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Low-fibrillated Bacterial Cellulose Nanofibers as a sustainable additive to enhance recycled paper quality

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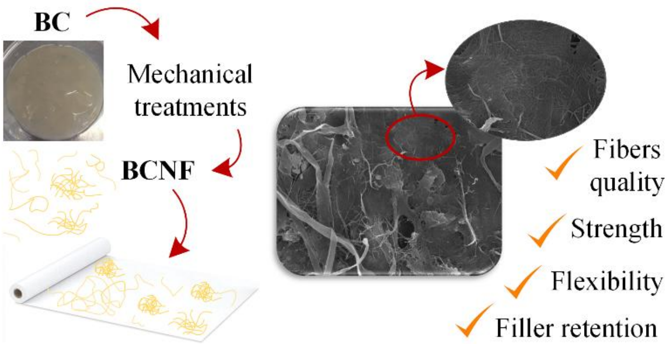
ABSTRACT

Bacterial cellulose is a biological macromolecule synthesized by bacteria of high purity and crystallinity. Bacterial cellulose nanofibers (BCNF) have been produced by soft homogenization and added to a recycled pulp to improve its quality. The benefits of BCNF on mechanical, physical and optical paper properties have been quantified and the retention mechanism of the BCNF in the paper network has been proposed. The use of BC to improve paper strength is usually limited by the decrease of tear index. The novelty of this work is that these two effects are decoupled by the addition of BCNF of low fibrillation (35.2%). In this way, some BCNF clusters are produced together with the individual nanofibers. Thus, with the addition of 3% BCNF, tensile and tear indexes as well as strain at break were improved by 11.1, 7.6, and 66.8%, respectively. Furthermore, the clusters were retained in the fiber network not only by hydrogen bonding, but also by physical retention within the gaps. Therefore, the addition of BCNF not only increases the mechanical properties of paper but also makes the handsheets more flexible and facilitates filler retention.

Keywords: bacterial cellulose nanofibers; improved recycled paper properties; retention mechanism

GRAPHICAL ABSTRACT



1. INTRODUCTION

Paper is the most recycled material in the world, and it is actually one of the best alternatives to replace plastics in the production of packages and bags. However, there are some challenges that recycled paper industry has to deal with. The most limiting is to keep the mechanical, physical and printing requirements of the product at the same time that the quality of the recycled paper is decreasing [1].

Nanocellulose is a biodegradable material that can contribute to an effective improvement of paper quality [2], and bacterial cellulose (BC), in particular, has superior properties than nanocelluloses of vegetal origin. Its high purity is one of the main distinctive of this biological macromolecule, since vegetal cellulose is always combined with hemicellulose and lignin, between other less abundant compounds [3]. In addition, its nanometric diameter but micrometric fiber length provide it a high surface area along with a high resistance, crystallinity and degree of polymerization and thus average molecular weight [4]. The BC is extruded by aerobic bacterial strains, especially of the genus *Komagataeibacter*, that are mainly isolated from rotten fruits and wastes of vinegar fermentation [5].

When these bacteria are cultured in static mode, they create a membrane on the surface of the culture broth due to their natural movement in search of oxygen. This membrane is a structurally stable hydrogel composed of a nanofiber network that contains fibers with diameters between 20-100 nm and up to 99% water in its structure [4]. Although these membranes have been widely used without further modification, e.g. for the fabrication of organic light emitting diodes or scaffolds for tissue engineering [6, 7], the nanofibers must be separated to use them as strengthening agents of a matrix [8]. Between the used methods for BC application, high speed disintegration at 16,000 r/min [9, 10] effectively improve the mechanical properties of different virgin pulps, such as unbleached softwood

[9] and hardwood kraft pulp [10] unbeaten birch and pine sulfate pulps [11] between others [12]. High speed disintegrated BC has been also used to improve other properties of paper, such as the flame retardant behavior of a softwood pulp [13]. This treatment produces a microfibrillation of the cellulose, getting ribbons with diameters in the range of 40-60 nm. On the other hand, it is also possible to obtain a nanofibrillation of the BC by acid hydrolysis, typical procedure used to isolate vegetal-derived cellulose nanocrystals (CNC) [5]. However, to the best knowledge of the authors, BC has not been nanofibrillated by high-pressure homogenization for any application. In this paper the enhancement of paper properties and, thus, recycled paper is studied.

The use of BC to improve tensile strength of paper is limited by the consequent decrease of tear index. The novelty of this work is the use of low fibrillated BC nanofibers (BCNF) with the presence of individual nanofibers and small unfibrillated clusters that can decouple this two effects. In this way, new opportunities to improve paper properties are foreseen. These BCNF have been produced from a soft homogenization of BC membranes, obtained through the culture of *Komagataeibacter sucrofermentans* in static mode. The benefits of the addition of different proportions of BCNF on the mechanical, physical and optical properties of a recycled paper have been assessed. Moreover, scanning electronic microscopy (SEM), X-Ray diffraction (XRD) and ash measurements, were used to elucidate the mechanism of BCNF retention within the fiber network.

2. EXPERIMENTAL SECTION

2.1 Materials

Komagataeibacter sucrofermentans CECT 7291, obtained from the Spanish Type Culture Collection (CECT), was the cellulose-producing bacterial strain used in this study. A three-component retention system frequently used in newsprint mills was supplied by BASF (Ludwigshafen, Germany): polyamine with a high molecular weight and a cationic charge density of 0.035 meq/g as coagulant; polyacrylamide (PAM) with a high molecular weight and a cationic charge density of 3.66 meq/g as flocculant; and hydrated bentonite clay. All other reagents and nutrients were of analytical grade and were supplied by Sigma-Aldrich.

2.2 Preparation and characterization of BCNF

Cell growth was carried out in a medium composed of 20 g/L fructose, 5 g/L yeast extract and 3 g/L peptone (M10) in static mode at 30 °C for 4 days . Then, the produced cellulose was removed to isolate bacteria in a high population as described by Santos, et al. [14]. When BC pellicles were isolated, they were suspended in water at a concentration of 1%, pulped for 60 min at 3000 rpm and homogenized in three batches at 600 bar in a laboratory homogenizer (PANDA PLUS 2000, supplied by GEA Niro Soavi, Parma, Italy) to obtain the BCNF.

Nanofibrillation degree, cationic demand (CD) and polymerization degree (PD) were determined as described by Merayo, et al. [15]. Nanofibrillation degree was determined through centrifugation of a suspension of 0.1 wt% BCNF at 4500 x g for 30 min. Nanofibrillation degree was calculated by the ratio between the remaining amount of BCNF in the supernatant and the total amount of BCNF [16]. CD was measured by colloidal titration using a Charge Analysing System (CAS) supplied by AFG Analytic GmbH (Leipzig, Germany). 0.00025 N poly-diallyl-dimethyl-ammonium chlorides (PDADMAC) was used as standard titration reagent. Then, CD was calculated through the eq. (1).

$$CD = \frac{V_{PDADMAC} \cdot C_{PDADMAC}}{V_{sample} \cdot C_{sample}} \quad (1)$$

Where $V_{PDADMAC}$ corresponds to the volume of PDADMAC spent in the titration, V_{Sample} means the volume of the suspension of BCNF used in the test, $C_{PDADMAC}$ is 0.00025 N and C_{sample} is the concentration of BCNF during the titration. PD of the BCNF was calculated through the determination of limiting viscosity number (η) according to ISO 5351/1, where the method in cupri-ethylene-diamine (CED) solution was used. Then, PD was related to η using $\eta = 0.42 \cdot PD$ when $PD < 950$ and $\eta = 2.28 \cdot PD^{0.76}$ when $PD > 950$ [17, 18].

Crystallinity index (Cr.I) was examined through XRD using a Philips X'Pert MPD X-ray diffractometer with an autodivergent slit fitted with a graphite monochromator using Cu-Kα radiation operated at 45 kV and 40 mA. XRD patterns were recorded from 3 to 80 ° at a scanning speed of 0.64 °/min. Segal's method was used to calculate Cr.I, according to eq. (2) [19].

$$Cr.I\ (\%) = \frac{I_{002} - I_{am}}{I_{002}} \cdot 100 \tag{2}$$

I_{002} is the intensity of the 002 interference at $2\theta = 22.5^o$ and I_{am} is the intensity of the amorphous scatter at $2\theta = 18^o$.

2.3 Handsheet preparation and characterization

A mixture of 60% old newsprint and 40% old magazine was used to prepare the recycled paper to simulate a newsprint furnish. Different proportions of BCNF, 0.5, 1.5, 3 and 6% relative to the total dry weigh, were added to the paper and diluted with hot water to reach a final concentration of 1 wt%. The mixture was pulped using a Messmer pulp disintegrator (Mavis Engineering Ltd, London, UK) at 3000 rpm for 10 min. After disintegration, the polyamine was added to the pulp at a concentration of 1.25 mg/g and stirred at 300 rpm for 15 min. The PAM and the bentonite were added separated 30 s one after the other with continuous stirring. Handsheets were prepared with a basis weight of 60 g/m^2 in a normalized Rapid-Köthen handsheet former (PTI, Vorchdorf, Austria) according to ISO 5269/2 (2004).

Handsheets were conditioned at 23 °C and 50 % humidity for 24 h. Grammage was determined following ISO 536. Mechanical, physical and optical characterizations were performed using an AUTOLINE 300 from Lorentzen & Wettre (Stockholm, Sweden). Tensile (TI) and tear indexes were calculated by dividing the tensile and tear strengths of the paper by its grammage. In addition, the physical properties of porosity, beta formation and thickness were measured. Homogeneity of the formed handsheets was determined through the standard deviation of 400 microgrammage measurements using a Beta formation tester (Ambertec, Espoo Finland). The bulk was calculated based on the ratio between the thickness and grammage.

The morphology of the handsheets was analyzed by SEM with a JEOL JSM 6335F at an accelerating voltage of 15 kV. These analyses were carried out in the National Center of Electronic Microscopy of Spain.

In addition, XRD analysis of handsheets was carried out to evaluate the presence of the different mineral fillers in the paper matrix. Again, a Philips X'Pert MPD X-ray diffractometer with an autodivergent slit fitted with a graphite monochromator using Cu-Kα radiation operated at 45 kV and 40 mA was used.

Finally, the main fillers used in the paper industry, $CaCO_3$ and kaolinite, were determined through ash measurements at 525ºC and 900ºC, according to ISO 1762 and ISO 2144. As stated in ISO 2144, both fillers does not decompose at 525ºC, but when they are submitted to 900ºC, only 56% of CaCO3 and 86-89% of kaolinite are retained. Therefore, the calculation of the filler contents has been made according to these proportions.

3. RESULTS AND DISCUSSION

3.1 BCNF characterization

The characterization results of the BCNF are shown in Table 1. The high entanglement of bacteria during culture, leads to the formation of membranes composed by a resistant network of nanofibers. The strength of the BC membranes causes a great difficulty in the production of highly fibrillated suspensions of BCNF. Thus, a low nanofibrillation degree has been observed, being 35.2%; as a result, some BCNF clusters were added to the handsheets as well as individual nanofibers.

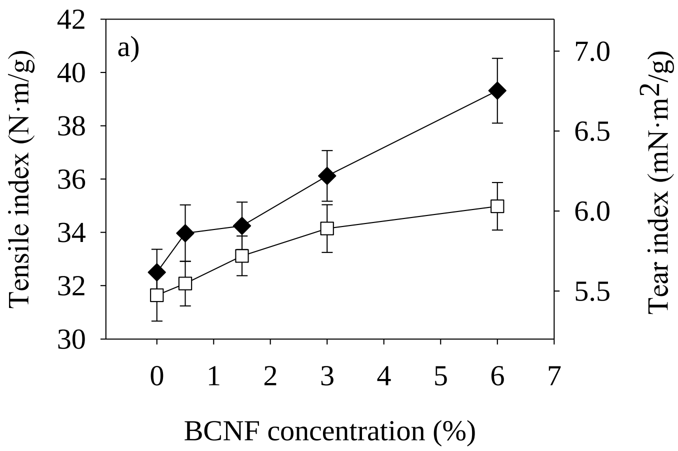
This low nanofibrillation degree also explains the low value of cationic demand, being 0.174 meq/g, compared to typical values for high fibrillated CNF, which are in the order of 0.465 meq/g [16]. As expected, PD and Cr.I values were much higher than either any cellulose fibers or CNF obtained in the literature [20]. It is mainly due to the static culture of bacteria, which allows them to move in a slow and direct way, forming very long and crystalline nanofibers [5].

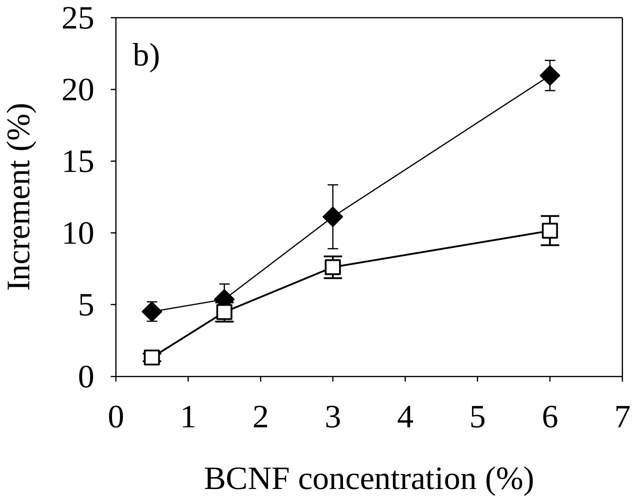
Table 1. Results of BCNF characterization

Property	Units	Value
Nanofibrillation degree	%	35.2
Cationic demand	meq/g	0.174
PD	-	1932
Cr.I	%	98.4

3.2 Effect of BCNF concentration on mechanical properties of recycled paper

Figure 1a shows that increasing BCNF content tended to an increase in the TI of the recycled paper. The addition of low concentrations of BCNF (0.5 – 1.5%) caused the TI to increase by approximately 5% (Figure 1b). Higher concentrations of BCNF further improved the TI (11 and 21% at concentrations of 3 and 6%, respectively). These improvements are slightly lower than those obtained with vegetable-derived CNF. For example, an improvement of approximately 20% in TI was obtained with the addition of 0.5% and 1.5% CNF from corn stalk and eucalyptus, respectively [16]. This may be due to the strong intermolecular attraction between BCNF due to hydrogen bonding and entanglement of bacteria during the culture process, which makes BC difficult to separate into individual nanofibers. Therefore, the low nanofibrillation degree, 35.2% (Table 1) compared to 86% for corn CNF and >95% for eucalyptus CNF [16], resulted in a smaller effect on paper strength. However, the effect might not only be due to the nanofibrillation degree but also to the different mechanisms of action of BCNF compared to CNF.





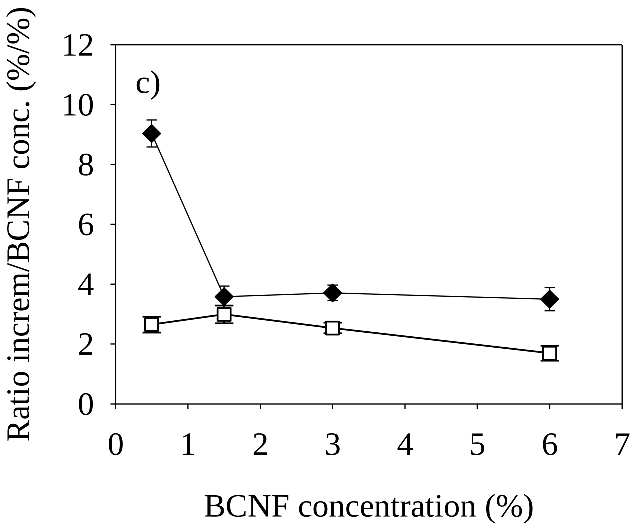


Figure 1. Evolution of a) tensile and tear indexes, b) relative improvements in tensile and tear indexes and c) ratio between the improvements in the tensile and tear indexes to BCNF concentration versus BCNF concentration. Symbols on the graphs represent the following: ♦ tensile index and □ tear index

The tear index increased with increasing concentrations of BCNF from 5.5 without BCNF to 5.9 $mN \cdot m^2/g$ with 3% BCNF and to 6.0 $mN \cdot m^2/g$ with 6% BCNF (Figure 1a). These data represent improvements of 7.6 and 10.1%, respectively (Figure 1b). According to Hassan, et al. [21], tear strength of paper is determined by the total number of fibers involved in the breaking of the handsheet, the fiber length and the number and strength of the interfiber bonds. They also explained that the number of fibers involved in the breaking process is related to the grammage and flexibility of the sheet. Thus, in rigid sheets, stress is concentrated in small areas, meaning only a few fibers are involved, but when sheets are more flexible, the force is transmitted from one fiber to another over a much larger area. In their study, the tear index was not affected by microfibrillated cellulose (MFC) when MFC content was lower than 30%, but it was strongly decreased when the concentration was higher than 30%. They explained that the large number of hydrogen bonds could be the reason for this decrease.

Based on that explanation, the more flexible the handsheets, the higher the tear index, which agrees with the results in this study. Thus, because BCNF clusters are added to the pulp instead of individual nanofibers, the number of hydrogen bonds formed between fibers is not as high as it was with CNF. Therefore, BCNF interacted with fibers, not only making stronger composites but also making the paper more flexible and favoring the transmission of the breaking force throughout the paper. However, when the degree of nanofibrillation is higher, the TI increases at low concentrations, but the tear index is strongly affected [16, 22]. These results are in accordance with different studies in which CNF were added to deinked pulps [23] or thermo-mechanical pulps [24].

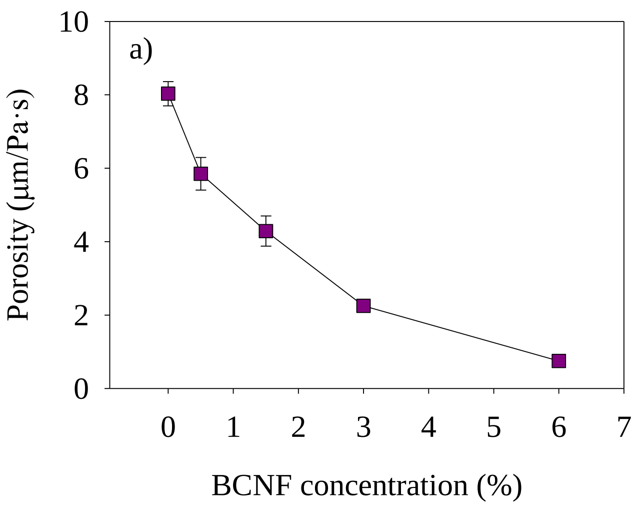
In this study, this relationship has been decoupled, thus both TI and tear index were improved with increasing concentrations of BCNF. However, increasing concentrations of BCNF also involve a concomitant increase in costs. The cost mainly includes both chemical and energy expenses. Therefore, generally the maximum TI and tear index obtained with the minimum BCNF concentration is desired. This has to be optimized based on the needs of each industrial paper product. The ratios between the improvements in strength (TI or tear index) and the increases in the BCNF concentrations were calculated as shown in Figure 1c. The maximum ratio of TI/BCNF concentration (9.0 %/%) was obtained at the BCNF concentration of 0.5%, decreased until 3.6 %/% at a concentration of 1.5%, and then remained constant thereafter (BCNF concentrations of 3 and 6%). Therefore, concentrations of 1.5% or higher have the same ability to improve TI. However, slight differences were found in the ratio of tear index/BCNF concentration. For the lower concentrations of BCNF evaluated, 0.5, 1.5 and 3%, the ratios varied in the range of 2.6-3.0 %/% and then decreased down to 1.7 %/% when the concentration of BCNF increased to 6%.

Although 0.5% of BCNF resulted in the highest ratio among the increases in TI and the concentration of BCNF used, this concentration only cause a 5% increase in TI, which may be not enough to justify the use of BCNF. When looking for improvements of 10-20%, the efficacy of using 1.5% BCNF is the same as using 6%. Therefore, if greater improvements in TI are desired, the BCNF concentration should be increased up to at least 3% to improve the TI by at least 10%.

Strain at break obtained from tensile strength measurements was improved with increasing concentrations of BCNF, and reached a value of 1.37% with 6% BCNF compared to 0.82% without them. Therefore, BCNF not only enhanced the strength of the paper but also provided the paper with some elasticity. This behavior is consistent with the results of Yousefi, et al. [25], who improved paper with BCNF and obtained a TI of 142.3 Nm/g instead of 11.2 Nm/g and a strain at break of 6.5% instead of 1.5% for nanopaper and regular paper, respectively.

3.3 Effect of BCNF concentration on physical and optical properties of paper

Physical and optical properties of the handsheets were also measured due to the importance of those properties for the machine runnability and printing quality of the paper. It has been previously reported that for CNF [20], porosity decreased with increasing concentrations of BCNF since they are retained at the gaps between fibers (Figure 2a). With the addition of only 0.5% BCNF, the porosity decreased from 8.0 to 5.8 µm/(Pa·s), and it reached 0.7 µm/(Pa·s) at a BCNF concentration of 6%. This result also indicates that BCNF are being retained in the handsheets and are not lost during paper formation. The decrease in porosity improves printing properties and barrier paper properties which is very important for advanced paper applications.



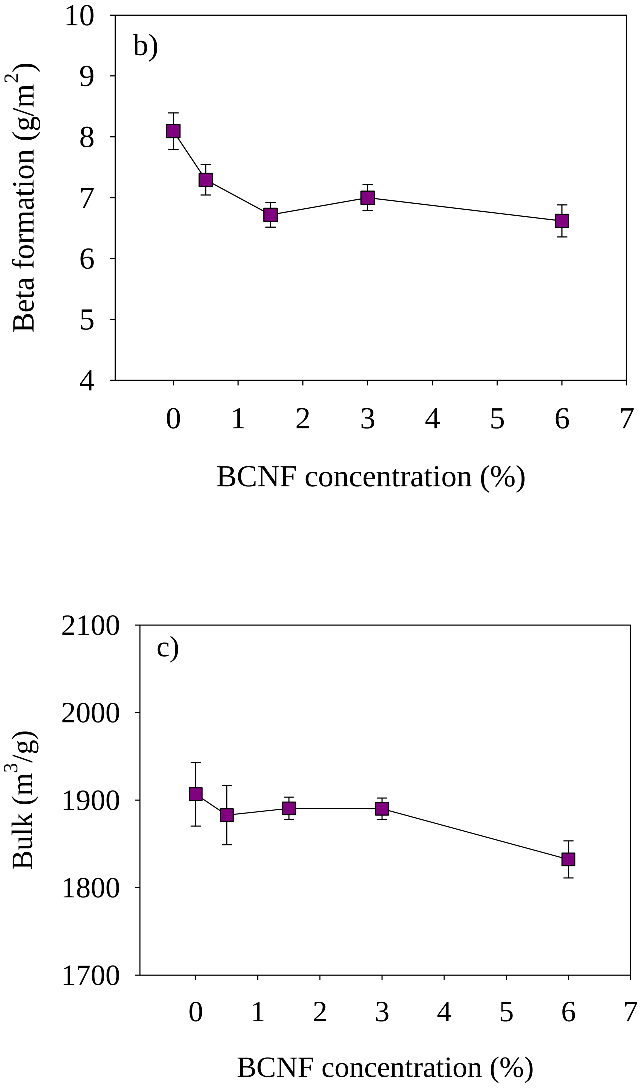


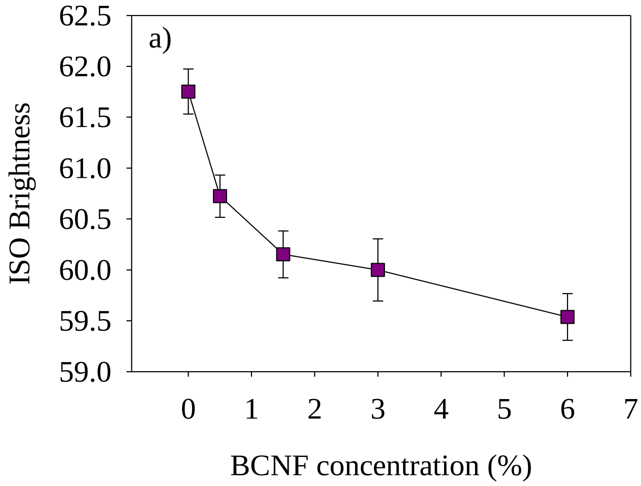
Figure 2. Evolution of physical properties of handsheets with changes in BCNF concentration: a) porosity, b) grammage standard deviation and c) bulk

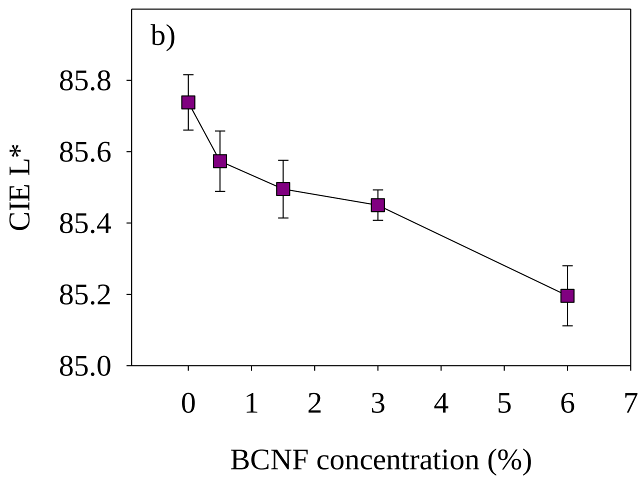
Because beta formation is the standard deviation of 400 microgrammage measurements, higher values indicate poorer handsheet formation. In this study, beta formation decreased when the concentration of BCNF was low, from 8.1 to 7.3 and 6.7 g/m^2 at concentrations of 0, 0.5 and 1.5%, respectively (Figure 2b). However, higher concentrations of BCNF did not further improve handsheet formation. Therefore, the reduction in porosity did not affect the homogeneity of the paper, since most of the pores were covered homogeneously by BCNF. Thus, the quality of handsheet formation was maintained at BCNF concentrations higher than 1.5%, although porosity was further reduced.

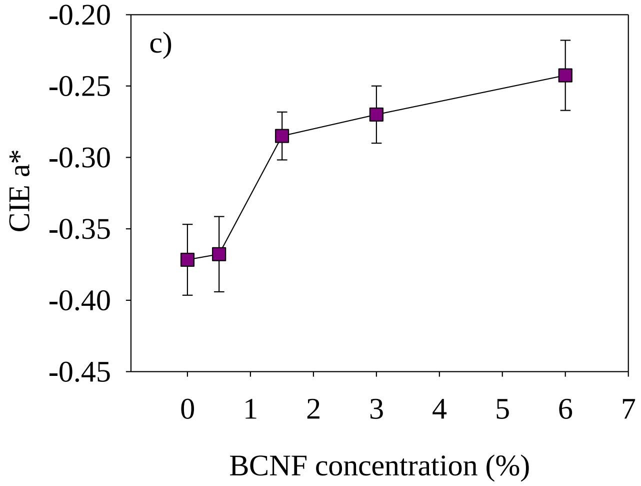
The bulk of the handsheets decreased when a concentration of 6% BCNF was used (Figure 2c). This behavior is likely due to the replacement of the original fibers with the same amount of high-quality nanofibers, which are situated at the gaps between macroscopic fibers thus decreasing the thickness of handsheets with the same grammage. A concentration of 6% BCNF was needed to affect handsheet bulk and, at that concentration, the bulk decreased to 1830 compared to 1890 m^3/g when no BCNF were added. Up to a concentration of 3% BCNF, the bulk was constant. According to the results of beta formation, the high standard deviations for the measurements in which there was a low BCNF concentration (0 and 0.5%) indicate a high variation of thickness and therefore worse formation.

Figure 3 shows the evolution of optical properties with increasing concentrations of BCNF. ISO-brightness was affected by the presence of BCNF, and it was reduced from 61.7% to 60.7% with only 0.5% BCNF. However, with concentrations of 1.5% or greater, the reduction was less pronounced; however, it decreased to an ISO-brightness of 59.5% with 6% BCNF. Balea, et al. [16] suggested that this is because brightness is measured through the light reflectance produced by fibers, fines and fillers at the paper sheets, and the small size of the CNF and BCNF makes them disperse or reflect only a small amount of visible radiation. Therefore, brightness decreased with the addition of these nanocelluloses.

Colorimetric constants are also considered important properties for the quality of the final paper, and they usually need to be within a limited range that varies depending on the requirements of the company. In this case, CIE L* decreased and CIE a* and CIE b* increased with increasing concentrations of BCNF. Therefore, according to the CIELAB color space, increasing concentrations of BCNF made the handsheets appear more black, red and yellow. This color tendency was strongly affected by concentrations below 1.5% BCNF and remained more stable thereafter (Figure 3).







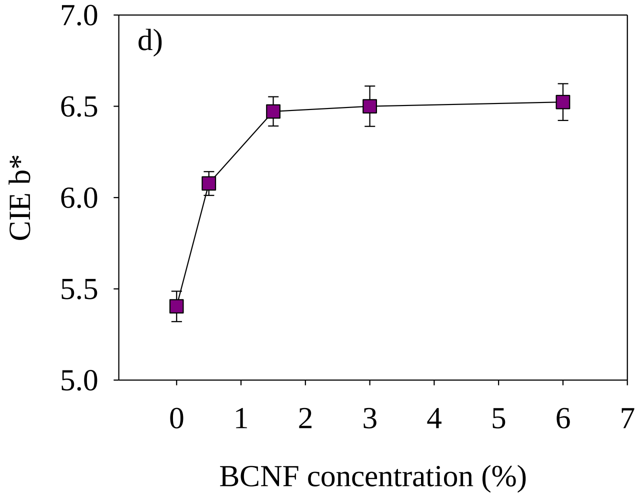


Figure 3. Evolution of optical properties of handsheets with BCNF concentration: a) ISO Brightness, b) CIE L*, c) CIE a* and d) CIE b*

Considering these data, low concentrations of BCNF did not strongly affect the physical and optical properties of paper, but deviations in thickness were still high and the increase in the TI was low. The optimum concentration in terms of efficacy in increasing mechanical properties proposed before (0.5% BCNF) is no longer viable since porosity, beta formation and deviation in thickness measurement are still high and can be improved. Therefore, considering the obtained improvements in the mechanical indexes and physical and optical properties, the recommended concentration is 3% BCNF. At this concentration, the TI increased by 11.1%, strain at break was enhanced in 66.8%, tear index increased 7.6%, porosity decreased from 8.0 to 2.2 µm/Pa·s, beta formation reached its minimum value of 7.0 g/m^2, bulk was kept almost constant at 1890 m^3/g and brightness and colorimetric constants remained almost constant at concentrations higher than 1.5% BCNF. The improvement in the formation, even at the highest studied concentration (6%) is due to the mechanism of retention of BCNF in the fiber network.

3.4 Hypothesis of the BCNF retention mechanism to enhance the paper strength

The mechanism traditionally proposed for the retention of vegetal CNF in the paper sheets is based on their interaction with the components of the pulp, mainly fibers and fines, through hydrogen bonding, in the presence of mineral fillers [26]. This was observed in the FESEM images of Hii, et al. [26], where highly fibrillated CNF are bonded with the fibers of the pulp.

BCNF are retained within the fiber network not only because of the hydrogen bonding between nanofibers and fibers but also because of their retention within the gaps between macroscopic fibers and on the fibers surface. This is due to their low degree of nanofibrillation, only 35.2%, which means that BCNF were added as clusters of nanofibers, more than individual nanofibers. Since these clusters are tightly bound by both hydrogen bonding and entanglement of BCNF during bacterial culture, they strengthen the handsheets and make them more flexible as shown in Figure 1.

To confirm this hypothesis, the handsheets surfaces were analyzed by SEM (Figure 4). At low concentration of BCNF (Figure 4a and b), it is difficult to identify BCNF clusters in the micrographs of the handsheets among the mixture of fibers, fines and fillers. The thin fibrils observed in these images may not only be due to the presence of some individual BCNF but also to some deteriorated fibers because of the recycling process, which causes fibrillation of fibers. This is clearly shown in the study by Delgado-Aguilar, et al. [23] in which they observed the change in fiber size triggered by beating.

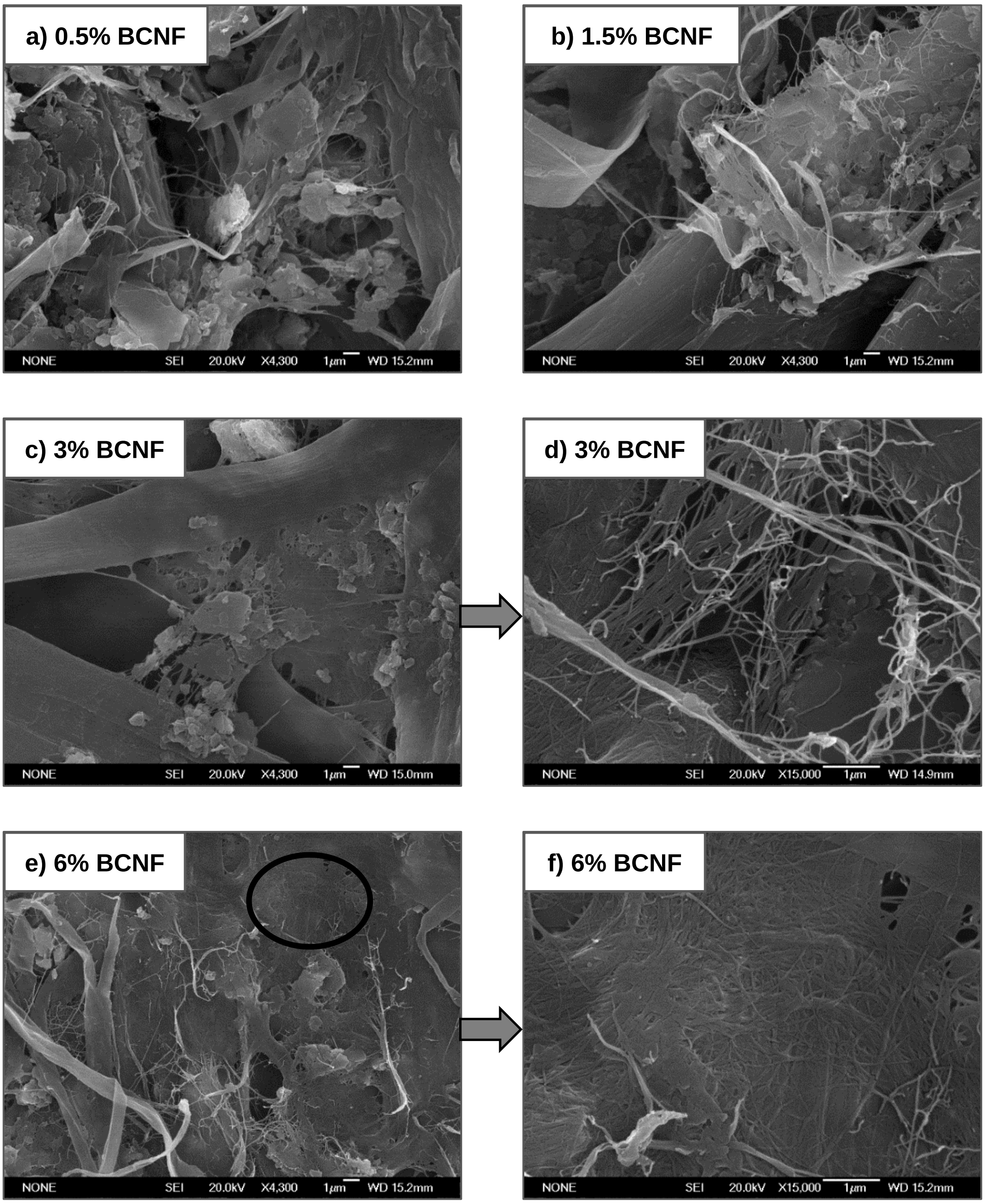


Figure 4. SEM images of the handsheets with different concentrations of BCNF: a) 0.5% BCNF, b) 1.5% BCNF, c) and d) 3% BCNF, and e) and f) 6% BCNF

When the BCNF concentration was increased up to 3% (Figure 4c and d), some BCNF clusters start to be visible. They were identified because of the homogeneous width of BCNF and their entanglement. These images confirm the initial hypothesis proposed that these BCNF are retained in the gaps between fibers, linking the fibers of the pulp and partially covering them. In addition, mineral fillers are retained in the handsheets in the proximity of the BCNF clusters. Thus, not only chemical retention through flocculants takes place, but also a physical retention because of the gap filling with the nanofibers net.

The covering effect of BCNF on recycled fibers is clearly observed when their concentration increased up to 6% BCNF (Figure 4 e and f) and it can be considered an improvement of the recycled fibers. These BCNF clusters are linked together to form a microscopic web that acts like a membrane easing filler retention, in view of the very small pore size.

Results from XRD analysis are represented in Figure 5, where typical cellulose I associated peaks, obtained at $2\theta = 15\text{-}17^{\circ}$, 22.5º and 35º are shown [27]. The other peaks in the XRD pattern indicate the presence of other crystalline materials. They correspond to the two mineral fillers used in the recycled paper industry: kaolinite and calcium carbonate. The peak at around 29.5º is the most intense peak of the XRD pattern of $CaCO_3$. On the other side, the observed peaks at 12.5º and 25º in all samples are attributed to kaolinite [28]. However, this material has many other minority peaks associated to its pattern, which cannot be observed due to the presence of the other components. Therefore, the quantification of the filler contents in each sample made through *The International Centre for Diffraction Data database* (ICDD) is not reliable. Moreover, no big difference between samples can be extracted from Figure 5.

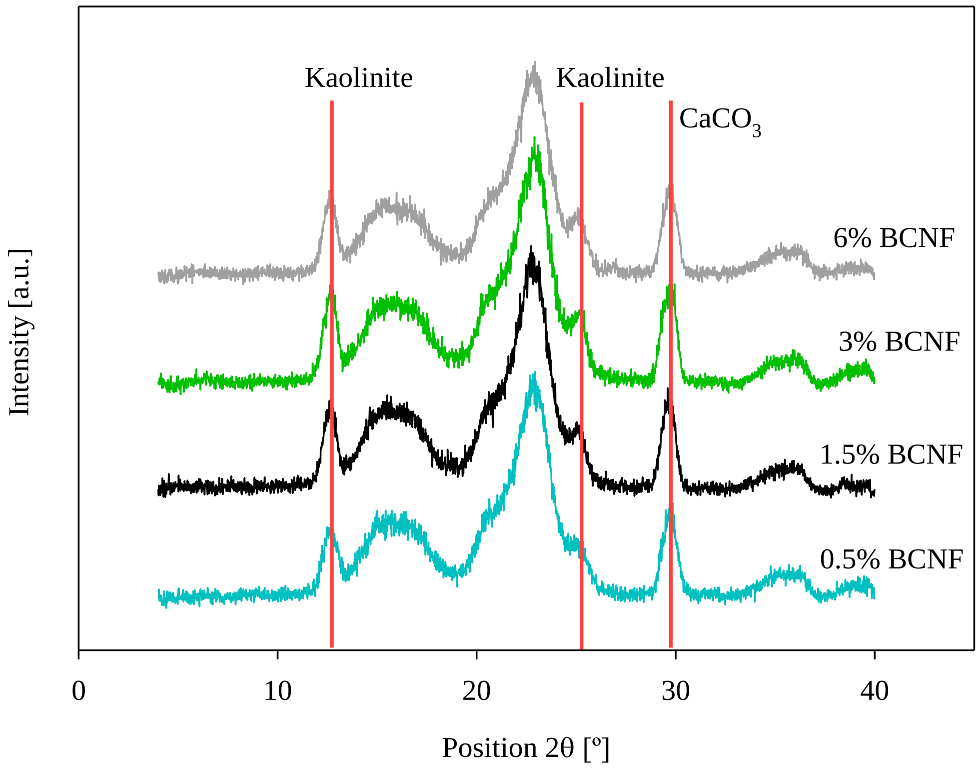


Figure 5. XRD patterns of papers enhanced with different BCNF concentrations. Red vertical lines show the different positions for the mineral fillers of recycled paper: kaolinite and $CaCO_3$

Then, filler content has been determined through ISO standards and showed in Figure 6. Both $CaCO_3$ and kaolinite contents are kept almost constant when concentration of BCNF is below 3%. However, they slightly decreased when the BCNF concentration is 6%, from 20.3 to 18.5%. The found reason is that the dose of the retention aids has been optimized to retain mineral fillers within the paper sheet. However, BCNF probably interact with the retention system, thus, this dose is adequate to retain both fillers and BCNF, when the last is not high.

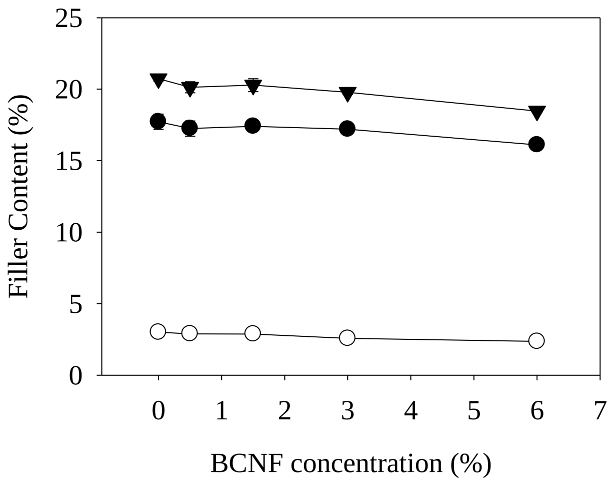


Figure 6. Mineral filler contents in handsheets prepared at different BCNF concentrations. Symbols on the graphs represent the following: ○ $CaCO_3$ filler content (%), ● kaolinite filler content (%) and ▼ total mineral filler content (%)

However, as the specific surface area of BCNF is much higher than that of cellulose fibers, retention aids interact with these nanofibers as well as with the mineral fillers prior to recycled fibers. Thus, the retention of mineral fillers is favorable in the proximities of BCNF as showed in SEM images (Figure 4). When the dose of BCNF is below 3%, both BCNF and mineral fillers are retained within the paper network. However, when BCNF concentration is increased to 6%, the amount of retention aids is not high enough to allow the chemical retention of all mineral fillers. Despite this fact, the reduction in the mineral filler content is not as high since they are physically retained by the BCNF clusters. Therefore, an optimization of the wet-end aids, taking into account not only the filler retention but also the BCNF addition would be necessary to improve the drainage step and reduce costs [29]. Then, a deeper research on the synergy between the retention system and the strength additives is still needed.

4. CONCLUSIONS

BCNF have been produced by a soft homogenization treatment of BC pellicles and applied to a recycled pulp in order to enhance the properties of the produced paper. The improvement of tensile strength of paper by BC is limited by the decrease of tear index. The novelty of this work is the use of low fibrillated BCNF with the presence of individual nanofibers as well as small clusters that decouple these two effects. This makes paper sheets more flexible and facilitates the retention of mineral fillers in the proximities of the BCNF clusters. By the addition of 3% BCNF, all measured mechanical properties have been improved: TI by 11.1%, tear index by 7.6% and strain at break by 66.8%. In addition, the optical properties of the produced papers are kept as high as the unmodified paper when BCNF concentration was below 1.5%. Finally, a high homogeneity is observed in the produced handsheets according to the beta formation, the porosity and the bulk results.

The BCNF retention mechanism is not only due to the hydrogen bonding of BCNF with the fibers, like in the case of high fibrillated CNF, but also to the physical retention of these clusters within the gaps. This fact together with the high affinity between BCNF and fillers due to the high specific surface area of BCNF, confirm a higher filler retention in their proximities, as observed in SEM images.

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