniguchi and Okamura 1998). Moreover, cellulose nanopaper has been fabricated by dewatering vacuum filtration (Henriksson *et al.* 2008). As a reinforcing element, NFC has several advantages, such as a fine diameter, large aspect ratio, biocompatibility, the possibility of functionalization, and high strength and modulus (Berglund 2005). These properties make NFC an attractive material to be used as an additive in paper to improve mechanical properties such as burst, tearing, and tensile stress. The benefits of using NFC as reinforcement in paper have been explored only recently, but there are signs of improvement in permeability and tensile index Eriksen *et al.* 2008; Mörseburg and Chinga-Carrasco 2009; Taipale *et al.* 2010; Zhang *et al.* 2012). The improvement in mechanical properties of paper after the addition of NFC can be compared with the properties of paper made from both unbeaten and slightly beaten pulps.

The aim of this work was to investigate the mechanical and physical properties of NFC-reinforced pulp and compare them to the traditional beaten pulps used in the fabrication of printing/writing paper and offset writing paper. Firstly, the properties of pulps beaten in PFI mill were compared to those of pulps beaten in industrial PFI systems and, afterwards, the incorporation of NFC in PFI-beaten pulps at different refining levels was evaluated. For this, in the present study paper from a *Eucalyptus* suspension beaten in a PFI mill, paper from an unbeaten suspension reinforced with different amounts of NFC, and paper from a mildly beaten suspension reinforced with NFC were prepared, and their physical and mechanical properties analyzed.

EXPERIMENTAL

Materials

For the preparation of NFC, commercial bleached hardwood *Eucalyptus* pulp from La Montañanesa (Grupo Torraspapel, Zaragoza, Spain) was used as starting material. The pulp was used in its dry form. For the oxidation process prior to defibrillation, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), sodium bromide (NaBr), sodium hypochlorite solution (NaClO), and sodium chlorite ($NaClO_2$) were acquired from Sigma-Aldrich and used as received without further purification.

For the preparation of paper sheets, bleached *Eucalyptus* pulp in its dry form was used as received. Cationic starch and silica colloidal (Vishtal *et al.* 2011), used as retention agents, were kindly given by Torraspapel S. A. (Sarrià de Ter, Girona, Spain).

Preparation of Nanofibrillated Cellulose (NFC)

Eucalyptus pulp was subjected to TEMPO-mediated oxidation. The process was carried out under neutral pH conditions, according to the methodology reported by Besbes *et al.* (2011). Five grams of cellulose fibers were suspended in 0.05 M sodium phosphate buffer solution (500 mL, pH 7) that contained TEMPO (25 mg) and NaBr (250 mg). Sodium chlorite solution (1.13 g, 10 mM) and sodium hypochlorite solution (1.13 g, 10 mM) were added to the slurry. Next, the mixture was stirred at 500 rpm and 60 ºC for 2 hours. Oxidation was stopped by adding 100 mL of ethanol.

The resulting oxidized fibers were filtered and washed two times. Finally, the fiber suspension was cooled at room temperature before being washed with water and filtrated.

The fibrillation process was performed by passing a 1 to 2 wt% fiber suspension through a high-pressure homogenizer (NS1001L PANDA 2K-GEA). Operation conditions were 600 bar pressure and 60 to 70 ºC. The process was repeated 5 to 6 times, such that a transparent gel-like product was obtained. From previous works (Besbes *et al.* 2011), the diameter of the produced NFC was between 30 to 40 nm. The suspension of NFC was submitted to 180,000 revolutions in a disintegrator (ISO 5263) every time before its use, to promote NFC dispersion.

Preparation of Paper Handsheets for Mechanical Testing

Dried, bleached *Eucalyptus* pulp was used as the primary raw material. The Kappa number found was 0.6, the viscosity presented average values of 855.2 cm^3/g, and the brightness was 91.1%.

The pulp was disintegrated in water with a disintegrator at 180,000 revolutions. After that, the suspension was filtered to eliminate excess water. Fiber slurry at 10 wt% was then prepared and beaten in a PFI mill (NPFI 02 Metrotec S.A.) at 1000, 1250, 2500, and 3750 revolutions. The beaten slurry was then dispersed in water and stirred. While stirring, silica colloidal and cationic starch were added as retention agents in amounts of 0.8 and 0.5 wt%, respectively. Stirring continued for 30 minutes at 500 rpm in order to assure good dispersion of all the substances.

In the case of NFC-reinforced paper, NFC was added to the slurry during the disintegration process. The amount of NFC was calculated to obtain 3%, 6%, and 9 wt% NFC-reinforced paper sheets. The handsheets for mechanical testing were prepared in a sheet formator (ISP mod. 786 FH). Handsheets were made according to ISO 5269-2 and conditioned in a weather chamber at 25 ºC and 50% humidity for 48 hours before mechanical testing.

Physical Characterization

Schopper-Riegler freeness and Canadian Standard Freeness

Rate of drainage (ºSR) was determined in a Schopper-Riegler Tester (mod. 95587 PTI) following ISO 5267/1 standard. Canadian Standard Freeness (CSF) was calculated from a freeness conversion table.

Water retention value

This parameter measures the amount of water chemically bonded to cellulose. First, 100 mL of pulp was vacuum filtered and divided into four equal portions, which were then centrifuged at 4000 rpm for 15 minutes to eliminate non-bonded water. Once centrifuged, the four pulp portions were dried at 105±2 ºC for 12 hours in containers of previously measured weight. The average water retention value was then calculated from the difference between the humid and dried weights of the four portions.

Specific surface (σ) and specific volume (α)

These two parameters were determined by the measurement of the permeability coefficient of a pad of fibers as a function of the pad concentration (Pulmac apparatus) and the application of the Kozeny-Carman equation, adapted to the case of pulp fibers swollen in water (Robertson and Mason 1949; Cowan 1970; Rouger and Mutjé 1984),

$$\left(B_o C^2\right)^{1/3} = \left(\frac{1}{5.5\sigma^2}\right)^{1/3}(1 - \alpha C) \tag{1}$$

where $B_o = [Q\eta L / (\Delta pA)]$ is the permeability coefficient (cm^2), Q is the volume rate of flow through the pad (cm^3/s^{-1}), Δp is the pressure drop across the pad (atm), A is the pad cross section area (cm^2), L is the pad depth (cm), η is the viscosity of water (cp), C is the solid concentration of the pad (g/cm^{-3}), σ is the specific surface area (cm^2/g^{-1}), and α is the hydrodynamic specific volume (cm^3/g^{-1}).

Morphological Characterization

Fiber morphology

Fiber morphology of the pulp, as well as the fines content was determined using a MorFI Compact analyzer (TechPap) controlled with a computer. The equipment analyses 1000 mL of 1 wt% fiber suspension by analysing images taken from the aqueous fiber suspension with a CCD video camera. About 10,000 fibers were analysed by the software MorFi v8.2.

Scanning electron microscopy

SEM photography was obtained with a ZEISS DSM 960A, controlled from a computer workstation. Samples were previously prepared by coating the samples' surfaces with gold by sputtering.

Mechanical Characterization

Testing specimens for mechanical characterization were conditioned according to ISO standard 187. The results were obtained from the average of 10 tested samples.

Tensile index

Testing experiments were performed in a Hounsfield 42 universal testing machine equipped with 2.5 kN load cell. Testing was performed according to ISO standards 1924-1 and 1924-2. The gap between clamping jaws was set to 150 mm and cross head speed was set to 10 mm/min. Preload was set at 2 N. Testing specimens were cut into paper strips 15 mm in width and 210 mm in length.

Burst index

Burst index was determined in a Burst Tester (mod. EM-50 IDM) and testing experiments were performed according to ISO 2758. Testing specimens were cut into 100 x 100 mm pieces.

Scott bond

Testing samples were cut to paper strips with dimensions of 25.4 x 200 mm. Scott bond specimens were tested in an internal bond tester (mod. IBT 10A IDM). Testing conditions were set according to TAPPI test method T569.

Tear index

Tear index refers to the tearing strength in relation to the basis weight. Tear index testing was performed in an Elmendorf Tearing Tester (mod. F53.98401 Frank PTI); testing conditions were according to ISO 1974. Testing samples were cut into 63 x 76 mm pieces.

Opacity

Opacity is defined as the ability of light to pass through a paper sheet. It was determined in a Technibrite ERIC950 brightness tester (mod. TB-1C/IR Technidyne Corporation) in accordance with TAPPI standard 425M-60.

Porosity

Porosity was obtained with a Gurley Porosimeter (Papelquímia). Testing was performed according to ISO 5636/5. Paper samples, measuring 50 x 100 mm, were cut and marked on both sides for easy identification. All results were obtained from the average of at least 10 tested samples.

RESULTS AND DISCUSSION

Effect of PFI beating on *Eucalyptus* pulp

The physical and morphological properties of slurry prepared from bleached *Eucalyptus* pulp beaten by means of PFI mill at different revolutions are summarized in Table 1.

Table 1. Physical and Morphological Properties of Slurries from Bleached *Eucalyptus* Pulp under Different Beating Revolutions

Rev.	ºSR	CSF (mL)	WRV (%)	σ (m^2/g)	α (g/cm^3)	l_w (μm)*	d^F (μm)	f** (%)
0	16	696	65.4	1.05	2.2	811	15.9	11.1
1250	23	549	104.6	2.2	2.9	798	16.8	11.3
2500	31	414	118.2	3.05	3.55	774	16.9	12.2
3750	43	267	141	4.8	3.5	744	17.8	12.7

* Mean weighted in length
** Percentage in length
Abbreviations: Revolutions (Rev.), Schopper-Riegler (ºSR), Canadian Standard Freeness (CSF), water retention volume (WRV), specific surface (σ), specific volume (α), fiber length (l_w), fiber diameter (d^F), fines (f)

Schopper-Riegler and Canadian Standard Freeness (ºSR and CSF, respectively) are two tests that measure the amount of water that is drained from a fiber suspension poured on a fine screen. Drainability is related to the fiber surface conditions and fiber swelling, so it can be used to determine the extent of beating in a pulp. Table 1 shows how the evolution of ºSR and CSF was progressive with the degree of beating. The highest increases of these two parameters were observed in suspensions beaten at 3750 revolutions. The water retention value (WRV) indicates the fiber's ability to uptake water and swell. Similar to ºSR and CSF, WRV is related to the fiber's bonding ability and increases gradually with the extent of beating. The result is an important enhancement in the capability of creating hydrogen bonds between fibers. However, high ºSR results in drainage difficulties in the slurry, which leads to runnability problems during paper formation (Norell *et al.* 1999; Hubbe and Heitmann 2007).

Specific surface and volume values increased gradually with the beating intensity. On the other hand, fiber length decreased slightly (9%), whereas diameter increased 11.9%. The increase in σ and α results in greater availability of –OH groups, which leads to a higher water retention value. Consequently, ºSR and CSF are closely related to the increase in specific surface and volume (Carrasco *et al.* 1996; Taipale *et al.* 2010).

Fines formation was low and showed a linear evolution along with the beating degree. PFI laboratory beating causes less damage to the fibers in contrast to industrial beating, which usually produces higher amounts of fines.

Microphotographs (Fig. 1) of unbeaten and beaten bleached *Eucalyptus* fibers show the general appearance of fibers before and after beating.

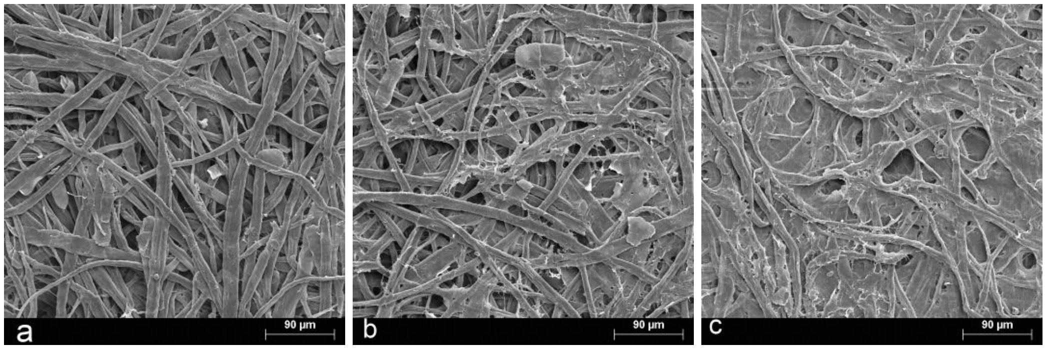

Fig. 1. SEM of bleached *Eucalyptus* fibers at different revolutions: a) unbeaten fiber, b) fibers beaten at 1000 revolutions, and c) fibers beaten at 3750 revolutions. Magnification 200x.

Fibers from unbeaten slurry (Fig. 1a) show a smooth and well-preserved surface without any appreciable damage or external fibrillation. Numerous empty spaces between fibers can also be observed. Beaten slurries (Fig. 1b) present fibril formation on the fiber surface. These fibrils increase the surface area, allow better interaction between fibers, increase hydrogen bonding, and fill the empty spaces of the paper sheet. These features become more evident as the intensity of beating is gradually increased (Fig. 1c).

Table 2. Physical and Mechanical Properties of Handsheets from Bleached *Eucalyptus* Pulp Beaten at Different Revolutions

Rev.	ºSR	CSF (mL)	T. I. (Nm/g)	B. I. (KPam^2/g)	S. B. (J/m^2)	Tear Index (100*gf*m^2/g)	Opacity (%)	G. P. (s)
0	16	675	25.7	1.25	72.6	38.6	84.4	2
1000	22	568	41.3	2.65	301	63.9	81.6	23
1250	23	525	47.6	3.2	357.9	68.4	80.5	25
2500	31	425	64.5	4.25	729.8	65.3	76.5	67
3750	43	275	85.5	4.65	1095.3	50.1	72.5	204

Abbreviations: Revolutions (Rev.), Schopper-Riegler (ºSR), Canadian Standard Freeness (CSF), tensile index (T. I.), burst index (B. I.), Scott bond (S. B.), and Gurley porosity (G. P.)

In Table 2, mechanical and physical properties of unbeaten and beaten slurries are presented. A direct consequence of the extent of beating is the enhancement of the mechanical properties of slurries. One of the aims of the present work was to determine the effect of PFI beating on the properties of *Eucalyptus* pulps and compare it with the industrial beating applied for the production of printing/writing papers. From the results, it is observed that physical and mechanical properties for writing/printing paper and offset paper are achieved with PFI beating at 1250 revolutions. The analysis of the individual properties is given below.

Tensile index is a useful mechanical parameter of pulp, which describes the tensile strength in relation to the amount of material being loaded. It mainly depends on the degree of fiber bonding and it is usually studied to determine the capability of bonding between fibers. Tensile index was enhanced 1.85, 2.5, and 3.3 times, at 1250, 2500, and 3750 revolutions, respectively, compared to the unbeaten slurry. In this study, tensile index's increasing tendency was a linear function of ºSR/CSF and revolutions applied.

Burst strength index measures the maximum perpendicular pressure that paper is able to resist before rupture. The ratio of the burst strength to the amount of tested material is known as the burst index. In beaten slurries, burst index showed increases of 156% at 1250 revolutions when compared to unbeaten pulp, whereas the increase was of 240 and 272%, respectively, at 2500 and 3750 revolutions.

Paper internal cohesion (Scott bond or Z-directional strength) is the ability of paper to resist tensile loading perpendicular to the plane of the testing specimen. After exceeding the Z-directional strength of a testing sample, a rupture in the structure takes place without affecting the surface. As in tensile and burst index, Scott bond is closely related to the fiber bonding. Samples beaten at 1250 revolutions showed increases of 393%, rising to 905% and 1409% at 2500 and 3750 revolutions, respectively.

Tear index refers to the tearing strength in relation to the basis weight. It is a function of the fiber orientation, fiber strength, fiber length, and bonding degree between fibers. In contrast to the other mechanical properties mentioned previously, tear index showed its maximum increase at 1250 revolutions. It is known that in pulps with a low degree of bonding (as in unbeaten slurries), tearing index increases when bonding between fibers improves. However, when the bonding degree is already high (as in beaten slurries), tear index is determined by the fiber strength. Therefore, the tear index will show a maximum at a certain beating degree without any further improvement (Levlin 1998).

The extent of beating also reflects on the paper's opacity. Good opacity is important in printing papers in order to prevent printed images or text from being seen from the reverse side of the sheet. Opacity is a function of paper thickness, the amount of filler, the bleaching degree, and the beating degree. Beating makes paper denser, but excessive beating results in lower opacity. This is clearly seen in Table 2 where the lowest opacity values were at 3750 PFI revolutions.

Porosity is indicative of the absorption capacity of paper and its ability to adsorb ink during printing. Similar to opacity, porosity is an indirect indicator of the slurry's beating degree. Intense beating decreases porosity, making it more difficult for air to pass through paper, requiring longer periods of time to do the Gurley porosity test. At 3750 revolutions, porosity is higher, whereas the unbeaten slurry shows little resistance to air passing.

Incorporation of NFC in *Eucalyptus* pulp

In order to evaluate the influence of NFC in *Eucalyptus* pulp, NFC was introduced into unbeaten *Eucalyptus* pulp. The experiments were intended to determine the viability of using NFC as a substitute of the PFI beating process.

For this reason, different amounts of NFC were incorporated in unbeaten *Eucalyptus* pulp. In Table 3, the physical and mechanical properties of slurries reinforced with different percentages of NFC are summarized.

One of the main characteristics of NFC is its high specific surface. The NFC used for this work had diameters between 30 and 40 nm with a calculated specific surface of 76 m^2/g. The ºSR exhibited a gradual increase corresponding to the amount of NFC added. The slurry reinforced with 3 and 6 wt% NFC presented ºSR values of 29 and 45 respectively.

Table 3. Physical and Mechanical Properties of Handsheets from Bleached *Eucalyptus* Pulp and Reinforced with NFC

NFC (wt%)	ºSR	CSF (mL)	T. I. (Nm/g)	B. I. (KPam^2/g)	S. B. (J/m^2)	Tear Index (100*gf*m^2/g)	Opacity (%)	G. P. (s)
0	18	651	25.7	1.25	72.6	37.9	83.9	2
3	29	445	31.9	2.2	216.2	46.6	85.7	7.5
6	45	248	42.8	2.9	343.4	58.3	83.4	28.4
9	54	178	51.3	3.4	469	68.3	84.6	52

Abbreviations: Nanofibrillated cellulose content (NFC), Schopper-Riegler (ºSR), Canadian Standard Freeness (CSF), tensile index (T. I.), burst index (B. I.), Scott bond (S. B.), and Gurley porosity (G. P.)

Hurter (2002) reported that industrial printing/writing papers show breaking lengths of 4120 m. At laboratory level (PFI mill), this value was observed in pulps with ºSR of 36. It is also worth mentioning that the industrial value of ºSR used was 33. However, further addition of NFC led to a poorer drainage rate than beating did. Thus, the slurry reinforced with 9 wt% NFC experienced a ºSR increase of 200% compared to the non-reinforced suspension, while the slurry beaten at 3750 revolutions presented increases of 168.75%. From these results, it can be stated that high amounts of NFC can lead to higher ºSR/CSF values than beating does.

Mechanical properties of pulp clearly improved after the addition of NFC, and this improvement rose progressively with the percentage of NFC. Tensile index was enhanced by 24.5% with 3 wt% NFC, reaching 67% and 100% for slurries reinforced with 6 and 9 wt% NFC, respectively. Results obtained at 9 wt% were superior to those of *Eucalyptus* pulp beaten at 1250 revolutions, but did not come close to values observed in slurry beaten at 2500 or 3750 revolutions.

The presence of NFC in the slurry enhanced the interaction of cellulose fibers by filling the empty spaces between fibers during the paper sheet formation, helping to create a better bonding area and leading to mechanical properties similar to those obtained after beating. This effect can be observed through SEM microphotography shown in Fig. 2.

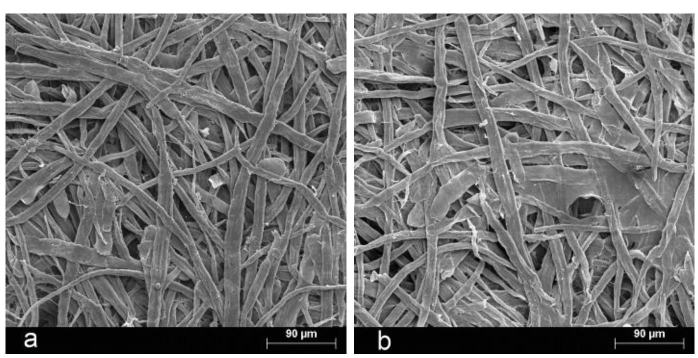

Fig. 2. SEM microphotographs of: a) paper without reinforcement and b) reinforced with 6% NFC. Magnification 200x

It is possible to observe the difference between unbeaten slurry (Fig. 2a) and slurry reinforced with 6 wt% NFC (Fig 2b). The presence of NFC produced a similar visual effect to PFI beaten slurries. Samples reinforced with 6 wt% NFC show fibrils entangled among the fibers, filling up some of the empty spaces in the paper. In this case, NFC acted as filler in a similar way as fibrils made by beating.

Burst index exhibited a similar tendency to tensile index. The best improvements were observed in slurries with 9 wt% NFC (2.72 times in comparison to non-reinforced slurry). Nevertheless, this improvement was still less than the values obtained for slurry beaten at 2500 revolutions. The Scott bonding was also enhanced compared to the unbeaten slurry, but this improvement was less than the results seen in beaten suspensions. Slurry reinforced with 9 wt% NFC exhibited an internal cohesion about 6.5 times higher than suspension without any reinforcement. In contrast, this parameter was 10 times higher in the slurry beaten at 2500 revolutions.

However, tear index presented results very similar to those of the slurry beaten at 2500 revolutions. Suspensions reinforced with 9 wt% NFC exhibited increases of 80%, similar to the growth seen in slurries beaten between 1250 and 2500 revolutions. In this case, the tear index did not show a maximum value, as it was observed in beaten slurry. Further addition of NFC should be carried out in order to determine whether a maximum value can be achieved or not.

An important feature observed in the experiments was the evolution of porosity in NFC-reinforced suspensions. If the beaten slurries (Table 2) are compared with the NFC-reinforced ones (Table 3), it is observed that the intense beating produced a less porous and compact paper, in contrast with what the addition of NFC does. Results obtained in samples with 9 wt% NFC presented lower values of air passing times (Gurley porosity) those achieved with beating at 2500 and 3750 revolutions. Interestingly, the opacity remained almost constant during the addition of NFC, because the fiber was not damaged. The obtained results demonstrated that mechanical properties of unbeaten slurry can be improved with the addition of NFC; however, the improvements observed by adding 9 wt% NFC were still not as good as properties of pulp beaten at 2500 and 3750 revolutions. Moreover, the addition of 9 wt% NFC produces a strong increase in ºSR, which is not desirable, since poor levels of drainage lead to runnability problems (Vishtal *et al.* 2011).

Therefore, a third group of experiments were carried out by introducing NFC in slightly beaten *Eucalyptus* pulp. In this case, *Eucalyptus* pulp beaten at 1000 revolutions was chosen, and it was reinforced with 6 wt% of NFC at maximum. On the one hand, the use of mildly-beaten pulps aims to decrease the intensity of beating in papermaking. On the other hand, the NFC reinforcement up to 6 wt% at max will avoid the drainage problems observed at higher amounts of NFC.

The physical and mechanical properties of handsheets produced with slightly beaten *Eucalyptus* pulp and reinforced with NFC are summarized in Table 4.

Table 4. Physical and Mechanical Properties of Handsheets from Bleached *Eucalyptus* Pulp Beaten at 1000 Revolutions and Reinforced with NFC

NFC (wt%)	ºSR	CSF (mL)	T. I. (Nm/g)	B. I. (KPam^2/g)	S. B. (J/m^2)	Tear Index (100*gf*m^2/g)	Opacity (%)	G. P. (s)
0	27	475	41.3	2.65	301	63.9	81.6	23
3	34	375	50.9	3.75	675.1	64.2	81.8	43
6	48	225	60.2	4.85	976.8	65.5	81.5	63

Abbreviations: Nanofibrillated cellulose content (NFC), Schopper-Riegler (ºSR), Canadian Standard Freeness (CSF), tensile index (T. I.), burst index (B. I.), Scott bond (S. B.), and Gurley porosity (G. P.)

The ºSR values from pulp for writing/printing paper are around 30 to 32 ºSR, which corresponds to the values between those of non-reinforced beaten slurry and 3% NFC-reinforced beaten slurry. Further addition of NFC created high ºSR values.

As expected, the mechanical properties exhibited important enhancements. Tensile index increased about 45% after the addition of 6 wt% NFC. Comparing these results with those obtained from unbeaten slurry reinforced with NFC, it is clear that the combination of slight beating and NFC yielded better results than the exclusive addition of NFC, even compared to the maximum amount of NFC added for this study. Beaten slurry with 6 wt% NFC presented tensile index values very close to those observed in suspension beaten at 2500 revolutions.

Samples with 6 wt% NFC exhibited burst indices slightly higher than slurries beaten at 2500 revolutions and suspension reinforced with 9 wt% NFC. The improvement was about 83% for the 6 wt% NFC formulation. The internal cohesion, or Scott bond, showed very similar behavior to tensile and burst index; the highest value was found in pulp reinforced with 6 wt% NFC. This result was much better than that observed in unbeaten pulp reinforced with 9 wt% NFC, but still slightly behind suspension beaten at 2500 revolutions.

Tear index presented little variation from one sample to another with no decreasing tendency after reaching a maximum, similar to what happened in beaten pulps, though such a maximum may be achieved if more NFC is added to the pulp. Porosity also exhibited similar values to samples beaten at 2500 revolutions and reinforced with 9 wt% NFC.

The overall results showed that the addition of NFC to slurry beaten at 1000 PFI revolutions can produce modifications in physical and mechanical properties very similar to those shown by pulp beaten at 2500 PFI revolutions. The exclusive addition of 9 wt% NFC to unbeaten slurry produced results close to those required in writing/printing and offset printing paper, but with ºSR/CSF values that were too high. Opacity was basically unaffected by the presence of NFC as it was observed in unbeaten/reinforced pulp.

It is clear that the addition of NFC to *Eucalyptus* pulp can reduce the need for intense beating. The existence of NFC helped create better bonding between fibers by forming entanglements among them in a similar manner to fibrils after beating. This improvement leads to better physical and mechanical properties.

It is necessary to carry out further investigation into the combination of beating degrees and the amount of NFC added to the suspension. The reduction in beating means less energy consumption, which is of particular interest to the papermaking industry. From an industrial point of view, the level of beating has evolved from producing pulps with 40 ºSR to pulps with 30 to 32 ºSR for coated paper used in printing/writing and offset printing paper, equivalent to 2500 revolutions in a PFI mill. This level of beating can be achieved under a specific energy consumption of 150 kWh/ton of beaten pulp, but this value can increase to 200 kWh/ton in the case of pulps with higher ºSR.

Nevertheless, the energy consumed in the production of NFC must be carefully analyzed in order to understand the actual energetic advantages of using NFC as a partial substitute for beating in the papermaking industry.

CONCLUSIONS

1. In this study, paper sheets from bleached *Eucalyptus* pulp and also reinforced with *Eucalyptus*-NFC were produced. Three different approaches of papermaking were used. In the first approach, a fiber suspension of PFI-beaten pulp was converted into handsheets. In the second approach, unbeaten *Eucalyptus* slurry was reinforced with 3%, 6%, and 9 wt% NFC. In the third approach, *Eucalyptus* slurry was slightly beaten and then reinforced up to 6 wt% at max of NFC. Physical, morphological, and mechanical properties were determined and analyzed. The effect of PFI beating compared to that of industrial beating was conducted, and the influence of the use of NFC as paper additive was analyzed, in terms of their ability as substitute of the refining process.
2. Beating with a PFI mill improved mechanical properties of paper sheets. Properties of printing/writing papers were achieved from slurries after beating at 1250 PFI revolutions, and with excellent drainage of the pulp (23ºSR).
3. Slurries reinforced with NFC presented properties similar to those of beaten pulps. The best mechanical and physical results were obtained from slurry with 6 to 9 wt% NFC. However, the use of this amount of NFC showed drainage difficulties (45-54ºSR). In general, and for a same value of properties (for instance same tensile index), the use of NFC exhibited always higher drainage difficulties.
4. Handsheets from slightly beaten slurry and reinforced with 3 wt% of NFC presented mechanical properties similar to those of printing/writing and offset papers. This demonstrates that it is possible to reduce the intensity of beating by adding NFC as additive in papermaking.
5. It is worth mentioning that while porosity tends to decrease significantly with beating, the use of NFC prevents the loss in porosity of paper sheets. Opacity remained almost invariable with the presence of NFC in the slurry.
6. It is necessary to carry out further research about the combination of different degrees of beating and the amount of NFC needed to obtain physical and mechanical properties suitable for different types of paper. From the present work, it is possible to conclude that NFC from *Eucalyptus* can be used as paper additive, at a level of 3 wt% of slightly-beaten pulps for the production of printing/writing papers.

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