

Towards a new generation of functional fiber-based packaging: cellulose nanofibers for improved barrier, mechanical and surface properties

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Abstract The present work shows the suitability of using industrial fluting papers as raw material for the development of four different substrates, enzymatically refined and/or containing cellulose nanofibers (CNF) in bulk. These four substrates were deeply studied and treated with different coating formulations, containing CNF, polyvinyl alcohol (PVA), native starch and alkyl ketene dimer, with the purpose of evaluating the benefits of using fiber-based packaging paper with improved mechanical, physical and barrier properties. The results showed that if CNF are coated in combination with PVA the tensile properties of paper can be significantly improved, as well as the grease resistance, whereas the air permeability and water vapor transmission rate decrease. The obtained papers present interesting vapor and air barrier properties, at the same time that unconceivable limits of breaking length are achieved (6.44 km). In addition, when a second layer of alkyl ketene dimer was coated on both sides of paper, the water contact angle was significantly improved, being higher than 115°.

Overall, the present work shows the feasibility of recycled fibers for the production of high value-added papers that can be used for packaging purposes due to their improved barrier and mechanical properties, and contributes therefore for the bio-based circular economy.

Keywords Cellulose nanofibers · Polyvinyl alcohol · Recycled paper · Packaging · Barrier properties

Introduction

The CEPI roadmap to 2050 outlines that the key for a sustainable economy is the higher utilization, and in a more efficient way, of the natural resources. The world's population is increasing day by day, a total of 9 billion people being expected by the year 2050. Taking into account that consumers' behavior depends on the economic, resource constraints, technology, societal values, style of governance and planet's capacity to support its population and corresponding lifestyle, several actions towards the development of new materials and products based on renewable resources must be developed (CEPI 2011). In fact, the European consumption of packaging papers increased from about 25 million tons in 1991 to about 39 million tons in 2015, and it is expected to keep

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growing (CEPI 2016). This substantial growth mainly comes from the environmental awareness of society, which is boosting the transition from a plastic to a fiber-based society in the packaging field. A proof of that is the COST Action FP1405 (ActinPak), which aims at developing knowledge-based network on sustainable, active and intelligent fiber-based packaging, in order to find new market applications and to overcome current technological, industrial and societal limitations (COST 2014).

As a result of the increasing interest on fiber-based products, especially those obtained from recovered paper, the quality of fibers is becoming increasingly important and there is a clear need to adopt concurrent strategies to further improve the efficiency of the recovery processes. However, this is challenging if a certain quality degree is required. In fact, during recycling, dinking and refining, fibers experience structural damages that need to be compensated with additional treatments. In addition, paper industries are adopting strategies to save resources and decrease the final production cost, such as decreasing the products basis weights or increasing their mineral filler content (Hubbe 2014).

During the last decade, cellulose nanofibers (CNF) have emerged as high value-added products derived from renewable resources, mainly composed by cellulose and hemicellulose, with improved properties with respect to common cellulosic fibers and a wide range of applications (Henriksson et al. 2007; Isogai et al. 2011; Hii et al. 2012). There is extensive literature on the use of CNF as paper strength additive in bulk, where the advantages of this nanostructured cellulose-based additive are extensively discussed in terms of contributing to the mechanical, physical and barrier properties, as well as paper products life span (Lavoine et al. 2012, 2014; Delgado-Aguilar et al. 2015b; Boufi et al. 2016). This is particularly relevant for the packaging sector, which is moving from plastic to fiber-based products. However, considering that the supply of virgin cellulosic resources is limited and that the world's population is increasing, the transition to recycled fibers based products is needed in order to assure a sustainable growth.

Fluting grade papers are mainly composed of recycled fibers. They are commonly used in corrugated cardboard, which is very sensitive to atmospheric conditions, a fact that limits its packaging potential (Allaoui et al. 2009). Actually, depending on

the application, the high porosity of paper against plastic is a drawback for the abovementioned transition to fiber based products. Syverud and Stenius (2009) were among the first to report air permeability results of MFC-coated papers. They found that as the amount of microfibrillated cellulose (MFC) on the surface was increased, air permeability was significantly decreased, at the same time that surface porosity was reduced. This was later confirmed by Aulin et al. (2010) and Nygård (2011). Moreover, Hult et al. (2010) found that microstructured cellulose fibers, properly combined with shellac, could improve grease resistance and moisture barrier and provide hydrophobic character to coated papers.

This work aims at developing high-performance fluting-based papers by using bulk treatments, such as enzymatic refining and incorporation of CNF in bulk, and different coating formulations. These formulations are based on CNF in combination with other coating compounds (native starch, alkyl ketene dimer and polyvinyl alcohol) to further improve their behavior in terms of barrier, mechanical and surface properties.

Materials and methods

Fluting paper was kindly provided by Saica S.A. (Spain) and bleached kraft eucalyptus pulp (BKPE), the raw material for the production of cellulose nanofibers (CNF), was supplied by ENCE Energía y Celulosa (Spain). Polyvinyl alcohol (Kuraray POVAL 4-98) was provided by Archroma (Spain) and it was totally hydrolyzed. Native starch, colloidal silica, cationic starch and alkyl ketene dimer (AKD) were provided by Torraspapel, S.A. (Spain). Endo- β -1,4-glucanases (Serzym 50) was supplied by SERTEC-20 S.L. (Spain), with an activity of 84,000 CMU/g at 60 °C at pH of 4.8 over a carboxymethylcellulose (CMC) substrate, and were used for enzymatic refining treatment. All chemicals for the CNF production and characterization were provided by Sigma Aldrich (Spain) and were used as received, except Novozym 476, which was provided by Novozymes A/S (Denmark), containing 2% of endo- β -1,4-glucanases with an activity factor of 4500 CNF-CA/g of cellulose, also tested over a CMC substrate.

Cellulose nanofibers production

Cellulose nanofibers were prepared by TEMPO-mediated oxidation followed by high-pressure homogenization. Prior to CNF production, the BKEP was first disintegrated by means of a laboratory pulper at 3000 rpm during 30 min, and then refined in a PFI mill for 4000 revolutions to promote fiber swelling and fibrillation (Zimmermann et al. 2010). TEMPO-mediated oxidation was performed with 15 mmol of sodium hypochlorite per gram of fiber, following a methodology reported elsewhere (Saito and Isogai 2004). This concentration was selected according to previous experiments (Tarrés et al. 2016a). Briefly, 15 g of BKEP were dispersed in distilled water containing TEMPO (0.016 g/g of fibers) and NaBr (0.1 g/g of fibers) at room temperature. The mixture was kept under stirring for 15 min to ensure good dispersion of all the substances. Then, 15% NaClO solution was added dropwise to the slurry, keeping the pH at 10. Once all the NaClO had been added, pH was maintained by adding a 0.5 M NaOH solution. The oxidation was considered to be finished when the pH remained constant at 10 without the incorporation of any oxidant. The reaction took about 5 h. The oxidized fibers were thoroughly washed with distilled water and kept at 4 °C for further use. These CNF, referenced as CNF-T, were only added as coating, and not in bulk.

In addition, cellulose nanofibers were also obtained by enzymatic hydrolysis, carried out according to a methodology reported elsewhere (Henriksson et al. 2007) but changing several parameters (Tarrés et al. 2016c). BKEP was dispersed at 1.5 wt% consistency in water in a laboratory pulper for 30 min at 3000 rpm. Then, the fibers were filtered until 10 wt% consistency and refined in a PFI mill for 4000 revolutions. This process was carried out to swell the fibers and thus to promote the activity of enzymes. Briefly, refined fibers were suspended in water again (until reaching a pulp consistency of 5 wt%), and 0.1 N HCl was dropped until a pH of 5 was reached. Then, the suspension was heated until 50 °C under constant stirring to avoid temperature gradients. At this step, the enzyme cocktail was dropped into the suspension and stirred for 4 h. The enzymatic process was stopped by heating the suspension at 80 °C for 15 min, leading to a strong decrease of the enzyme activity (De Marco and Felix 2007). Enzyme dosage was set at 160 g/Tn. The enzymatically hydrolyzed pulp then was washed with

distilled water and kept at 4 °C. These CNF were only added in bulk, and not as coating agent. They were referenced as CNF-E.

After the chemical or enzymatic pretreatment, the fibers were subjected to high-pressure homogenization in a Panda Plus 2000 homogenizer from Gea Niro Soavi (Italy) following the sequence of 3 times at 300 bar, 3 times at 600 bar and 3 times at 900 bar. This sequence has been previously reported to avoid clogging in the pressure chambers of the homogenizer (Tarrés et al. 2016b).

Cellulose nanofibers characterization

The cationic demand of the CNF suspension, understood as the amount of highly charged cationic polymer required to neutralize the nanofibers surface, was measured using a Mütek PCD 04 particle charge detector from BTG International Ltd (United Kingdom). For this, CNF were first dispersed in a poly-DADMAC solution (0.1 wt%). The contact time between CNF and poly-DADMAC was set at 10 min. Then, the suspension was centrifuged and the supernatant was titrated with the anionic standard polymer Pes-NA. Both the polymers were supplied by BTG.

Regarding the carboxyl content, it was determined by ionic exchange between two defined pHs (2.8 and 10). This methodology is based on the ionic exchange that takes place between carboxylic groups from cellulose and zinc cations from an aqueous suspension. First, cellulosic fibers must be demineralized by means of adding 50 mL of zinc acetate to 0.8 g of fibers at pH 1. Then, the suspension was kept under gentle stirring for 30 min and then washed with excess of zinc acetate and finally with deionized water. Next, fiber was redispersed in 250 mL of zinc acetate at pH 7 and filtered. The filtrate was titrated with EDTA 0.01 M using black eriochrome as indicator. The titration was carried out at pH 10.

The yield of fibrillation was determined by centrifugation (4500 rpm, 20 min) of a 0.1 wt% CNF aqueous suspension. The individual cellulose nanofibrils were found in the supernatant, whereas non-fibrillated and partially fibrillated material remained in the precipitate at the bottom of the vessel. The degree of polymerization (DP) of the oxidized cellulose fibers was determined from intrinsic viscosity measurements, according to the existing bibliography. The viscosimetric average molecular weight was

calculated according to previously published works (Henriksson et al. 2007). Transmittance was determined in a 0.1 wt% CNF aqueous suspension using a Shimadzu UV-160A ultraviolet–visible (UV–Vis) spectrophotometer.

The fibrils diameter and specific surface area were determined according to a methodology reported elsewhere, based on calculations from cationic demand and carboxyl content (Espinosa et al. 2016). Briefly, it was considered that the interaction between the CNF surface and the added cationic polymer (poly-DADMAC) occurred through two different mechanisms: on the one hand, part of the polymer got retained by ionic interaction between carboxylic groups from CNF and the polymer thereof. On the other, the rest of the consumed poly-DADMAC was assumed to be retained by hydrogen bonding and Van der Waals forces. This assumption can be performed due to the high-molecular weight of the poly-DADMAC that was used, hindering the penetration into the cellulose fibers cell walls (Lizundia et al. 2016). In addition, diameters were also determined by transmission electron microscopy (TEM) using a Zeiss EM 910.

Preparation of the fluting paper sheets

Commercial fluting paper was teared in small pieces and disintegrated in a pulper equipped with an helicoidal rotor. The process was carried out at 50 °C and 1 wt% of NaOH under constant stirring (1000 rpm) for 15 min. The amount of added water was the required to achieve 5 wt% of pulp consistency. In the case of CNF-reinforced papers, CNF-E were added in a second disintegration stage (90 min at 3000 rpm) at laboratory scale. The amount of added CNF-E was calculated to obtain 3 wt% of the reinforced paper sheets weight. Afterwards, colloidal silica and cationic starch were added as retention agents in the amounts of 0.8 and 0.5 wt%, respectively, under gentle stirring at 500 rpm for 20 min (González et al. 2013).

On the other hand, enzymatic refining was carried out according to a methodology reported elsewhere (Delgado-Aguilar et al. 2015c). In a typical experiment, 75 dry g of 5 wt%-consistency pulp was stirred and heated at 65 °C. The pH was set at 4.8 by the addition of diluted HCl. At this point, enzymes solution (350 g/Tn of dried pulp) were added to the

slurry, and stirring was continued for 30 min. The enzymatic hydrolysis was stopped by heating the suspension at 80 °C, as reported elsewhere (Henriksson et al. 2007). The resulting enzyme-treated pulp was finally washed with distilled water to eliminate remaining enzyme and reagents.

Paper sheets were prepared in a Rapid-Köthen sheet former (ISP mod. 786FH) according to ISO standard 5269-2 and conditioned at 23 °C and 50% of relative humidity for 48 h before testing.

Coating of the paper sheets

Four different agents were used for the preparation of the coating formulations: (1) CNF-T, (2) Native starch, NS, (3) Polyvinyl alcohol, PVA and (4) Alkyl ketene dimer, AKD. Several coating formulations were prepared by the combination of these agents, as listed in Table 1.

The coating formulations were prepared by dispersion in an Ultraturrax T25 (IKA, Germany) at 20,000 rpm during 60 s. Then, the suspensions were dispersed using a sonicator Q700 for 10 min (5 min pulse on, 2 min pulse off, and 5 min pulse on) at 60% of amplitude to remove any air bubble.

Coating was performed with an automatic bar coating equipment (RK Control Coater) in both sides of paper. Depending on the coating formulation, different layers were deposited. In the case of AKD coating, only one layer per side was applied. The rest of the formulations were coated twice per paper side. In some cases, a third layer of AKD was coated at both sides of paper. Figure 1 exemplarily shows the structure of the resulting coated fluting papers:

Each paper sample was air-dried after depositing each coating layer and after coating all the desired layers paper was submitted to vacuum-drying and conditioned at 23 °C and 50% of relative humidity before testing.

Recycled pulp and paper characterization

Pulp suspensions drainability was evaluated by measuring the Schopper-Riegler degree (°SR) following the ISO 5267-1 standard, whereas the morphological analysis (length, diameter and fines) was carried out by using a MorFi Compact analyzer (TechPap, France).

Paper handsheets were characterized in terms of: (1) structural properties: basis weight (ISO 536),

Table 1 Coating formulations used in this work

Reference	Water (%)	Native starch (%)	CNF-T (%)	PVA (%)	AKD (%)
CNF-T	99.55	–	0.45	–	–
NS_CNF-T	97.05	2.50	0.45	–	–
PVA	98.00	–	–	2.00	–
CNF-T_PVA	97.55	–	0.45	2.00	–
AKD	99.50	–	–	–	0.50

**Fig. 1** Schematic illustration of the structure of coated papers

thickness (ISO 534), density, porosity and morphology by FE-SEM; (2) mechanical properties: breaking length at constant elongation rate (ISO 1924-2); (3) barrier properties: water vapor transmission rate (WVTR) (TAPPI T448), Gurley porosity (ISO 5636-5); and (4) surface properties: water contact angle and grease resistance (TAPPI T559).

FE-SEM analysis was performed by means of a Zeiss DSM 960A microscope at 7 kV of acceleration voltage. For WVTR, a circular paper specimen was placed on the top of a self-made chamber containing 30 g of dried silica gel. Water absorption of silica gel was assessed by gravimetry until constant weight, meaning that silica gel was saturated. Water contact angle on paper surface was measured using a DSSA24 drop-shape analyzer from Krüss GmbH (Germany) equipped with Krüss Advance Software. Measurements were performed at room temperature with a frequency of two measurements per second. The total testing time was 30 s for each paper. For grease resistance assessment, twelve (from kit 1–12) different suspensions of castor oil, toluene and n-heptane were prepared.

Results and discussion

TEMPO-catalyzed oxidation has been extensively reported as an effective method for the production of cellulose nanofibers with unique properties, clearly superior in several aspects to other CNF prepared by alternative methods (Delgado-Aguilar et al. 2015a). In addition, such oxidative method leads to shorter CNF,

fact that makes them suitable to be used as coating agent in papermaking due to their capability to penetrate in the paper structure (Tarrés et al. 2016a). Table 2 shows the main characteristics of the both the TEMPO-oxidized and the enzymatic CNF prepared in this study.

The obtained CNF-T present a carboxyl content of 1526 $\mu\text{eq-g/g}$, indicating that the TEMPO/NaBr/NaClO oxidation in water at basic pH effectively oxidized C6 primary hydroxyl groups of cellulose to C6 carboxylate groups, which can be either in its acidic or salt form, depending on the pH after fiber washing (Isogai et al. 2011). This high amount of carboxylate groups promoted fibers fibrillation after TEMPO-catalyzed oxidation, apart from introducing several anionic and voluminous groups, thus leading to a high cationic demand. This fact significantly increased the specific surface of the CNF, reaching values of 347.2 m^2/g . If these CNF are assumed as perfect cylinders (which are not), a diameter of 7.7 nm can be calculated. TEMPO-mediated oxidation is also known for the depolymerization that imparts on cellulose chains which, according to Shinoda and collaborators (Shinoda et al. 2012), has a direct relationship with CNF length. Indeed, high oxidation degrees lead to shorter CNF, promoting thus the penetration in the paper web structure when they are used as coating (Tarrés et al. 2016a). This penetration is interesting mainly due to two aspects: one the one hand, if the CNF interact with paper fibers, they will improve some mechanical properties and, on the other hand, they also promote the barrier and surface properties.

Table 2 Characterization of the obtained CNF

Sample	CC ($\mu\text{eq-g/g}$)	CD ($\mu\text{eq-g/g}$)	σ (m^2/g)	d (nm)	T at 800 nm (%)	DP (–)	Length* (nm)	Aspect ratio	Yield (%)
CNF-E	42.1 \pm 3.1	255 \pm 29	103.7	25.7	44.6	320 \pm 3	615	23.9	29.4
CNF-T	1526 \pm 103	2239 \pm 91	347.2	7.7	83.4	197 \pm 8	87	11.3	97.1

* Calculated from $\text{Length (nm)} = 4.286 \cdot \text{DP} - 757$ (Shinoda et al. 2012). CC carboxyl content, CD cationic demand, σ specific surface, d diameter, T transmittance (at 800 nm); DP degree of polymerization

The carboxyl groups content of the CNF-E is smaller than that of the CNF-T, as expected, as well as the cationic demand and all the other parameters, except the aspect ratio. Indeed, CNF-E present about twice the aspect ratio of CNF-T, mainly due to their higher length. Therefore, they are not so adequate as CNF-T to be used as coating agent, but they have the potential to be used as reinforcing agent in paper bulk, due to their lower water retention capacity, higher aspect ratio and more competitive production costs (Tarrés et al. 2016c). Four different recycled fluting pulps were used for paper production, each one with the drainability and the morphological characteristics shown in Table 3.

The reference pulp presents a drainability of 41°SR, a typical value for brown-line recycled pulps (Biricik and Atik 2012; Moral et al. 2017). When this pulp was enzymatically refined, drainability was kept almost constant with no relevant changes in fibers morphology (length was just decreased from 844 to 768 μm). This effect was also observed in previous works (Delgado-Aguilar et al. 2015c). The incorporation of CNF-E into the pulp suspension significantly decreased the pulp drainability, due to the higher specific surface of CNF-E compared to fluting fibers. This higher specific surface, as expected, increased the nanofibers ability to retain more water and, thus, also increased the drainage time of the pulp suspension.

The CNF-E did not affect apparently the mean length and diameter of the fibrous material, but increased the amount of fines. This is understandable, since the equipment used for measuring the fibers dimensions is not able to detect fibers in the nanoscale. However, taking into account the fibrillation yield of CNF-E (Table 2), the increase on fine elements was somehow expected.

As previously described, the different pulps were used for the production of isotropic paper handsheets. In addition, each paper was used as substrate for the different coating formulations (Table 1). The basic properties of the samples coated with a single layer per paper side are listed in Table 4.

Comparing the uncoated papers, it is possible to see that the incorporation of CNF-E in the paper matrix increased significantly their density, making them less porous. This effect has been extensively reported and it can be attributed to the higher specific surface of CNF-E (compared to the fibers), at the same time that shrinkage inter-fiber forces occur. On the other hand, when analyzing the effect of enzymatic refining, no significant changes can be observed in terms of density. However, when CNF-E were added to the enzymatically treated fibers, the resulting papers presented a considerably lower porosity, showing that the paper structure was more closed. In addition, when the enzymatically treated fibers were combined with

Table 3 Characterization of the untreated and treated recycled fluting pulps

Pulp reference	Enzyme treatment	CNF-E (%)	°SR	Length (μm)	Diameter (μm)	Fines (%)	Aspect ratio
Fluting	No	0	41	844 \pm 12	20.9 \pm 0.3	13.45 \pm 1.10	40.38
Fluting_E	Yes	0	40	768 \pm 18	19.8 \pm 1.2	14.05 \pm 0.72	38.78
Fluting_CNF	No	3	54	825 \pm 9	20.5 \pm 0.6	23.13 \pm 0.93	40.24
Fluting_E + CNF	Yes	3	55	779 \pm 21	20.1 \pm 0.7	24.03 \pm 1.03	38.75

Table 4 Properties of the coated paper samples (effect of the different coating formulations on substrates with a single layer per side)

Substrate	Coating formulation	Basis weight (g/m ²)	Thickness (μm)	Density (g/cm ³)	Porosity (%)
Fluting	None	71.78 ± 0.72	135.42 ± 4.11	0.53	64.66
	CNF-T	72.13 ± 0.86	136.13 ± 3.06	0.53	64.68
	NS_CNF-T	75.11 ± 0.53	140.75 ± 4.58	0.53	64.42
	PVA	83.64 ± 0.74	143.89 ± 1.03	0.58	61.25
	CNF-T_PVA	80.66 ± 0.89	142.83 ± 3.49	0.56	62.35
	AKD	72.12 ± 0.91	138.12 ± 3.91	0.52	65.19
Fluting_E	None	72.20 ± 1.02	133.75 ± 4.71	0.54	64.01
	CNF-T	73.15 ± 0.69	132.98 ± 2.55	0.55	63.33
	NS_CNF-T	76.23 ± 0.85	141.91 ± 2.10	0.54	64.19
	PVA	84.57 ± 0.79	144.78 ± 4.84	0.58	61.06
	CNF-T_PVA	80.74 ± 0.61	141.11 ± 4.51	0.57	61.85
	AKD	73.09 ± 0.70	136.81 ± 3.12	0.53	64.38
Fluting_CNF	None	72.49 ± 0.39	124.33 ± 5.04	0.58	61.13
	CNF-T	73.09 ± 0.87	126.01 ± 3.55	0.58	61.33
	NS_CNF-T	74.16 ± 0.92	131.00 ± 1.03	0.57	62.26
	PVA	79.50 ± 1.09	133.11 ± 2.20	0.60	60.18
	CNF-T_PVA	77.68 ± 1.13	129.33 ± 1.57	0.60	59.96
	AKD	73.12 ± 0.93	128.61 ± 1.25	0.57	62.10
Fluting_E + CNF	None	73.01 ± 0.67	112.32 ± 0.97	0.65	56.67
	CNF-T	73.92 ± 0.84	113.39 ± 2.39	0.65	56.54
	NS_CNF-T	77.05 ± 0.95	128.22 ± 3.54	0.60	59.94
	PVA	78.20 ± 1.01	129.66 ± 1.87	0.60	59.79
	CNF-T_PVA	76.26 ± 0.98	126.22 ± 4.01	0.60	59.72
	AKD	74.05 ± 0.77	118.30 ± 3.94	0.63	58.27

CNF-E, the obtained paper porosities were much higher. The porosity of the substrate clearly affects the penetration of the CNF-T into the paper matrix and, as a consequence, their suitability to be used as coating agent and their impact on the paper mechanical properties, (Tarrés et al. 2016a). This effect can explain why when MFC is used, mechanical properties are not improved, even worsened (Lavoine et al. 2014).

The use of AKD increased porosity in all the substrates. This fact is completely understandable considering the hydrophobization effect of AKD as sizing agent [it blocks free hydroxyl groups, thus limiting the capacity of fibers to retain water as well as the fiber-to-fiber bonding, decreasing shrinkage forces between them and, at the same time, making the paper more porous (Lindström and Larsson 2008; Li et al.

2010)]. This paper “opening” effect of AKD was confirmed by FE-SEM (Fig. 2b). As discussed later, this effect can be beneficial for some surface properties (water contact angle), but it is expected to negatively affect barrier properties.

As visible in Table 4, the addition of CNF-T as coating agent, with or without NS, had no impact on paper density and on porosity (except when CNF-T and NS were applied on papers made of enzymatically refined fibers and density slightly decreased, may be due to an experimental error). However, when PVA was used (both containing CNF-T or not) the hand-sheets density increased significantly, meaning that the coating formulation perfectly penetrated into the paper structure. Nevertheless, in both cases, regardless the penetration of the coating formulation into the paper bulk, it became more closed, as depicted in

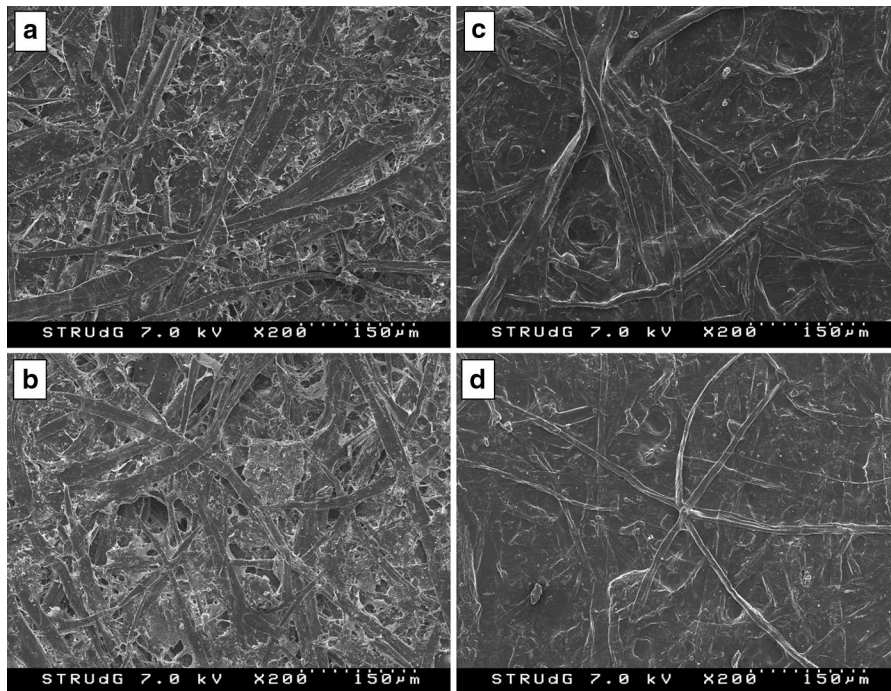


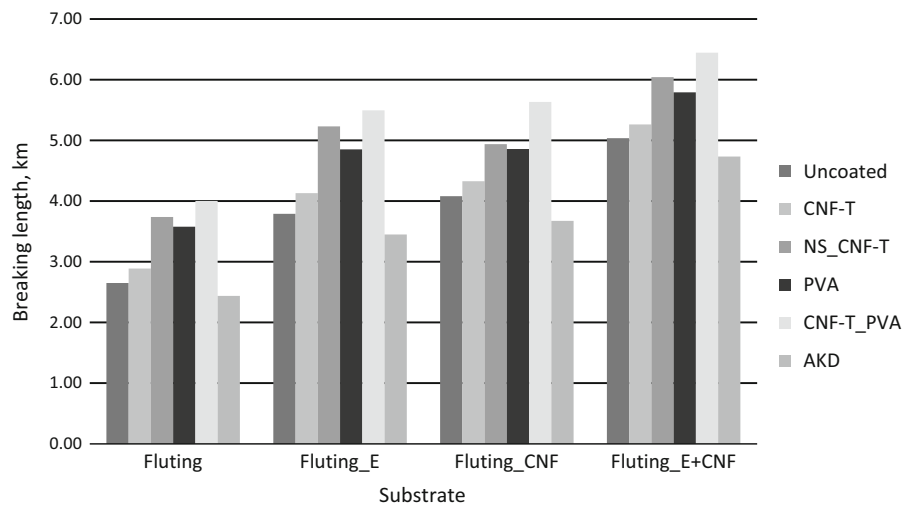
Fig. 2 FE-SEM images at large magnification of reference fluting paper **a** uncoated and coated with **b** AKD, **c** NS_CNF and **d** PVA. None of the papers contained CNF in bulk

Fig. 2. AKD was also used as second layer: those papers that were first coated with CNF-T, NS, PVA and their combinations, were subsequently coated with AKD. The basic properties were assessed and it was found that AKD increased the porosity of all substrates in at least 2%, mainly due to the aforementioned hydroxyl groups blocking effect.

The results of the breaking length of all samples are plotted in Fig. 3. As can be seen, the enzymatic refining increased this tensile property in 43%, the incorporation of 3 wt% of CNF-E in 54% and their combination (Fluting_E + CNF) in almost 95%, obtaining a final breaking length of 5042 m.

A positive effect of the enzymatic refining on brown-line papers, with the same magnitude, was

Fig. 3 Breaking length of single-coated and uncoated papers



already previously reported (Tarrés et al. 2017). For all paper substrates, the coating formulation CNF-T_PVA was the one leading to the higher tensile strength enhancement. This can be attributed mainly to two mechanisms: on the one hand, TEMPO-oxidized CNF have the ability to penetrate into the paper web and, thus, of increasing fiber-to-fiber bonding, as already reported elsewhere (Tarrés et al. 2016a); on the other hand, PVA is less viscous than NS, promoting the aforementioned penetration and, at the same time, due to its nature, imparting resistance to the fibrous matrix. The reinforcing capacity of PVA was corroborated by using it alone, leading to a breaking length increase of 35% in the case of the neat substrate and 15% in the case of the stronger substrate, the Fluting_E + CNF. The interesting point of increasing tensile strength of paper by means of coating different formulations is that there is no effect on pulp drainability, since it is a post-formation treatment. In this sense, it is possible to obtain fluting papers with 6.44 km of breaking length with a significantly small Schopper-Riegler degree. As expected, when AKD was coated to the prepared substrates, tensile strength was decreased, mainly due to the paper opening effect previously discussed.

Even though not being a good coating agent in terms of tensile properties enhancement, AKD is a good hydrophobizing agent, as well known, which creates ester groups on the cellulose chain. Table 5 shows the effect of coating AKD to uncoated and previously coated substrates in terms of water contact angle, 25 s after the drop deposition.

As expected, the uncoated papers were not able to stand the water drop on their surface due to their high hydrophilicity and porosity. The same result was obtained with the samples coated with PVA. This fact is understandable due to, the water-soluble character of PVA which, according to the supplier, was totally hydrolyzed. Interestingly, the use of NS in combination with CNF-T further improved the water contact angle of the substrates, in spite of the hydrophilic character of NS. Its use promoted the distribution and retention of the CNF-T on paper surface, generating a homogeneously distributed NS_CNF-T layer at paper's surface. The substitution of NS by PVA (coating formulation CNF-T_PVA) did not improve the water contact angle. In all cases, the results of the fluting substrates samples were significantly better than the one of the commercial paper.

Table 4 brings to the light the huge effect of coating paper with AKD: water contact angles close to 100° were obtained for all the not previously coated specimens. The same occurred when the substrate was coated before with PVA. Therefore, it is natural that the higher values correspond to those papers coated with CNF-T_PVA prior to AKD. In fact, the substrate that showed higher water contact angle was the one enzymatically treated and containing CNF in bulk using this coating sequence (115.38°). To understand this effect, two mechanisms need to be considered: on the one hand, the substrate itself presented lower porosity, limiting the penetration of CNF-T in the paper structure. On the other, due to this higher density, the coating formulation remained at the surface, creating a better distributed layer on the paper surface. In addition, as can be seen in Fig. 3, this paper, prior to AKD coating, showed 6.44 km of breaking length in an isotropic sheet former, where fibers are randomly oriented. Although AKD leads to a slightly decrease of the mechanical properties (close to 10% loss), one can expect that through the combination of enzymatic refining, CNF in bulk and a double coating of CNF-T_PVA plus AKD, fluting packaging papers with about 6 km of breaking length and a water contact angle of 115° can be obtained. It is true that this value can be easily achieved by using refined bleached kraft pulps and AKD coatings (extensively used at paper industry), but the use of recycled fluting, as in this study, promotes resources circularity, increasing the life span of the final product.

Similarly to the water contact angle, grease resistance was also determined using different kits (Table 6). It was found that grease resistance did not vary as function of the substrate. According to the supplier, PVA should exhibit a good performance in terms of grease resistance but better results were obtained with CNF-T and NS_CNF-T. Even though a value of 1 corresponds to a grease non-resistant paper.

Surprisingly, when CNF-T were combined with PVA, grease resistance was significantly increased. Although 3 is not a high value in the kit scale (maximum kit is 12) (Vaswani et al. 2005), the results reveal that a synergetic effect between both components of the coating formulation exists. Double-coated papers (second layer of AKD) were also submitted to grease resistance tests. As expected, the obtained papers showed poor grease resistance (kit 0), which is understandable since AKD has been extensively

Table 5 Water contact angle of the single and double coated substrates

Substrate	Coating formulation	Water contact angle (°)	
		No AKD	AKD coated
Commercial	None	16.37 ± 0.93	Not tested
	None	–	97.07 ± 5.09
	CNF-T	26.15 ± 1.74	103.12 ± 4.18
Fluting	NS_CNF-T	37.16 ± 3.21	108.66 ± 4.87
	PVA	–	99.60 ± 3.32
	CNF-T_PVA	38.87 ± 1.29	106.26 ± 3.21
Fluting_E	None	–	99.03 ± 3.10
	CNF-T	28.16 ± 2.51	101.30 ± 4.02
	NS_CNF-T	34.01 ± 4.53	106.88 ± 2.65
	PVA	–	98.19 ± 1.77
Fluting_CNF	CNF-T_PVA	38.10 ± 3.67	107.13 ± 1.54
	None	–	98.23 ± 2.97
	CNF-T	30.02 ± 2.87	102.69 ± 2.83
	NS_CNF-T	38.34 ± 4.68	107.28 ± 4.01
Fluting_E + CNF	PVA	–	100.13 ± 5.08
	CNF-T_PVA	39.04 ± 3.64	112.35 ± 3.42
	None	–	101.26 ± 2.87
	CNF-T	29.19 ± 2.96	106.25 ± 4.14
	NS_CNF-T	38.22 ± 3.94	110.51 ± 3.03
Fluting_E + CNF	PVA	–	104.39 ± 4.61
	CNF-T_PVA	38.46 ± 2.69	115.38 ± 3.40
	None	–	101.26 ± 2.87

Table 6 Grease resistance of single-coated substrates

Substrate	Coating formulation	Grease resistance (kit)
Commercial	None	0
	None	0
Fluting	CNF-T	1
Fluting_E	NS_CNF-T	1
Fluting_CNF	PVA	0
Fluting_E + CNF	CNF-T_PVA	3

reported to be effective for selective oil removal due to its high oil absorption capacity (Tarrés et al. 2016b). In addition, as observed in Fig. 2, papers are significantly more porous, fact that promotes the entrance of grease into the paper structure. Also for the commercial paper, as for the non-coated fluting, the kit value was 0.

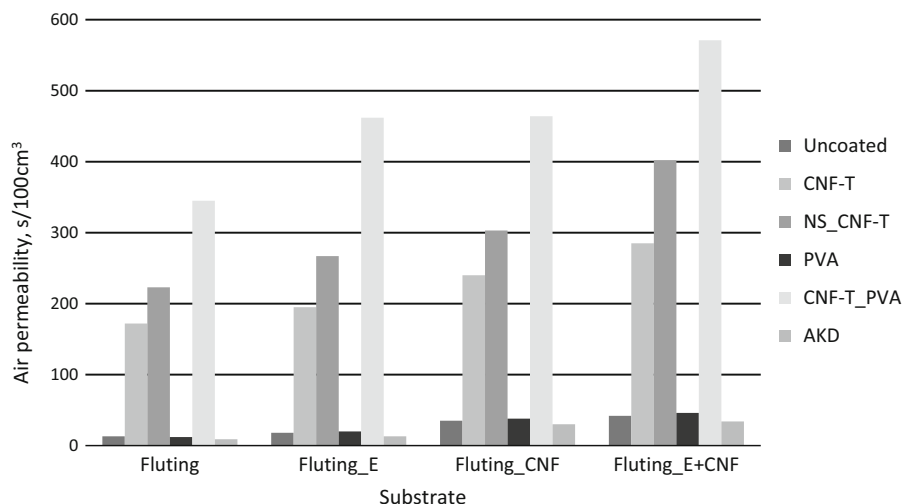
The air permeability results of both the coated and uncoated substrates are plotted in Fig. 4.

The neat fluting paper exhibits a high air permeability (13 s/100 cm³), in accordance with other works for similar basis weights (Balea et al. 2016). This permeability was slightly decreased with the

incorporation of CNF in bulk due to the increase of the shrinkage forces between fibers (generated by CNF) and the increase of paper density. The effect of enzymatic refining was even lower, mainly due to the lower effect on fiber morphology (Delgado-Aguilar et al. 2015c). As expected, the combination of both bulk treatments led to less porous papers and, thus, exhibiting lower air permeability.

The air permeability of both the commercial paper and the neat fluting paper was of the same: 14 s/100 cm³. When CNF-T formulation was used, air permeability was significantly decreased due to the aforementioned paper closing effect. This effect was

Fig. 4 Air permeability of single-coated and uncoated substrates



more pronounced when CNF-T were combined with NS (NS_CNF-T): values of 223 and 402 s/100 cm³ were obtained respectively for the Fluting paper and for the Fluting_E + CNF paper. The effect of PVA as coating, in terms of air permeability, was not significant, as in the case of water contact angle. However, when PVA was combined with CNF-T (CNF-T_PVA), air permeability was drastically decreased. This effect can be attributed to the already mentioned affinity between cellulose and PVA, leading to a extremely well bonded system able to cover the paper surface and penetrate into its structure (Tarrés et al. 2016a).

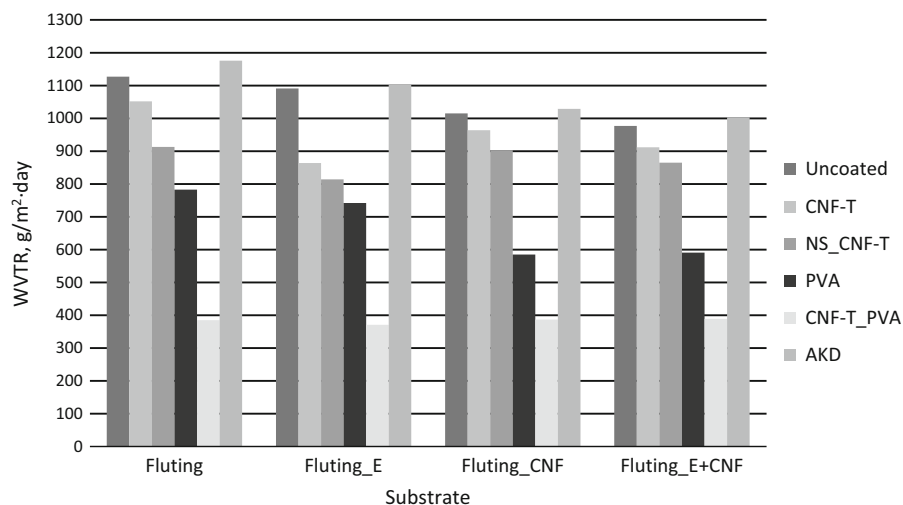
For the double-coated papers, it was found that the air permeability was slightly increased. As explained above, this is most certainly due to the fact that AKD

blocks the hydroxyl groups, which results in more porous structures.

Water vapor transmission rate (WVTR) of both single and double-coated papers was determined in order to assess their suitability to resist moisture (Fig. 5).

As expected, the use of CNF in bulk decreased the WVTR (from 1127 to 1015 g/m² day). This effect was also observed when the substrate was enzymatically refined. The incorporation of CNF-T significantly decreased the WVTR in all cases and, when they were combined with NS (NS_CNF-T) this effect was even more pronounced. However, PVA exhibited a better performance in terms of providing barrier to water vapor, since in all cases the WVTR was significantly lower than the one obtained both with CNF-T and

Fig. 5 Water vapor transmission rate (WVTR) of single-coated and uncoated substrates



NS_CNF-T. As for the other properties, the combination of CNF-T and PVA (CNF-T_PVA) was the one that, once coated on paper surface, had the best performance. In all cases, WVTR was lower than 400 g/m² day, while the uncoated substrates presented WVTR values from 977 to 1127 g/m² day. AKD was found to slightly increase the WVTR due to the hydroxyl groups blocking effect, as in the case of air permeability. Double-coated papers were also submitted to WVTR tests, showing that in all cases the amount of water passing through the paper increased in about 20%. Overall, enzymatically refined papers containing CNF in bulk and coated with CNF_T-PVA were those showing the best performance in terms of vapor barrier properties. The WVTR of the commercial paper was slightly smaller than that of the fluting paper (1083 g/m² day), most probably as a result of the lower paper porosity that can be achieved in a continuous paper machine and of the more homogeneous fiber orientation.

Conclusions

In this work, industrial fluting has been used as raw material for the development of four different substrates, enzymatically refined and/or containing cellulose nanofibers (CNF) in bulk. These four substrates were thoroughly studied and treated with different coating formulations with the purpose of evaluating the benefits of using fiber-based packaging paper with improved mechanical, physical and barrier properties. From the experiments, it can be concluded that the neat fluting paper exhibited poor mechanical properties (2.65 km of breaking length), high hydrophilicity, air permeability and WVTR. Enzymatic refining significantly improved the tensile properties of paper (43%), being this enhancement even higher when CNF were used in bulk: 54 and 90% for untreated and treated substrates, respectively. All coating formulations, except AKD, increased significantly the breaking length of the substrates, reaching unconceivable limits of tensile strength with such fibers. From all coating formulations, the one combining polyvinyl alcohol (PVA) and TEMPO-oxidized cellulose nanofibers (CNF-T) was that exhibiting better mechanical and barrier properties. Breaking length, air permeability, grease resistance and WVTR were significantly improved in all the substrates, especially in

those previously treated with enzymes and containing CNF in bulk. However, in terms of hydrophobicity, none of the coating formulations showed good performance unless they contained AKD. Nevertheless, AKD has been found to be detrimental for the abovementioned properties.

Overall, the present work shows how fluting grade paper, which is mainly composed by recycled fibers, can be used for high-performance packaging paper, with improved mechanical and barrier properties. This offers an opportunity of introducing such secondary fibers in high value-added market sectors, adding value to recovered paper and, thus, promoting circular economy.

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