

# Valorization of Corn Stalk by the Production of Cellulose Nanofibers to Improve Recycled Paper Properties

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Corn stalk, an agricultural waste, was valorized by the production of cellulose nanofibers (CNF), which were tested for improving recycled paper properties. CNF from eucalyptus kraft pulp (E-CNF) was used as a reference. Addition of 0.5% wt. CNF produced from corn organosolv pulp (C-CNF) to recycled paper increased the tensile index by 20%, whereas the same improvement with E-CNF was achieved at 1.5% wt. Tensile index was further enhanced by increasing the E-CNF, whereas C-CNF achieved its maximum effect at this dose. Different recycled furnish compositions were studied to evaluate C-CNF as a product additive. C-CNF improved tensile strength in all the different recycled furnishes studied. The tensile index improvement caused by C-CNF did not depend on the proportions of old newspaper and old magazine paper used. Addition of C-CNF to recycled corrugated board fluting increased the tensile strength, but to a slightly lower extent than in the case of recycled newsprint paper.

**Keywords:** CNF; Corn stalk; Agricultural waste; Recycled paper; Nanocellulose; Paper properties

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## INTRODUCTION

The papermaking industry is challenged by the increased use of secondary fibers and stricter quality requirements for final paper products (Confederation of European Paper Industries, CEPI 2014). Secondary fibers inherently reduce the paper quality, especially its strength (Nazhad 1994). Paper strength is a result of the strengths of individual fibers plus the strengths of bonds between those fibers. Strength may be enhanced by refining the pulp; however, recycled fibers are not usually refined to avoid higher degradation of these fibers. Consequently, additives are commonly used to moderately increase strength properties effect (Lindström *et al.* 2005).

Natural aids and nanomaterials are increasingly important as strength additives (Brodin *et al.* 2014). Cellulose-based nanomaterials interact between them and with cellulosic fibers *via* hydrogen bonds (Taipale *et al.* 2010) that form nanofilm coating layers (Schlosser 2008; Lavoine *et al.* 2014) or increase the fiber network strength (Ahola *et al.* 2008; Eriksen *et al.* 2008). The advantages of nanocellulose materials are the low cost of their raw material, renewability, non-abrasive properties, high specific strength, and safer handling (Besbes *et al.* 2011). They are obtained by mechanical defibrillation (cellulose nanofibrils, CNF), acid hydrolysis (nanocrystalline cellulose, NCC), and bacterial fermentation of different organic substrates (bacterial nanocellulose, BNC) (Eichhorn *et al.* 2009; Osong *et al.* 2016).

CNF has been studied as a reinforcement agent in virgin paper applications due to its large surface area, its ability to promote hydrogen bonding, and, thus, its improvement of paper strength (Taipale *et al.* 2010; González *et al.* 2012; Petroudy *et al.* 2014). The retention of CNF in the paper web is not easy due to its small size and anionic charge; it commonly requires retention aids (Ahola *et al.* 2008; Manninen *et al.* 2011; González *et al.* 2012; Petroudy *et al.* 2014). On the other hand, when CNF is retained, the drainage rate may decrease (Taipale *et al.* 2010; Manninen *et al.* 2011; González *et al.* 2012; Petroudy *et al.* 2014), and mechanical paper properties may be altered, such as tensile and tear indexes (Taipale *et al.* 2010; González *et al.* 2012; Petroudy *et al.* 2014). Therefore, an integral optimization would be required, in which not only improvement of mechanical properties would be considered, but also drainage rate and solids retention, optimizing retention aids as well as CNF doses.

The effect of CNF on paper strength is influenced by the amount of CNF added to the pulp (Manninen *et al.* 2011), the source of fibers in the furnish studied, the raw material, and the production process used to obtain CNF. The effect of source of fibers, applying the same CNF, has been neglected when comparing softwood and hardwood pulps (Silva *et al.* 2010). CNF production using homogenization achieves higher increments in tensile strength than CNF produced by grinding (Eriksen *et al.* 2008); moreover, tensile strength increases with the intensity of mechanical treatment used to produce CNF because higher intensity results in more homogenous material with higher amounts of cellulose nanofibers (Silva *et al.* 2010; Spence *et al.* 2011). In fact, a decrease in average CNF particle size is linearly correlated with an increase in tensile strength (Eriksen *et al.* 2008; Silva *et al.* 2010). In addition, TEMPO oxidation pretreatment improves mechanical properties better than enzymatic pretreatment, when both use similar homogenization processes (Silva *et al.* 2010).

Physical properties of paper are also affected by CNF. In packaging applications, barrier properties are of special interest to prevent oxygen transfer through paper. With increased CNF concentration, the density of the paper increases, and the air permeability, porosity, and thickness decrease because the pores between fibers are blocked or reduced by CNF (Eriksen *et al.* 2008; Taipale *et al.* 2010; Manninen *et al.* 2011).

Most studies focus on improving the mechanical properties of paper produced from virgin pulps (Ahola *et al.* 2008; Eriksen *et al.* 2008; Mörseburg and Chinga-Carrasco 2009; Syverud and Stenius 2009; Silva *et al.* 2010; Taipale *et al.* 2010; Manninen *et al.* 2011; González *et al.* 2012), but extensive studies about CNF in recycled paper are still needed. CNF may be a feasible alternative for improving the mechanical properties of recycled paper (Delgado-Aguilar *et al.* 2014). Salam *et al.* (2013) demonstrated improvements in tensile and burst indexes when microcrystalline cellulose was added to old corrugated board (OCC) pulp. Though agricultural sources of CNF have been limited, published results are encouraging, and the use of CNF from agricultural residues is of great interest (Hassan *et al.* 2011; Petroudy *et al.* 2014).

It is difficult to compare the effect of CNF, whose raw material is virgin wood fibers *vs.* other sources, because they were added in different pulps. In this work, an agricultural waste, corn stalk pulp prepared by organosolv cooking, was used as a source for CNF production. The potential benefits of corn CNF in recycled paper were assessed, and the results were compared with eucalyptus bleached kraft pulp CNF as a reference. CNF was tested in several recycled pulps including recycled newsprint paper, with different proportions of recovered old newspaper (ONP) and recovered old magazine paper (OMG), and OCC fluting.

## EXPERIMENTAL

### Production of CNF

CNF was obtained from two different cellulose sources. Never-dried, refined *Eucalyptus globulus* ECF bleached kraft pulp (EBK) with a Canadian Standard Freeness (CSF) of 540.8 mL was obtained from Torraspapel S.A. (Zaragoza, Spain). Never-dried corn stalk organosolv pulp (Corn) was prepared in the laboratory by cooking with 40% ethanolamine at 165 °C during 60 min and washed with distilled water to remove the ethanol and dissolved lignin. This pulp was refined at 5000 rpm in a PFI mill to reach a CSF of 170 mL and a Kappa index of 16.8. The amount of uncooked compounds in the corn pulp was 5.4%, and the extractive compounds added up to 0.55%. This pulp was obtained by organosolv cooking to avoid the environmental impact of the kraft process, and it was not bleached in order to minimize the required treatment and its environmental impact. Nanofibrillated material was obtained by TEMPO-mediated oxidation using 5 mmol of NaClO per gram of EBK pulp and 15 mmol of NaClO per gram of Corn pulp, as described in Saito *et al.* (2007). The different composition of the pulps required different amounts of the NaClO oxidant. The EBK pulp was almost pure cellulose and was previously oxidized during kraft cooking and bleaching, but the Corn pulp was obtained *via* an organosolv process. Thus, it contained many impurities, as shown by the Kappa index and the percentage of non-cooked compounds (5.4% wt). These compounds react with NaClO and reduce cellulose oxidation during the TEMPO reaction (Okita *et al.* 2009). The amount of NaClO was adjusted to obtain similar oxidation in both pulps. After oxidation, pulps were cleaned with distilled water and filtered and/or centrifuged at 4500 × g until the pH was 7. Finally, the pulp was homogenized six times at 600 bar in a PANDA PLUS 2000 laboratory homogenizer (GEA Niro Soavy, Parma, Italy), obtaining the CNF with concentration around 0.3 to 0.5% wt, which was the range of concentrations used for their application.

### CNF Characterization

The yield in nanofibrillation was determined by centrifugation of the CNF suspension with 0.1% solid content at 4500 × g for 20 min (Gonzalez *et al.* 2014). The CNF fraction was isolated in the supernatant, and the yield was calculated as the proportion of dry solids in the supernatant *versus* total dry solids in the sample.

CNF was characterized by atomic force microscopy (AFM) with a multimode AFM Nanoscope IIIa (Bruker, Billerica, USA), with an FESP probe oscillating at 86.5 kHz. To prepare the CNF sample for AFM, a drop of diluted CNF suspension (0.3 to 0.5 % wt) was dried on mica substrate at ambient temperature (Henriksson *et al.* 2008; Mandal and Chakrabarty 2011). Microscopic analyses were carried out in the National Centre of Electronic Microscopy at the Complutense University of Madrid.

Transmittance readings of 0.1% wt. CNF suspensions diluted were performed between 400 and 800 nm on a Cary 50 Conc UV-visible spectrophotometer (Varian Australia PTI LTD, Victoria, Australia).

The amount of carboxylate groups in oxidized fibers was determined by conductimetric titration of the pulp after TEMPO treatment and cleaning but before homogenization. A pulp sample containing 0.15 g of dry matter was added to 5 mL of 0.01 M NaCl, and the pH was adjusted to 2.5 to 2.8 by adding 0.1 M HCl to protonate all carboxylate groups.

Deionized, distilled water was added to a total volume of 55 mL. With continuous stirring, 0.05 M NaOH was added to the sample in 0.2-mL increments, and the conductivity was recorded after each addition. The amount of carboxylic groups was calculated from the curve of conductivity *vs.* amount (meq) of NaOH added (Habibi *et al.* 2006).

Cationic demand (CD) measurements were taken by colloidal titration of diluted CNF suspensions (0.05 to 0.1 %wt.) with 0.001 N-polyDADMAC on a Mütek PCD04 particle charge detector (BTG Instruments GmbH, Herrsching, Germany).

Polymerization degree (PD) was calculated from the limiting viscosity number (intrinsic viscosity) of the CNF suspensions, which was determined by the ISO 5351 standard (2010) and based on the Mark-Houwink-Sakurada (MHS) equation (Flory 1953; Tanford 1961) (Eq. 1),

$$H = K \cdot M^a \quad (1)$$

where  $M$  is the molecular weight (g/mol),  $\eta$  is the intrinsic viscosity (mL/g), and  $K$  and  $a$  are constants.

Different  $K$  and  $a$  values have been reported; the values given by Henrikson *et al.* (2008) are the most commonly used ( $K = 2.28 \cdot 10^{-4}$  dL/g,  $a = 0.76$ ). PD was calculated from the molecular weight of the polymer by dividing it by 162 g/mol, which is the molecular weight of the anhydroglucose monomer.

## Cellulose Pulps

Cellulose pulps were prepared with 20 g of dry recovered paper in water using a Messmer pulp disintegrator (Mavis Engineering Ltd, London, UK) at 30000 rpm for 1 h. Different recovered papers were used: (i) deinked newsprint paper in different proportions of old newspaper/old magazine (70/30, 60/40, 50/50, and 30/70); and (ii) OCC fluting, which is the center part of OCC cardboard. The recovered paper was soaked for at least 24 h before disintegration to favor fiber swelling. To retain CNF after paper disintegration, pulp suspensions were mixed with cationic starch (7.5 mg per g of dried pulp) for 20 min at 500 rpm (Taipale *et al.* 2010; González *et al.* 2012). Optimization of CNF dose was performed using newsprint recycled paper with 60/40 proportion, whose characterization is shown in Table 1.

The cationic starch was supplied by SOLAM (Emlichheim, Germany). Following supplier recommendations, 0.3 g of powder starch was heated in 200 mL of ultrapure water at 85 to 90 °C for 15 min with continuous stirring and then cooled at room temperature. Water (300 mL) was added to a final concentration of 0.5% starch.

Morphological analysis was performed with a Morfi analyzer model V7.9.13.E (Techpap, France) (Moral *et al.* 2010).

## Sheet Preparation and Characterization

Handsheets were prepared with basis weight of 60 g/m<sup>2</sup> in a normalized Rapid-Köthen handsheet former (PTI, Vorchdorf, Austria) according to the ISO 5269/2 (2004) and DIN 54358/1 (1981) standards. The handsheets were physically, optically, and mechanically characterized with use of an AUTOLINE 300 from Lorentzen & Wettre (Stockholm, Sweden).

**Table 1.** Characterization of 60/40 recycled paper pulp

Fibers		
	Units	DIP 60/40
Length Weighted in Length	µm	892
Average Width	µm	20.7
Coarseness	mg/m	0.166
Macrofibrils	%	1.74
Broken Ends	%	34.7
Average Angle	°	131.0
Kinked Fibers	%	13.38
Average Curl	%	5.47
Pulp		
	Units	DIP 60/40
Fibers	number x 10 <sup>6</sup> /g	13.48
Aggregates	number/g	78723
Fines	number/g	121719
Ash	g/L	0.8
Cationic demand	µeq/L	168
Conductivity	µS/cm	1083
Soluble and colloidal COD	mg/L	104

## RESULTS AND DISCUSSION

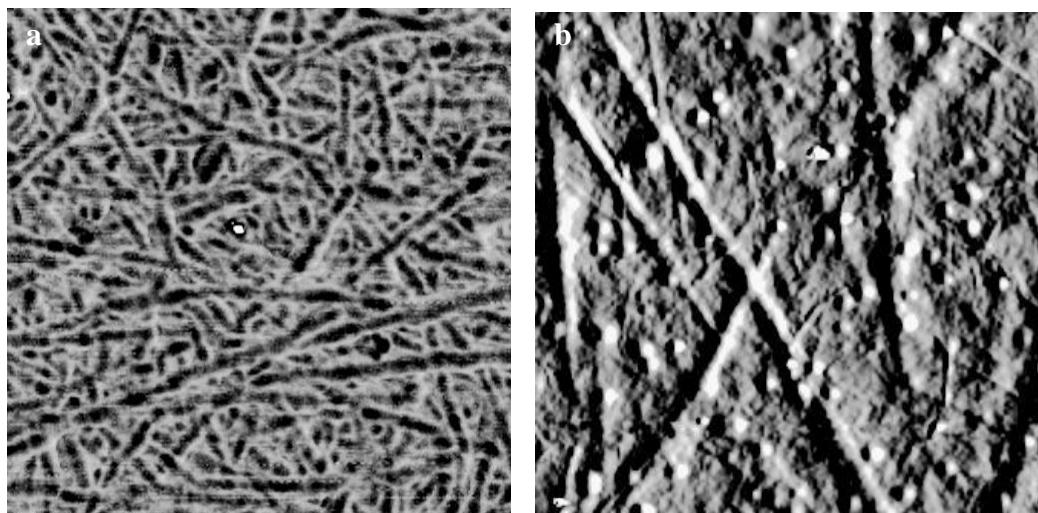
### Obtaining CNF from Agricultural Waste: Characterization and Comparison with Eucalyptus CNF

CNF can be obtained from corn pulp by TEMPO oxidation and subsequent homogenization. During CNF production, the total solids were decreased by the intensive oxidation and cleaning steps. Thus, production efficiency was defined as the amount of CNF obtained with regard to the input of cellulose pulp before applying TEMPO pretreatment. The production efficiency of CNF from corn pulp (C-CNF) was 56%; 44% of the corn pulp solids were lost. These losses probably resulted from the oxidation of impurities or physical losses during the cleaning step. In the CNF obtained from EBK pulp (E-CNF), production efficiency was 64%, which is higher than the production efficiency of C-CNF. As the production process was the same for both pulps, the difference was due to the pulp itself. Corn pulp was not bleached, and it contained uncooked compounds. These compounds may have been degraded during TEMPO oxidation, which reduced the amount of solids after this step. In contrast, EBK pulp contained bleached, nearly pure fibers, such that losses were minimized during CNF production.

The nanofibrillation yield was quantified as the amount CNF out of the total product obtained after TEMPO pretreatment and homogenization processes. C-CNF yield was 86%; therefore, 86% of the solids in the product obtained was C-CNF. The remaining 14% was impurities deposited during centrifugation. The E-CNF yield was higher than 95%, indicating that there were neither fines nor fibers in the E-CNF suspension. Therefore, the

higher losses from corn pulp resulted from the different pulping methods. The proportion of fibers in corn pulp was lower than in EBK pulp, and these impurities decreased production efficiency and nanofibrillation yield. Theoretically, C-CNF efficiency and yield could be increased by purifying the corn pulp, for example by bleaching the pulp and removing the lignin. Kappa index of C-CNF was measured and found to have values of 6.13, which indicates a reduction in lignin content in comparison with corn pulp. Therefore, there was a consumption of lignin during the TEMPO oxidation. Part of the NaClO added was consumed in parallel reactions with lignin and, probably, other impurities of the pulp and subsequently removed in the washing steps.

When CNF was characterized by AFM (Fig. 1), differences in fibrillation and homogenization were noted, although CNF aggregates and elemental nanofibrils with 6-nm diameter were observed in all cases. C-CNF suspensions showed high homogenization grade with mostly individual nanofibrils and few bundles, but E-CNF suspensions had a wider diameter distribution and more bundles. Therefore, nanofibril dispersion was higher in C-CNF than in E-CNF. E-CNF presented long nanofibril bundles larger than 30 nm in diameter and several  $\mu\text{m}$  long, but elementary fibrils were also observed. Some bundles of E-CNF showed wider points due to curling or “kinking”.



**Fig. 1.** AFM phase images of: a) C-CNF (500x500 nm) and b) E-CNF (4x4  $\mu\text{m}$ )

The presence of bundles in E-CNF was reflected in its transmittance values (Table 2). Lower transmittance at 400 nm in E-CNF was probably due to its higher amount of bundles. This difference in transmittance value disappeared at 800 nm because bundles did not absorb at this wavelength. However, bundles did not precipitate during centrifugation because they are not fines or fibers; consequently, the E-CNF yield was not affected.

Generally, C-CNF transmittance was high despite its lower yield. Therefore, particles deposited during the centrifugation of C-CNF were not cellulose fines or fibers, which would disperse the light at 800 nm; it follows that they were probably non-cellulosic materials with densities larger than cellulose. Moreover, the colloidal or dissolved lignin from corn stalk in C-CNF suspension did not affect the transmittance measurement (Xiao *et al.* 2001).

**Table 2.** Characterization of the CNF Suspensions

	Transmittance (%)		Oxidation Degree (mmol COOH/g)	CD (meq/g)	PD (monomers)	Yield (%)
	400 nm	800 nm				
E-CNF	83.5	94.8	0.59	0.465	440	>95
C-CNF	89.9	95.0	0.52	0.198	541	86

The higher the carboxylic content of the oxidized pulp is, the easier the mechanical treatment would be. Eucalyptus pulp had more carboxylic acids than corn pulp, although less HClO was used to prepare E-CNF. This result reflects the consumption of HClO to degrade uncooked compounds and lignin in corn pulp. Reduction of these impurities implies that the CD value (Table 2) was mostly due to anionic charges in nanofiber, which was lower than in E-CNF. PD was slightly lower for E-CNF because its higher oxidation degree favored cellulose breakage during homogenization. Thus, C-CNF contained more homogenized and dispersed nanocellulose material than E-CNF, and it had a higher polymerization degree. While the production efficiency and nanofibrillation yield of C-CNF obtained from unbleached organosolv corn pulp were lower, these values may be improved by reducing impurities.

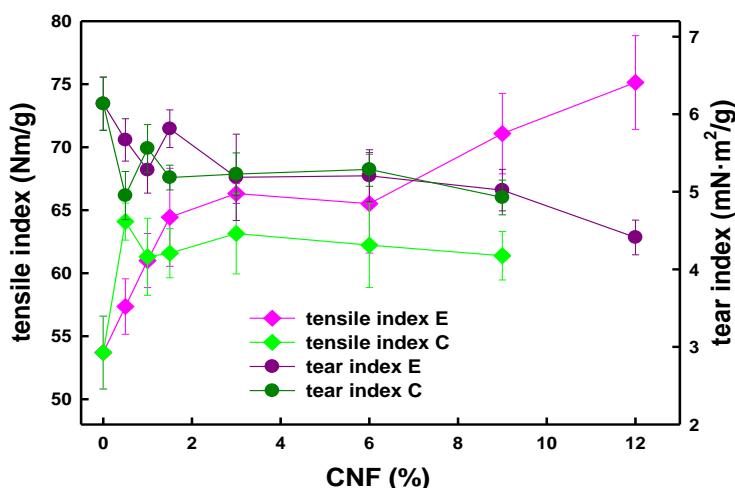
### CNF as a Recycled Paper Additive. Dosage Optimization

The objective of this work was to add CNF to recycled paper pulp to improve the mechanical properties of recycled paper products, mainly tensile index, without affecting the wet end process of papermaking. However, CNF can negatively affect other mechanical properties, *e.g.*, tear index. Moreover, the effect on physical and optical properties must also be considered in order to select the optimal CNF dose. The recycled paper selected to test C-CNF effects was newsprint recycled paper with an ONP/OMG proportion of 60/40 because it is commonly used in newsprint mills.

Tensile index varied based on the type and amount of CNF (Fig. 2). C-CNF increased the tensile index to its maximum value at 0.5% C-CNF, which was 19.4% higher than without C-CNF. A completely different behavior was observed when E-CNF was added, such that increasing E-CNF improved the tensile index. At 1.5% E-CNF, a 20% increase in tensile index was achieved. Further increases in tensile index occurred at the 9% and 12% E-CNF doses (40% increase at 12% E-CNF). However, these extremely high doses would increase costs and cause difficulties for CNF dispersion in the pulp and in the drainage step. CNF interacted with fibers as well as with cationic starch. Adding cationic starch without CNF to the recycled pulp resulted in an increase in tensile strength; CNF addition also increased tensile strength on their own. The specific surface of CNF is quite higher than that for the fibers; consequently cationic starch interacts most probably to a greater degree with CNF than with fibers. Therefore, in presence of CNF, cationic starch is consumed interacting with CNF instead of fibers and tensile strength provided by cationic starch is reduced. This reduction becomes more important as CNF dose increased. Moreover, at lower doses of the C-CNF, interaction with cationic starch was not favored because C-CNF were efficiently dispersed before the addition of CS, forming hydrogen bonds with the fibers such that the amount of fibers related to the amount of C-CNF was relatively high. As the C-CNF dose increased, interaction between C-CNF and cationic starch was becoming more important, in competition with the interaction of cationic starch with fibers, which were decreasing, as well as hydrogen bonds among C-CNF and fibers.

Therefore, strength decreased due to the fact that cationic starch was consumed with C-CNF and this effect could not be counterbalanced by the increase in strength produced by C-CNF. In the case of lower doses of E-CNF, their effect on tensile strength was lower than the effect of C-CNF, probably due to the dispersion of CNF in the fiber network, being easier the dispersion of C-CNF than the dispersion of E-CNF, which could be dispersed in form of aggregates or bundles. As the dose of E-CNF increased, the interaction with the cationic starch was evident in the flat part of the E-CNF profile. At doses between 1.5 and 6%wt the effect of the cationic starch on the tensile strength was canceled because of its interaction with E-CNF, which was more probable than with fibers. Higher doses achieved a further increase in tensile strength probably because the excess of E-CNF dose was used to promote new hydrogen bonds with the fibers.

At low doses, C-CNF provided better results than E-CNF, obtaining the same improvement in tensile index with 3-fold less C-CNF. C-CNF has the added advantage of valorizing an agricultural waste. However, tensile index was not increased by increasing C-CNF, whereas more E-CNF achieved a higher tensile index.

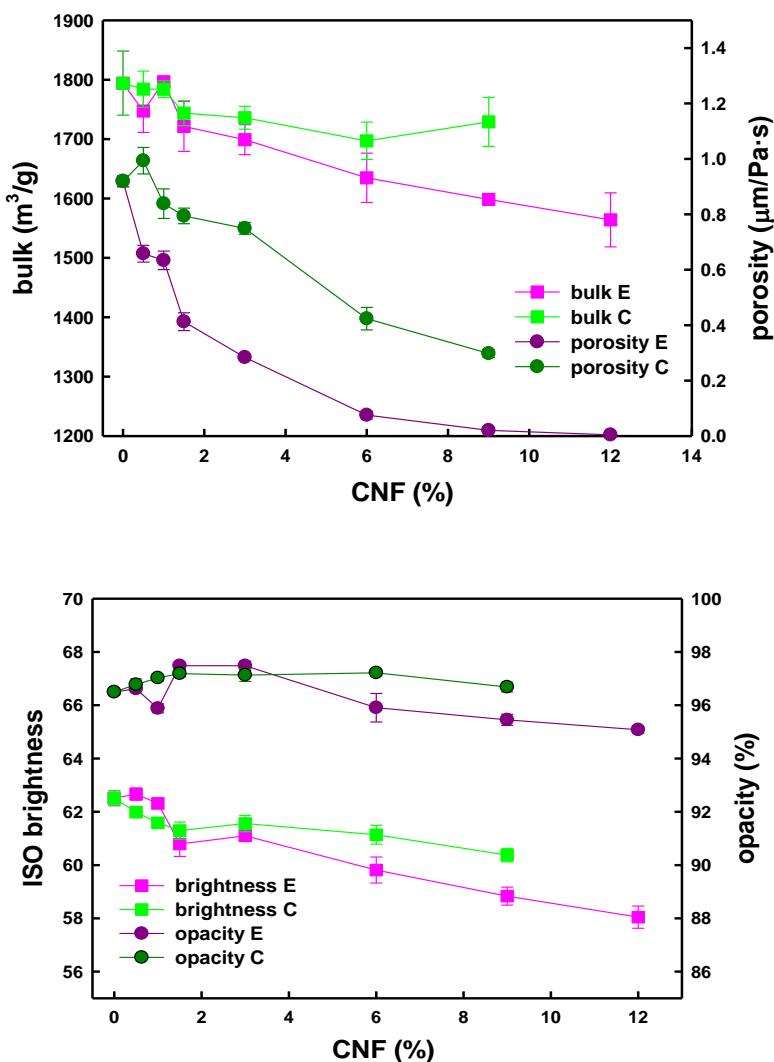


**Fig. 2.** Effect of C-CNF and E-CNF dose on tensile and tear indexes of hand sheets prepared with ONP/OMG of 60/40

The effects of C-CNF and E-CNF on tear index were also measured (Fig. 2). C-CNF had a higher impact on this property, as observed for many dry strength additives, such as C-PVA (Fatehi *et al.* 2009), combined C-PVA and A-PAM (Cho *et al.* 2010), and molasses (Ashori *et al.* 2013). This effect also reported when different types of CNF were used as additives in deinked pulp (Delgado-Aguilar *et al.* 2014), semi-bleached soda bagasse pulp (Petroudy *et al.* 2014), and thermo-mechanical pulp (TMP) (Eriksen *et al.* 2008). However, other reports show an increase in tear index when CNF from hardwood and softwood, including E-CNF, is added to hardwood bleached kraft pulps (Silva *et al.* 2010; González *et al.* 2012). Therefore, the origin of fibers used in the furnish also influences CNF effects on mechanical properties. This reduction in tear index is related to the increase in the number of bonds caused by the replacement of fibers and fines by the same mass of nanofibers, which are much smaller and much more numerous than fibers and fines. This is in accordance with the observations of other authors on tear index, which depends on the fiber length and the number of binding points. Yu (2001) showed a decrease in tear index with increasing fiber-fiber bonding, and Seth and Page (1988) showed that

tear index increased with fiber length, particularly with a lower degree of bonding. C-CNF addition decreased tear index more than E-CNF because the amount of nanoelements (*i.e.*, nanofibrils and bundles of nanofibrils) per gram of C-CNF was much higher than in E-CNF, which had more aggregates. The higher amount of nanoelements increased the number of bonds and, therefore, decreased tear index.

Finally, C-CNF effects on other physical and optical properties were studied. The bulk and porosity of the handsheets decreased and density increased with increasing C-CNF, especially for doses higher than 1 %wt. (Fig. 3). This result was expected because nanofibrils placed on the spaces between fibers had blocked the pores. Therefore, decrease in porosity is an indicator of the retention of the CNF in the handsheets.



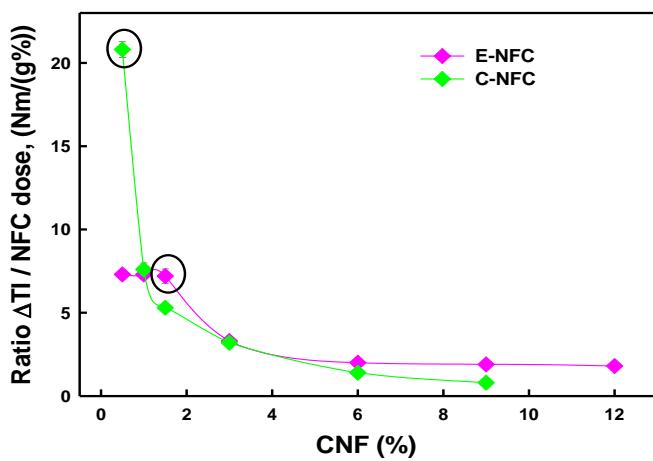
**Fig. 3.** Effect of C-CNF and E-CNF dose on bulk, porosity, brightness, and opacity

The effect of C-CNF addition was similar to but lower than E-CNF and also in accordance with previous work for deinked pulp (Delgado-Aguilar *et al.* 2014) and virgin pulp (González *et al.* 2013). Decreases in porosity improved the barrier properties of paper, which is interesting with regard to improving packaging properties. Moreover, the low air

permeability indicated a low surface porosity, which is beneficial for printing (Syverud and Stenius 2009).

Increasing additions of C-CNF slightly reduced brightness (Fig. 3), as expected by its higher Kappa index. C-CNF contained some residues of colored compounds, which reduced the brightness. However, low doses of E-CNF did not decrease brightness because it did not have impurities, but higher doses reduced brightness more so than C-CNF. Brightness is caused by the light reflected by fibers, fines, and fillers in the sheet; however, nanofibrils are too small to reflect or disperse high amounts of visible radiation ( $\lambda > 600$  nm). As a consequence, nanofibrils are transparent to visible radiation, and high amounts of CNF with such a small dimension leads to reduced brightness. When high doses of E-CNF were added, their distribution in the pulp may have been hindered by its high viscosity; the number of zones with high E-CNF concentration, which are less bright and more transparent, would increase. Opacity was also decreased, but it was not affected at doses lower than 6 %wt. (Fig. 3) because E-CNF dispersion was favored at lower doses. This result differed from observations by Delgado-Aguilar *et al.* (2014), who reported decreased opacity with low CNF doses, probably due to the dispersion and distribution of CNF in the pulp. For C-CNF, its low viscosity ensured its homogeneous distribution in the pulp, even at high doses. Because of this good distribution, high C-CNF doses affected brightness and opacity less than E-CNF.

Brightness, bulk, and porosity were not greatly affected by low doses of C-CNF (Fig. 4). However, porosity strongly decreased when the optimal dose of E-CNF (1.5% wt) was used. This result was expected because of nanofibrils in the gaps between fibers, which are more noticeable at higher E-CNF doses. Finally, opacity slightly increased at low CNF doses, but the increase caused by C-CNF was much lower than that for E-CNF.



**Fig. 4.** Ratio between the improvement of tensile index and the CNF dose

The optimal dose of CNF was established as the lowest dose resulting in the highest increase in tensile index and the lowest reduction of tear index, bulk, and brightness. This calculation accounts for factors in CNF production including chemicals, water, and energy, and the increased energy required for pulp mixing at increased CNF dose. Moreover, high doses of CNF reduce the drainage rate (Taipale *et al.* 2010; González *et al.* 2012). The effects on tear index, bulk, brightness, and opacity were negligible at low doses of CNF. Therefore, the ratio between the tensile index and dose was used to optimize the CNF dose

(Fig. 4). The highest ratios were obtained with a C-CNF dose of 0.5% wt. and with E-CNF doses of 0.5, 1, and 1.5% wt. The optimum C-CNF dose was 0.5% wt. because it achieved the highest ratio, and there was a sharp decrease at higher doses of C-CNF. In contrast, similar ratios were achieved by 0.5, 1, and 1.5% wt. of E-CNF, decreasing at higher doses. As these three doses all produced the maximum efficiency, the optimal dose was selected based on tensile index. Therefore, 1.5% wt. was selected, as it achieved the same improvement as the optimum dose of C-CNF, which was 1.5 times higher than the 1% E-CNF dose.

The lower dose of C-CNF required to increase tensile index can be explained by the lower electrostatic repulsive forces between C-CNF and fibers. The anionic charge of C-CNF is lower than that of E-CNF; the higher polymerization degree of C-CNF contributed to the strength of the paper sheet. The interaction between C-CNF and the pulp components, especially fines and fibers, was favored by the cationic starch added to form hydrogen bonds.

### **Application of CNF in Different Recycled Paper Products**

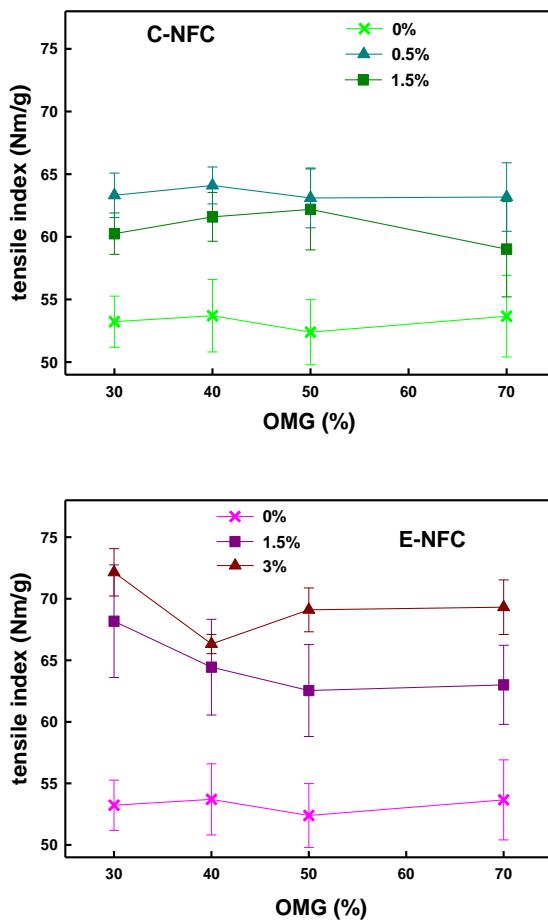
The raw material used to produce recycled products had a noticeably effect on the paper properties and the behavior of additives. OMG and ONP have different characteristics, *e.g.*, the higher filler content of OMG, which affects the morphology and ash content of mixed pulps (Table 3).

**Table 3.** Morphology and Ash Content of Extreme ONP/OMG Mixtures

Fibers			
	Units	DIP 30/70	DIP 70/30
Length Weighted in Length	µm	857	911
Average Width	µm	20.9	21.1
Coarseness	mg/m	0.178	0.155
Macrofibrils	%	2.15	1.76
Broken Ends	%	39.0	34.7
Average Angle	°	131.1	130.9
Kinked Fibers	%	11.63	13.24
Average Curl	%	5.48	5.65
Pulps			
	Units	DIP 30/70	DIP 70/30
Fibers	number x 10 <sup>6</sup> /g	13.30	14.10
Aggregates	number/g	76355	78256
Fines	number/g	211005	116126
Ash	g/L	1.3	0.6

The 30/70 ONP/OMG pulp mixture contained 100% more fillers than the 70/30 mixture. In addition morphology analyses of the pulps in presence of both CNF did not show differences with the pulp without CNF. Consequently, CNF were retained in the handsheets but they did not promote aggregation or any other morphological effect in the pulps.

The tensile strength of recycled paper was expected to decay with increasing OMG as a result of the increasing percentage of fillers. However, Fig. 5 shows that the OMG proportion had no effect when there was no CNF added to the different pulps. This may be due to the accumulative amount of dry strength additives remaining in the recovered paper used, which modulates the effect of the increasing filler content. Moreover, OMG was more fibrillated, as shown by the higher macrofibrillation index of pulp with 70% OMG (Table 3). Therefore, fillers contributed more to bonding, increasing the interaction among fibers and, therefore, tensile strength. As a result, the tensile strength of the sheets prepared with different ONP/OMG mixtures was similar.

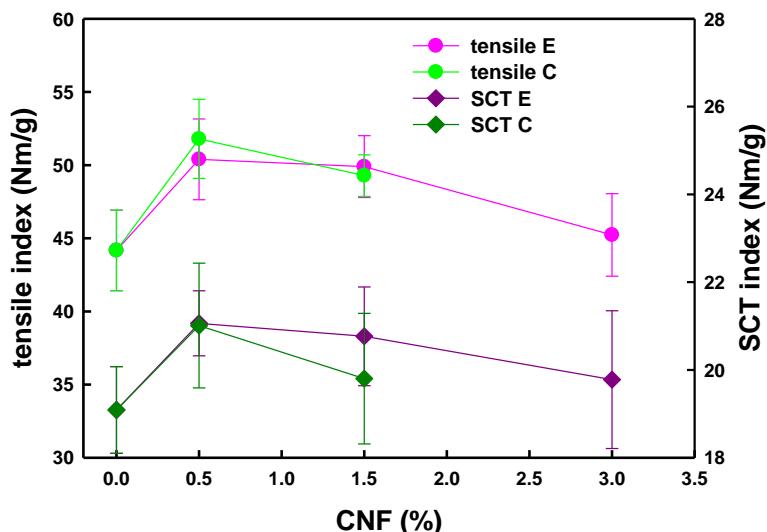


**Fig. 5.** Effect of CNF on tensile index of recycled paper with different proportions of OMG

The effect of C-CNF on tensile strength was similar regardless of the proportion of OMG. The optimal dose for C-CNF was confirmed for all ONP/OMG mixtures because there were no greater differences between 0.5% and 1.5% C-CNF (Fig. 5). The same dose of starch was used for all trials; therefore increasing CNF with the same amount of cationic starch did not result in an increase in tensile strength. This fact could indicate that the maximum amount of C-CNF retained by this cationic starch dose was 0.5%. Using E-CNF, the tensile strength of paper with 1.5% E-CNF decreased slightly with increasing OMG, although with 3% E-CNF there was a lower decrease; consequently, at high proportions of OMG, the highest tensile strength was obtained with 3% E-CNF. Therefore, the cationic

starch was able to retain a dose of E-CNF up to 3%. This indicates a higher interaction between cationic starch and E-CNF comparing with C-CNF.

Finally, the effect of CNF was studied on fluting paper from OCC cardboard. No differences were found between C-CNF and E-CNF (Fig. 6). The addition of 0.5% CNF increased the tensile index up to 17.3%. The slight reduction in tensile strength compared with ONP/OMG mixtures may have been related to the presence of lignin in this pulp (Kappa index of 62), which interferes with the interaction between fibers and CNF, affecting the mechanical properties of the handsheets formed.



**Fig. 6.** Effect of CNF on tensile index and SCT index of recycled fluting paper

Tensile strength is not the most critical mechanical property of board, so the effect of CNF on the short compression strength (SCT) of fluting was also measured. Figure 6 shows that the addition of CNF increased SCT to a lower extent than it increased the tensile index. SCT increased around 10% when 0.5% CNF was added to the fluting pulp, which was the maximum improvement regardless of the kind or dose of CNF. These results showed that CNF improved both tensile strength and SCT index.

## CONCLUSIONS

1. Producing CNF from corn stalk, an agricultural waste, is feasible.
2. C-CNF improved mechanical properties of recycled paper and board, reaching similar results as in E-CNF.
3. Production efficiency and yield in C-CNF was lower than that in E-CNF, but the lower C-CNF dose required may compensate for the lower yield because low doses limit negative effects on bulk and favor dispersion of C-CNF.

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