

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 cellulose nanofibers, polyvinyl alcohol, 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 tensile properties of paper can be significantly improved if CNF are coated in combination with PVA, at the same time that grease resistance was improved, air permeability and water vapor transmission rate were decreased. The obtained papers presented interesting barrier properties to vapor and air, at the same time that unconceivable limits of breaking length were achieved (6.44 km). In addition, when a second layer of alkyl ketene dimer was coated on both sides of paper, water contact angle was significantly improved, being higher than 115°, although the rest of the properties were slightly worsened. Overall, the present work shows the feasibility of using recycled fibers for the production of high value-added papers that could be used for packaging purposes due to their improved barrier and mechanical properties, promoting bio-based economy and circularity of the resources.

Keywords: cellulose nanofibers; polyvinyl alcohol; recycled paper; packaging; barrier properties

1 Introduction

The CEPI roadmap to 2050 outlined that the key to a sustainable economy is a higher utilization of natural resources and, in addition, in a more efficient way. The world's population is increasing day by day, and, by 2050, we are expected to be more than 9 billion people in Earth. Taking into account that consumers' behavior depends on economics, resource constraints, technology, societal values, style of governance and planet's capacity to support its population and their lifestyles, 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

35 million tons in 2015, and it is expected to keep growing (CEPI 2016). This substantial growth mainly comes
36 from the environmental awareness of society, which is boosting the transition from a plastic to a fiber-based
37 society in the field of packaging. A proof of that is COST Action FP1405 (ActinPak), which aims at
38 developing knowledge-based network on sustainable, active and intelligent fiber-based packaging in order
39 to overcome current technological, industrial and societal limitations pursuing new market applications of
40 fiber-based packaging (COST 2014).

41 As a result of the increasing interest on fiber-based products and, especially, those produced from recovered
42 paper, the fibers quality is becoming exposed due to the current implemented processes to recover the
43 original properties of paper. In this sense, there is a clear need to adopt concurrent strategies to further
44 increase the efficiency of such processes. However, this can become a challenge if a certain level of
45 properties is required, thus, during recycling, dinking and refining, fibers experience structural damages
46 that need to be compensated with additional treatments. Not only this but, for further palliating resources
47 consumption, paper industries are adopting strategies to save resources, such as decreasing basis weights
48 of their products or increasing the mineral filler content, facts that decrease the final production cost (Hubbe
49 2014).

50 During the last decade, cellulose nanofibers (CNF) have appeared as high value-added product derived
51 from renewable resources, mainly composed by cellulose and hemicellulose, with improved properties with
52 respect to common cellulosic fibers and a wide range of applications (Henriksson et al. 2007; Isogai et al.
53 2011; Hii C. et al. 2012). Concretely, there is extensive literature on the use of CNF as paper strength
54 additive in bulk, where the advances of using this nanostructured cellulose-based additive is extensively
55 discussed in terms of mechanical, physical and barrier properties, besides increasing the life span of paper
56 products (Lavoine et al. 2012, 2014; Delgado-Aguilar et al. 2015c; Boufi et al. 2016). However, under the
57 premise that packaging sectors aims at moving from plastic to fiber-based products, several challenges need
58 to be addressed, especially barrier and mechanical properties. In addition, considering that Earth has a
59 limited capacity to supply cellulosic resources and world's population is increasing, this transition needs to
60 be performed considering that most of the paper needs to be recycled to assure a sustainable growth.

61 Fluting grade papers are mainly composed by recycled fibers. They are commonly used in corrugated
62 cardboard, which is very sensitive to atmospheric conditions (Allaoui et al. 2009), fact that limits its use
63 itself as packaging material. In fact, depending on the application, the high porosity of paper against plastic
64 limits the abovementioned transition.

65 For all the above, the aim of this work is to develop high-performance fluting-based papers by means of
66 using bulk treatments, such enzymatic refining and incorporation of CNF in bulk, and deposition of
67 different coating formulations based on CNF prepared by TEMPO-mediated oxidation in combination with
68 other coating compounds (native starch, alkyl ketene dimer and polyvinyl alcohol) to further improve its
69 behavior in terms of barrier, mechanical and surface properties.

70 **2 Materials and methods**

71 Fluting paper was kindly provided by Saica S.A. (Spain) and bleached kraft eucalyptus pulp (BKEP), the
72 raw material for the production of cellulose nanofibers (CNF), was supplied by ENCE Energía y Celulosa
73 (Spain). Polyvinyl alcohol (Kuraray POVAL 4-98) was provided by Archroma (Spain) and it was totally
74 hydrolyzed. Native starch, colloidal silica, cationic starch and alkyl ketene dimer (AKD) were provided by

75 Torraspapel, S.A. (Spain). Endo- β -1,4-glucanases (Serzym 50) was supplied by SERTEC-20 S.L. (Spain),
76 with an activity of 84,000 CMU/g at 60 °C at pH of 4.8 over a carboxymethylcellulose (CMC) substrate,
77 and were used for enzymatic refining treatment. All chemicals for CNF production and characterization
78 were provided by Sigma Aldrich (Spain) and were used as received, except for Novozym 476, which was
79 provided by Novozymes A/S (Denmark), containing 2 % of endo- β -1,4-glucanases with an activity factor
80 of 4500 CNF-CA/g of cellulose, also tested over a CMC substrate.

81 **2.1 Cellulose nanofibers production**

82 Cellulose nanofibers were prepared by TEMPO-mediated oxidation. Prior to CNF production, the BKEP
83 was first disintegrated by means of a laboratory pulper at 3000 rpm during 30 minutes, and then refined in
84 a PFI mill for 4000 revolutions to promote fiber swelling and fibrillation (Zimmermann et al. 2010).
85 TEMPO-mediated oxidation was performed at 15 mmol of sodium hypochlorite per gram of fiber,
86 following a methodology reported elsewhere (Saito and Isogai 2004). This oxidation degree was selected
87 due to previous experimentation, where the incorporation of such CNF significantly improved mechanical
88 properties of paper when they were applied as coating (Tarrés et al. 2016a). Briefly, 15 g of BKEP were
89 dispersed in distilled water containing TEMPO (0.016 g per g of fibers) and NaBr (0.1 g per gram of fibers)
90 at room temperature. The mixtures was kept under stirring for 15 minutes to ensure good dispersion of all
91 the substances. Then, 15 % NaClO solution was added dropwise to the slurry, keeping the pH at 10. Once
92 all the NaClO had been added, pH was maintained through the dropwise addition of a 0.5 M NaOH solution.
93 The oxidation was considered to be finished when pH remained constant at 10 without the incorporation of
94 any oxidant. The reaction took about 5 hours. The oxidized fibers were washed with distilled water and
95 kept at 4 °C for further use. These CNF were only added as coating, and not in bulk. They were referenced
96 as CNF-T.

97 Enzymatic hydrolysis was carried out according to a methodology reported elsewhere (Henriksson et al.
98 2007) but changing several parameters (Tarrés et al. 2016c). BKEP was dispersed at 1.5 wt% consistency
99 in water in a laboratory pulper for 30 min at 3000 rpm. Then, the fibers were filtered until 10 wt%
100 consistency and refined in a PFI mill for 4000 revolutions. This process was carried out to swell the fibers
101 and thus to promote the activity of enzymes. Briefly, refined fibers were suspended in water again (until
102 reaching a pulp consistency of 5 wt%), and 0.1 N HCl was dropped until achieving a pH of 5. Then, the
103 suspension was heated until 50 C under constant stirring to avoid temperature gradients. At this step, the
104 enzyme cocktail was dropped into the suspension and stirred for 4 h. The enzymatic process was stopped
105 by heating the suspension to 80 C for 15 min, where the enzyme activity is strongly decreased (De Marco
106 and Felix 2007). Enzyme dosage was set at 160 g/Tn. The enzymatically hydrolyzed pulp then was washed
107 with distilled water and kept at 4 C. These CNF were only added in bulk, and not as coating agent. They
108 were referenced as CNF-E.

109 Once fibers had been pretreated, they were subjected to high-pressure homogenization in a Panda Plus 2000
110 homogenizer from Gea Niro Soavi (Italy) following the sequence of 3 times at 300 bar, 3 times at 600 bar
111 and 3 times at 900 bar. This sequence has been previously reported to avoid clogging in the pressure
112 chambers of the homogenizer (Tarrés et al. 2016b).

113 **2.2 Cellulose nanofibers characterization**

114 Cationic demand of the CNF suspension, understood as the amount of highly charged cationic polymer
115 required to neutralize CNF surface, was measured using a Mütek PCD 04 particle charge detector from

116 BTG International Ltd (United Kingdom). For this, CNF were first dispersed in a poly-DADMAC solution
117 and the excess was titrated with PES-Na, an anionic standard polymer, both supplied by BTG. The carboxyl
118 content was determined by ionic exchange between two defined pHs. This methodology is based on the
119 ionic exchange that takes place between carboxylic groups from cellulose and zinc cations from an aqueous
120 suspension. Yield of fibrillation was determined by centrifugation (4500 rpm, 20 min) of a 0.1 wt% aqueous
121 CNF suspension. The individual CNF were found in the supernatant, whereas non-fibrillated and partially
122 fibrillated material remained in the precipitate at the bottom of the vessel. The degree of polymerization
123 (DP) of the oxidized cellulose fibers was determined from intrinsic viscosity measurements, according to
124 the existing bibliography. The viscosimetric average molecular weight was calculated according to
125 previously published works (Henriksson et al. 2007). Transmittance was determined of a 0.1 wt% CNF
126 suspension using a Shimadzu UV-160A ultraviolet-visible (UV-Vis) spectrophotometer.

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

136 **2.3 Preparation of the fluting paper sheets**

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

144 On the other hand, enzymatic refining was carried out according to a methodology reported elsewhere
145 (Delgado-Aguilar et al. 2015d). In a typical experiment, 75 dry g of 5 wt%-consistency pulp was stirred
146 and heated at 65 °C. The pH was set at 4.8 by the addition of diluted HCl solution. At this point, enzymes
147 solution (350 g/Tn of dried pulp) were added to the slurry, and stirring was continued for 30 min. The
148 enzymatic reaction (hydrolysis) was stopped by heating the suspension at 80 °C, as reported elsewhere
149 (Henriksson et al. 2007). The resulting enzyme-treated pulp was finally washed with distilled water to
150 eliminate remaining enzyme and reagents.

151 Paper sheets were prepared in a Rapid-Köthen sheet former (ISP mod. 786FH) according to ISO standard
152 5269-2 and conditioned at 23 °C and 50 % of relative humidity for 48 h before testing.

153 **2.4 Coating of the paper sheets**

154 Four different agents were used for the preparation of the coating formulations: i) CNF-T, ii) Native starch,
 155 iii) PVA and iv) AKD. Several coating formulations were prepared by the combination of these agents, as
 156 it is reflected in Table 1.

157 **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

158
 159 Coating formulations were prepared by means of dispersion in an Ultraturrax T25 (IKA, Germany) at
 160 20,000 rpm during 60 seconds. Then, suspensions were dispersed using a sonicator Q700 for 10 min (5 min
 161 pulse on, 2 min pulse off, and 5 min pulse on) at 60 % of amplitude to remove any air bubble.

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



167
 168 **Figure 1.** Schematic illustration of the structure of coated papers

169 After depositing each coating layer, paper was air-dried to promote formulations deposition. After coating
 170 all the desired layers, paper was submitted to vacuum-drying and conditioned at 23 °C and 50 % of relative
 171 humidity before testing.

172 **2.5 Recycled pulp and paper characterization**

173 Pulp suspensions were characterized by means of Schopper – Riegler degree (°SR) following ISO 5267-1
 174 standard and morphological analysis (length, diameter and fines), carried out by using a MorFi Compact
 175 analyzer (TechPap, France).

176 Paper characterization was performed by determining: (i) basic properties: basis weight (ISO 536),
 177 thickness (ISO 534), density, porosity and morphology by FE-SEM; (ii) mechanical properties: breaking
 178 length at constant elongation rate (ISO 1924-2); (iii) barrier properties: water vapor transmission rate

179 (WVTR) (TAPPI T448), Gurley porosity (ISO 5636-5); and (iv) surface properties: water contact angle and
180 grease resistance (TAPPI T559).

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

189 **3 Results and discussion**

190 TEMPO-catalyzed oxidation has been extensively reported as an effective method for the production of
191 cellulose nanofibers with unique properties, clearly superior in several aspects to other CNF prepared by
192 alternative methods (Delgado-Aguilar et al. 2015a). In addition, such oxidative method also leads to shorter
193 CNF, fact that makes them suitable to be used as coating agent in papermaking due to their capability to
194 penetrate in the paper structure (Tarrés et al. 2016a). Table 2 shows the main characteristics of the prepared
195 CNF, which were subsequently coated on paper surfaces in combination with the rest of coating agents.

196 **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)

Carboxyl content (CC); Cationic demand (CD); Specific surface (σ); Diameter (d); Transmittance (T at 800 nm); Degree of Polymerization (DP)

197

198 The obtained CNF-T presented a carboxyl content of 1526 $\mu\text{eq-g/g}$, indicating that the
199 TEMPO/NaBr/NaClO oxidation in water at basic pH effectively oxidized C6 primary hydroxyl groups of
200 cellulose to C6 carboxylate groups, which could be either in its acidic or salt form, depending on the pH
201 after fiber washing (Isogai et al. 2011). This high amount of carboxylate groups promoted fibers' fibrillation
202 after TEMPO-catalyzed oxidation, apart from introducing several anionic and voluminous groups, leading
203 to a high cationic demand. This fact significantly increased the specific surface of the obtained CNF,
204 obtaining values of 347.2 m^2/g . If these CNF are assumed as perfect cylinders, which are not, a diameter of
205 7.7 nm can be calculated. TEMPO-mediated oxidation is also known for the depolymerization that imparts
206 on cellulose chains that, according to Shinoda and collaborators (Shinoda et al. 2012), has a direct
207 relationship with CNF length. Indeed, high oxidation degrees lead to shorter CNF, promoting thus the
208 penetration thereof in the paper web structure when they are used as coating (Tarrés et al. 2016a). Their
209 penetration into the paper structure is interesting mainly due to two aspects: one the one hand, if they
210 interact with paper fibers, they will impart some mechanical properties improvement and, on the other,
211 barrier and surface properties.

212 Comparatively, CNF-E showed lower carboxyl groups content, as expected, and lower cationic demand as
 213 well. In fact, the characteristics of CNF-E are significantly lower than CNF-T, except for aspect ratio.
 214 Indeed, CNF-E presented about twice the aspect ratio of CNF-T, mainly due to their higher length. In this
 215 sense, while it is true that they are much longer to be used as coating, they present potential application as
 216 reinforcing agent in paper bulk, since they have lower water retention capacity, higher aspect ratio and more
 217 competitive production costs (Tarrés et al. 2016c). As expected, specific surface was much lower than CNF-
 218 T.

219 Recycled fluting pulps were obtained by means of disintegration and several treatments were applied. A
 220 total of four different pulps were used for paper production, as reflected in Table 3, together with their basic
 221 characterization.

222 **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 ± 12	20.9 ± 0.3	13.45 ± 1.10	40.38
Fluting_E	YES	0	40	768 ± 18	19.8 ± 1.2	14.05 ± 0.72	38.78
Fluting_CNF	NO	3	54	825 ± 9	20.5 ± 0.6	23.13 ± 0.93	40.24
Fluting_E+CNF	YES	3	55	779 ± 21	20.1 ± 0.7	24.03 ± 1.03	38.75

223
 224 The reference pulp presented 41 °SR, a typical value for brown-line recycled pulps (Biricik and Atik 2012;
 225 Moral et al. 2017). When this pulp was enzymatically refined, drainability was kept almost constant with
 226 no significant changes in fibers' morphology, since length was merely decreased from 844 to 768 µm. This
 227 effect was also observed in previous works (Delgado-Aguilar et al. 2015d). The incorporation of CNF-E
 228 into the pulp slurry significantly decreased the pulp drainability, due to the higher specific surface of CNF
 229 compared to fluting fibers. This higher specific surface, as expected, confers them the ability to retain more
 230 water and, thus, increases the drainage time of the pulp slurry. The addition of such CNF-E into the pulp
 231 slurry did not affect the length and diameter of the fibers, but increased the amount of fines. This is
 232 understandable, insomuch as MorFi equipment is not able to detect fibers in the nanoscale. However, taking
 233 into account the fibrillation yield of CNF-E (Table 2), the increase on fine elements was something
 234 expected.

235 The different pulps were used for the production of isotropic papers, as described in the previous section.
 236 Each paper was used as substrate for the different coating formulations (Table 1) and basic properties such
 237 as basis weight, thickness, density and porosity were determined. Table 3 shows the basic properties of
 238 those papers having a single layer per paper side.

239 **Table 3.** Effect of different coating formulations on the prepared substrates

Substrate	Coating formulation	Basis weight (g/m²)	Thickness (µm)	Density (g/cm³)	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
	None	72.20 ± 1.02	133.75 ± 4.71	0.54	64.01
Fluting_E	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
	None	72.49 ± 0.39	124.33 ± 5.04	0.58	61.13
Fluting_CNF	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
	None	73.01 ± 0.67	112.32 ± 0.97	0.65	56.67
Fluting_E+CNF	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
	None				

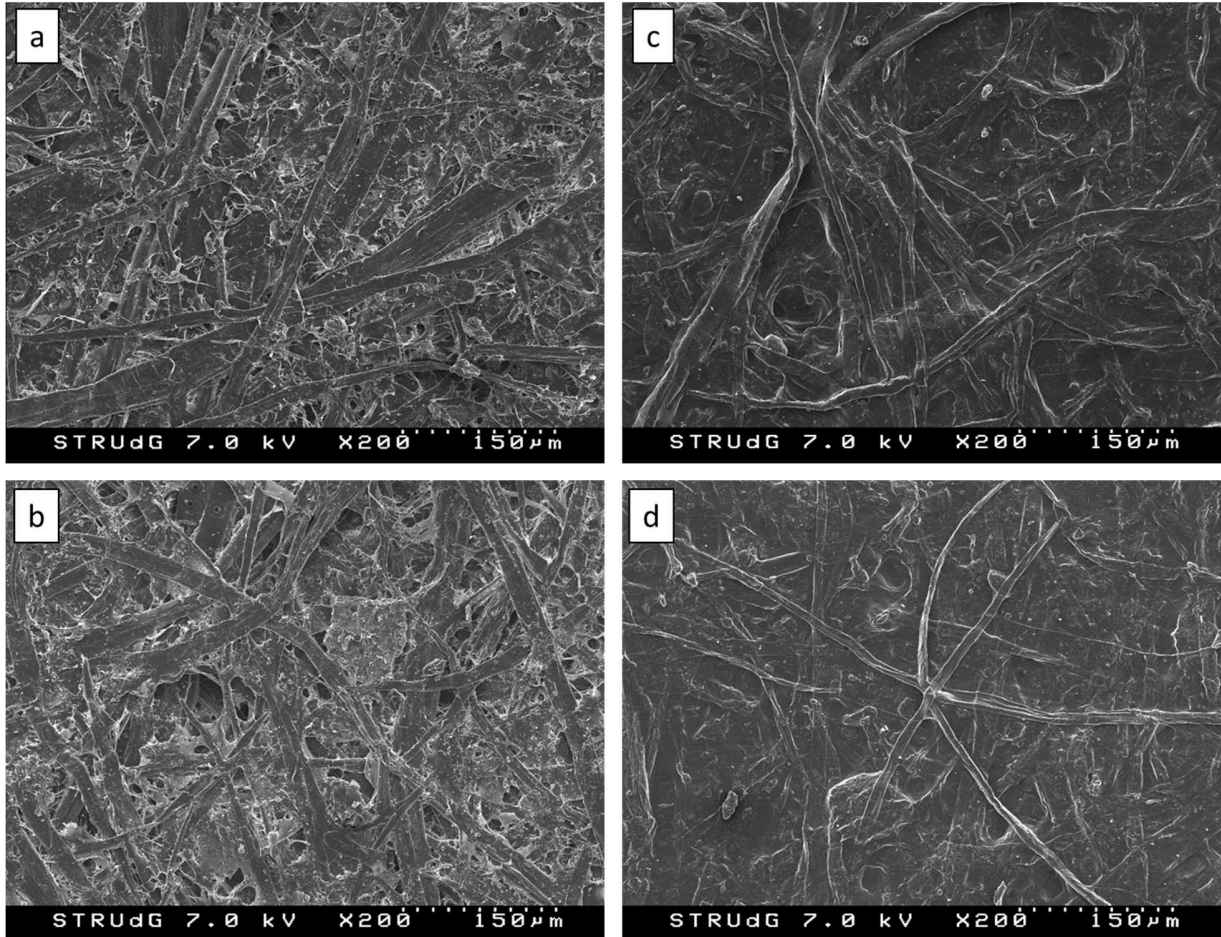
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241 Comparing the uncoated papers, it is possible to see that the incorporation of CNF-E in bulk in paper
242 substrates significantly increased their density, making them less porous. This effect has been extensively
243 reported and it is attributed to the higher specific surface of CNF-E (compared to fibers in the paper
244 substrate), at the same time that shrinkage inter-fiber forces take place. On the other hand, when analyzing
245 the effect of enzymatic refining, no significant changes can be observed in terms of density. However, when
246 CNF-E were added to the enzymatically treated fibers, the resulting papers presented a significantly lower
247 porosity, showing that paper pores were more closed. The porosity of the substrate clearly affects the
248 suitability of using CNF-T as coating agent, since they will limit the penetration thereof into the paper
249 structure (Tarrés et al. 2016a). The penetration of CNF-T into the paper structure will improve the
250 mechanical properties thereof because of their ability to generate new hydrogen bonds between fibers
251 (Tarrés et al. 2016a). This effect can explain why when microfibrillated cellulose (MFC) is used,
252 mechanical properties are not improved, even worsened (Lavoine et al. 2014).

253 The use of AKD increased porosity in all the substrates. Taking into account the hydrophobization
254 mechanism of AKD, this effect is completely understandable. AKD is commonly used as sizing agent in
255 papermaking industry, improving paper printability and water resistance. The incorporation of AKD,
256 indeed, blocks free hydroxyl groups, limiting thus the capacity of fibers to retain water. At the same time,
257 this effect is also limiting the creation of inter-fiber bonds, decreasing shrinkage forces between them and,
258 at the same time, making the paper more porous (Lindström and Larsson 2008; Li et al. 2010). This paper
259 “opening” effect was also observed by FE-SEM, where a more porous structure becomes apparent (Figure

260 2). Although this will be discussed later, this effect can be beneficial for surface properties (water contact
261 angle), but it is expected to negatively affect barrier properties.

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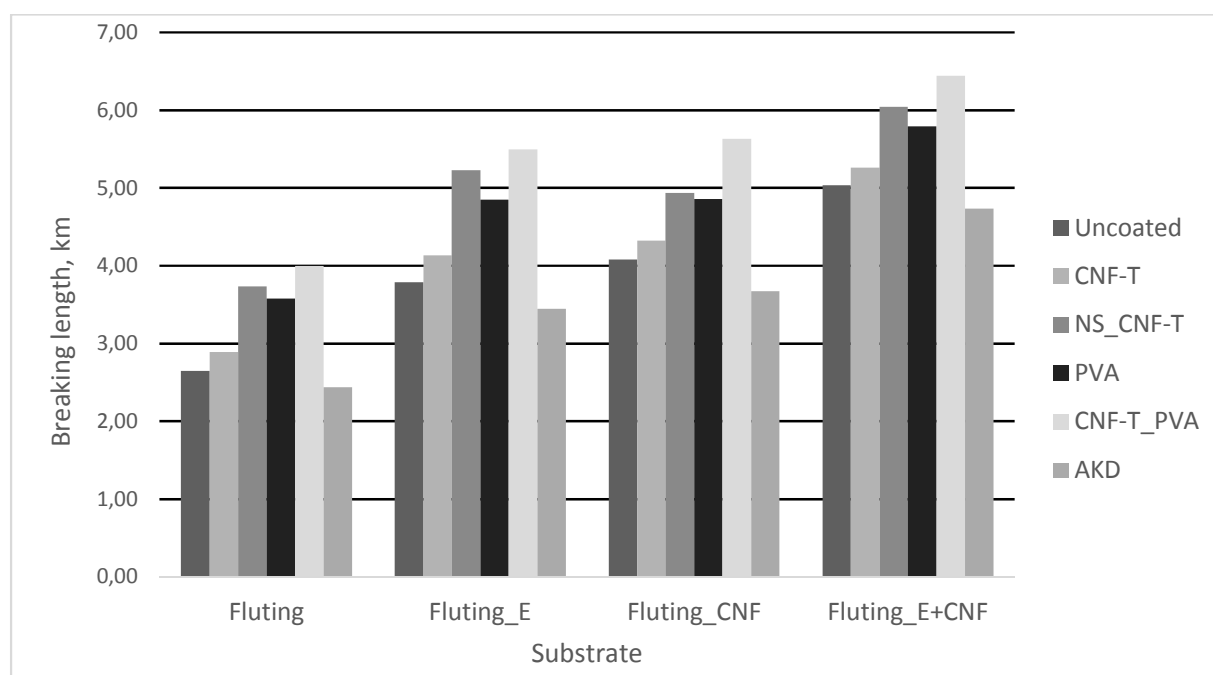


263

264 **Figure 2.** FE-SEM images at large magnification of reference fluting paper (a) uncoated and coated with
265 (b) AKD, (c) NS_CNF and (d) PVA

266 In terms of basic properties, the addition of CNF-T as coating, both in presence of NS and not, did not vary
267 neither paper density nor porosity. However, when PVA was used (both containing CNF-T and not) density
268 experienced a significant increase, meaning that the coating formulation perfectly penetrated into the paper
269 structure. Nonetheless, in both cases, regardless the coating formulation penetrated into the paper structure
270 or not, paper became more closed, as it is reflected in Figure 2. AKD was also used as second layer, meaning
271 that those papers that were first coated with CNF-T, NS, PVA and their combinations, where subsequently
272 coated with AKD. Basic properties were assessed and it was found that AKD increased the porosity of all
273 substrates in at least 2 %, mainly due to the aforementioned hydroxyl groups blocking.

274 The obtained papers, both coated and not, were tested at tensile. The results (Figure 3) showed that
275 enzymatic refining increased breaking length in 43 %, the incorporation of 3 wt% of CNF-E in 54 % and
276 their combination (Fluting_E+CNF) in almost 95 %, obtaining a final breaking length of 5042 m.



277

278

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

279 The effect of enzymatic refining on brown-line papers has been previously reported, and the obtained
 280 enhancement was of the same magnitude (Tarrés et al. 2017). The coating formulation CNF-T_PVA was,
 281 in all cases, the one that improved higher tensile strength enhancement of paper. This effect can be attributed
 282 mainly to two mechanisms: on the one hand, TEMPO-oxidized CNF have been reported to have the ability
 283 to penetrate into the paper web and, thus, creating new inter-fiber bonds (Tarrés et al. 2016a). On the other,
 284 PVA was less viscous than NS, promoting the mentioned penetration and, at the same time, due to the
 285 nature of the used polymer, imparting resistance to the paper. The reinforcing capacity of PVA was
 286 corroborated by using it as coating formulation, leading to a breaking length increase of 35 % when it was
 287 coated over the neat substrate and 15 % in the case of the stronger substrate, the Fluting_E+CNF. The
 288 interesting point of increasing tensile strength of paper by means of coating different formulations is that
 289 there is no effect on pulp drainability, since it is a post-formation treatment. In this sense, it is possible to
 290 obtain fluting papers with 6.44 km of breaking length with significantly lower Schopper – Riegler degree.
 291 As expected, when AKD was coated to the prepared substrates, tensile strength was decreased, mainly due
 292 to the paper opening effect previously discussed.

293 Even though AKD seems not to be a good candidate to be coated on paper substrates in terms of properties
 294 enhancement, it is interesting due to its hydrophobization capacity by means of the creation of esters on the
 295 cellulose chain. Table 4 shows the effect of coating AKD to uncoated and previously coated substrates in
 296 terms of water contact angle after 25 seconds of the drop deposition.

297

Table 4. Water contact angle of the single and double coated substrates

Substrate	Coating formulation	Water contact angle (°)	
		No AKD	AKD coated
Fluting	None	-	97.07 ± 5.09

	CNF-T	26.15 ± 1.74	103.12 ± 4.18
	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
	None	-	99.03 ± 3.10
Fluting_E	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
	CNF-T_PVA	38.10 ± 3.67	107.13 ± 1.54
	None	-	98.23 ± 2.97
Fluting_CNF	CNF-T	30.02 ± 2.87	102.69 ± 2.83
	NS_CNF-T	38.34 ± 4.68	107.28 ± 4.01
	PVA	-	100.13 ± 5.08
	CNF-T_PVA	39.04 ± 3.64	112.35 ± 3.42
	None	-	101.26 ± 2.87
Fluting_E+CNF	CNF-T	29.19 ± 2.96	106.25 ± 4.14
	NS_CNF-T	38.22 ± 3.94	110.51 ± 3.03
	PVA	-	104.39 ± 4.61
	CNF-T_PVA	38.46 ± 2.69	115.38 ± 3.40

298

299 As expected, those uncoated substrates were not able to stand the water drop on their surface due to their
300 high hydrophilicity and porosity. In addition, those coated with PVA also presented 0 ° of water contact
301 angle. This fact is understandable due to, first, the nature of the cellulosic fibers used for the formation of
302 the substrate and, second, the water-soluble character of PVA which, according to the supplier, was totally
303 hydrolyzed. Interestingly, the use of NS in combination with CNF-T further improved the water contact
304 angle of the substrates. Although the hydrophilicity of NS, its use promoted the distribution and retention
305 of the CNF-T on paper surface, generating a homogeneously distributed NS_CNF-T layer at paper's
306 surface. The substitution of NS by PVA (coating formulation CNF-T_PVA) did not improved the water
307 contact angle, meaning that, apparently, both had the function of promoting CNF-T distribution.

308 Table 4 brings to the light the huge effect of coating AKD on paper surfaces, thus those papers that were
309 not previously coated exhibited water contact angles around 100 ° in all cases. The same occurred when the
310 substrate had been previously coated with PVA. From all the above results, it comes that those papers
311 exhibiting higher water contact angle were those coated with CNF-T_PVA prior to AKD. In fact, the
312 substrate that showed higher water contact angle was the one enzymatically treated and containing CNF in
313 bulk using this coating sequence (115.38 °). To understand this effect, two mechanisms need to be
314 considered: on the one hand, the substrate itself presented lower porosity, limiting the penetration of CNF-
315 T in the paper structure. On the other, due to this higher density, the coating formulation probably remained
316 at the surface, creating a better distributed layer along the paper surface. In addition, as it can be seen in
317 Figure 3, this paper, prior to AKD coating, showed 6.44 km of breaking length in an isotropic sheet former,
318 where fibers are randomly oriented. While it is true that it has been found that AKD slightly decreases
319 mechanical properties, this effect can be quantified in a 10 % loss. Thus, one can expect that through the
320 combination of enzymatic refining, CNF in bulk and a double coating of CNF-T_PVA plus AKD, fluting

321 packaging papers with about 6 km of breaking length and a water contact angle of 115 ° can be obtained.
322 While it is true that this value could be easily achieved by means of using mechanically refined bleached
323 kraft pulps and AKD coating (extensively used at paper industry), the use of recycled fluting promotes
324 resources circularity, increasing the life span of the final product.

325 As in the case of water contact angle, grease resistance was also determined using different kits (Table 4).
326 It was found that grease resistance did not vary as function of the substrate. According to the PVA supplier,
327 the selected PVA should exhibit good performance in terms of grease resistance but, according to the
328 obtained results, CNF-T and NS_CNF-T were significantly better. However, a value of 1 is extremely low,
329 which means that these papers could be considered as grease non-resistant.

330 **Table 4.** Grease resistance of single-coated substrates

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

331
332 Surprisingly, when CNF-T were combined with PVA, grease resistance was significantly increased.
333 Although kit 3 is not much high (maximum kit is 12) (Vaswani et al. 2005), the obtained results bring to
334 the light that exists a synergetic effect between both components of the coating formulation. Double-coated
335 papers (second layer of AKD) were also submitted to grease resistance kit. As expected, the obtained papers
336 showed poor grease resistance, obtaining a value of 0 for all of them. This fact is understandable, thus the
337 use of AKD has been extensively reported to be effective for selective oil removal due to its high oil
338 absorption capacity (Tarrés et al. 2016b).

339 Air permeability of the obtained substrates, both coated and not, was also determined, leading to the results
340 shown in Figure 3.

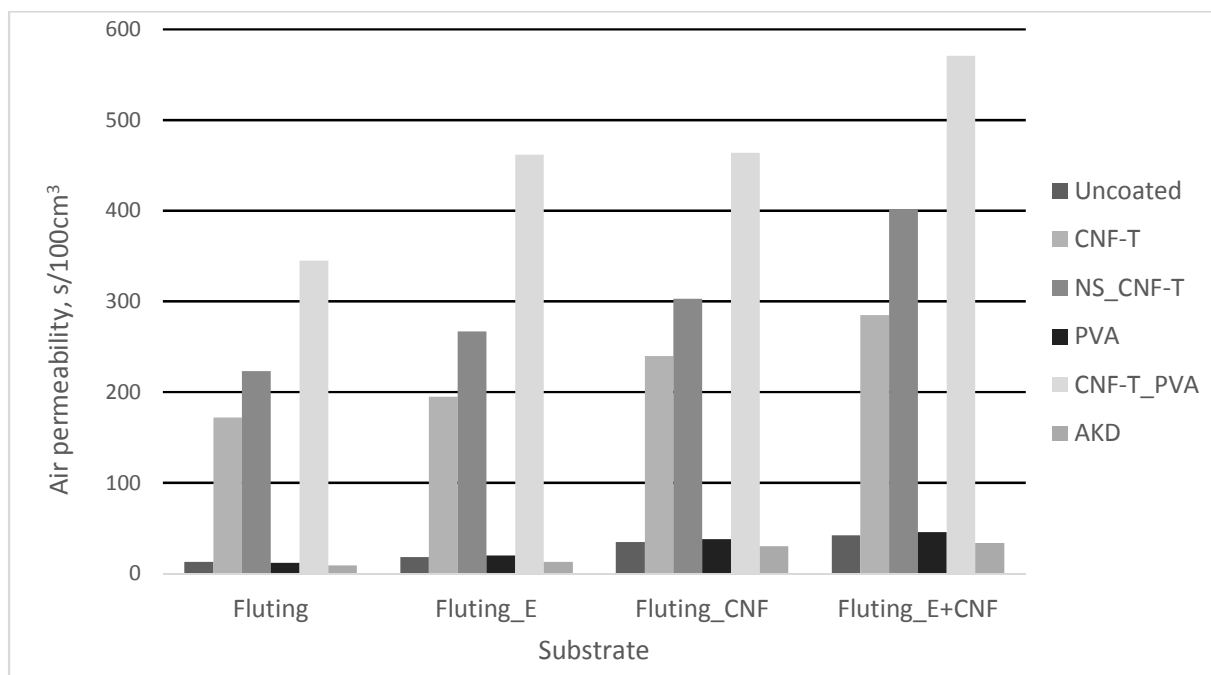


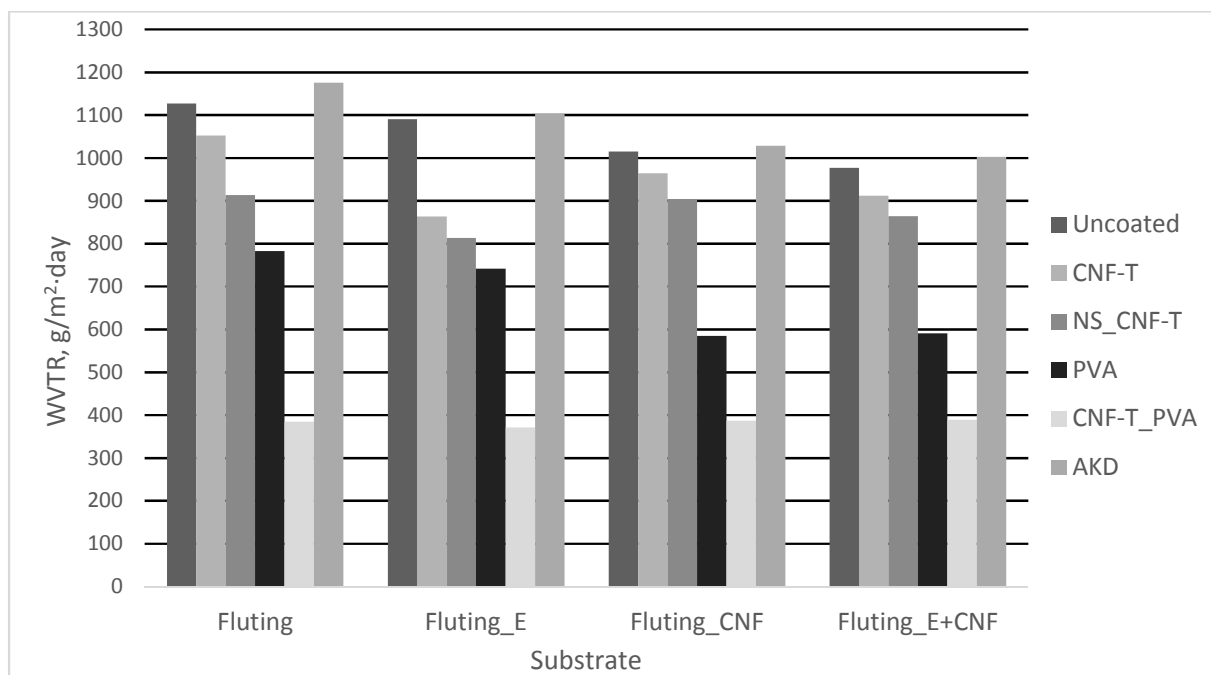
Figure 3. Air permeability of single-coated and uncoated substrates

The neat fluting paper exhibited high air permeability (13 s/100 cm³), as reported in previous 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 on paper density. The effect of enzymatic refining was even lower, mainly due to the lower effect on fiber morphology that generates (Delgado-Aguilar et al. 2015d). As expected, the combination of both bulk treatments let to less porous papers and, thus, exhibiting lower air permeability.

When CNF-T formulation was used, air permeability was significantly decreased due to the aforementioned paper closing effect. This effect was more pronounced when CNF-T were combined with NS (NS_CNF-T), obtaining values of air permeability from 223 (Fluting) to 402 s/100 cm³ (Fluting_E+CNF). The effect of PVA formulation as coating, in terms of air permeability, was not significant, as in the case of water contact angle. However, when this formulation was combined with CNF-T (CNF-T_PVA), air permeability was drastically decreased, increasing significantly the required time to pass 100 cm³ of air. This effect, as in the case of breaking length, can be attributed to the affinity between cellulose and PVA, leading to a extremely well bonded system (mainly due to hydrogen bonding) able to cover the paper surface and penetrate into its structure (Tarrés et al. 2016a).

In the case of double-coated papers, it was found that air permeability was slightly increased. As explained above, this effect could be understood by the fact AKD blocks hydroxyl groups, leading to more porous structures and, thus allowing the pass of air through the substrate.

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



363

364

Figure 4. Water vapor transmission rate (WVTR) of single-coated and uncoated substrates

365 As expected, the use of CNF in bulk decreased the WVTR (from 1127 to 1015 g/m²·day). This effect was
 366 also observed when the substrate was enzymatically refined. The incorporation of CNF-T significantly
 367 decreased the WVTR in all cases and, when they were combined with NS (NS_CNF-T) this effect was even
 368 more pronounced. However, PVA exhibited better performance in terms of providing barrier to water vapor,
 369 since in all cases the WVTR was significantly lower than the one obtained both with CNF-T and NS_CNF-
 370 T. As in the rest of the evaluated properties, the combination of CNF-T and PVA (CNF-T_PVA) was the
 371 one that, once coated on paper surface, had the best performance. In all cases, WVTR was lower than 400
 372 g/m²·day, while the uncoated substrates presented WVTR values from 977 to 1127 g/m²·day, meaning that
 373 it was decreased in about 60 %. AKD was found to slightly increase the WVTR due to the hydroxyl groups
 374 blocking, as in the case of air permeability. Double-coated papers were also submitted to WVTR tests,
 375 showing that in all cases the amount of water that passed through the paper increased in about 20 %. Overall,
 376 enzymatically refined papers containing CNF in bulk and coated with CNF_T-PVA showed the best
 377 performance in terms of vapor barrier.

378 4 Conclusions

379 In this work, industrial fluting has been used as raw material for the development of four different
 380 substrates, enzymatically refined and/or containing cellulose nanofibers (CNF) in bulk. These four
 381 substrates have been deeply studied and treated with different coating formulations with the purpose of
 382 evaluating the benefits of using fiber-based packaging paper with improved mechanical, physical and
 383 barrier properties. From the experimentation, it can be concluded that the neat fluting paper exhibited low
 384 mechanical properties (2.65 km of breaking length), high hydrophilicity degree, air permeability and
 385 WVTR. Enzymatic refining significantly improved the tensile properties of paper (43%), being this
 386 enhancement even higher with the incorporation of CNF in bulk, 54 and 90% for untreated and treated

387 substrates, respectively. All the coating formulations, except AKD, significantly increased the breaking
388 length of the substrates, reaching unconceivable limits of tensile strength with such fibers. From all the
389 coating formulations, the one combining polyvinyl alcohol (PVA) and TEMPO-oxidized cellulose
390 nanofibers (CNF-T) was the one that exhibited better properties, both mechanical and barrier. Breaking
391 length, air permeability, grease resistance and WVTR was significantly improved in all the substrates, with
392 special effect in those substrates previously enzymatically treated and containing CNF in bulk. However,
393 in terms of hydrophobicity, none of the coating formulations showed good performance unless they were
394 combined with AKD. However, the use of AKD has been found to be detrimental for the abovementioned
395 properties.

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

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403 **References**

- 404 Allaoui S, Aboura Z, Benzeggagh ML (2009) Effects of the environmental conditions on the mechanical
405 behaviour of the corrugated cardboard. *Compos Sci Technol* 69:104–110. doi:
406 10.1016/j.compscitech.2007.10.058
- 407 Balea A, Blanco Á, Monte MC, et al (2016) Effect of Bleached Eucalyptus and Pine Cellulose Nanofibers
408 on the Physico-Mechanical Properties of Cartonboard. *BioResources* 11:8123–8138.
- 409 Biricik Y, Atik C (2012) Effect of cellulase treatment of long fiber fraction on strength properties of
410 recycled corrugated medium. 11:12199–12205. doi: 10.5897/AJB12.506
- 411 Boufi S, González I, Delgado-Aguilar M, et al (2016) Nanofibrillated cellulose as an additive in
412 papermaking process: A review. *Carbohydr Polym* 154:151–166. doi:
413 10.1016/j.carbpol.2016.07.117
- 414 CEPI (2011) The Forest Fibre Industry: 2050 Roadmap to a low-carbon bio-economy. 1–46.
- 415 CEPI (2016) Key Statistics 2015.
- 416 COST (2014) Memorandum of Understanding COST FP1405 - ActinPak. 1–29.
- 417 De Marco JL, Felix CR (2007) Purification and characterization of a β -glucanase produced by
418 *Trichoderma harzianum* showing biocontrol potential. *Brazilian Arch Biol Technol* 50:21–29. doi:
419 10.1590/S1516-89132007000100003
- 420 Delgado-Aguilar M, González I, Tarrés Q, et al (2015a) Approaching a Low-Cost Production of Cellulose
421 Nanofibers for Papermaking Applications. *BioResources* 10:5345–5355. doi:
422 10.15376/biores.10.3.5330-5344

- 423 Delgado-Aguilar M, Recas E, Puig J, et al (2015b) Aplicación de celulosa nanofibrilada, en masa y
424 superficie, a la pulpa mecánica de muela de piedra: una sólida alternativa al tratamiento clásico de
425 refinado. *Maderas Cienc y Tecnol* 17:0–0. doi: 10.4067/S0718-221X2015005000028
- 426 Delgado-Aguilar M, Tarrés Q, Pèlach MÀ, et al (2015c) Are Cellulose Nanofibers a Solution for a More
427 Circular Economy of Paper Products? *Environ Sci Technol* 49:12206–12213. doi:
428 10.1021/acs.est.5b02676
- 429 Delgado-Aguilar M, Tarrés Q, Puig J, et al (2015d) Enzymatic Refining and Cellulose Nanofiber
430 Addition in Papermaking Processes from Recycled and Deinked. *BioResources* 4:5730–5743.
- 431 Espinosa E, Tarrés Q, Delgado-Aguilar M, et al (2016) Suitability of wheat straw semichemical pulp for
432 the fabrication of lignocellulosic nanofibres and their application to papermaking slurries. *Cellulose*
433 23:837–852. doi: 10.1007/s10570-015-0807-8
- 434 González I, Alcalá M, Arbat G, et al (2013) Suitability of rapeseed chemithermomechanical pulp as raw
435 material in papermaking. *BioResources* 8:1697–1708. doi: 10.15376/biores.8.2.1697-1708
- 436 Henriksson M, Henriksson G, Berglund LA, Lindström T (2007) An environmentally friendly method for
437 enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. *Eur Polym J* 43:3434–
438 3441. doi: 10.1016/j.eurpolymj.2007.05.038
- 439 Hii C., Gregersen Ø, Chinga-Carrasco G, Eriksen Ø (2012) The effect of MFC on the pressability and
440 paper properties of TMP and GCC based sheets. *Nord Pulp Pap Res J* 27:388–396. doi:
441 10.3183/NPPRJ-2012-27-02-p388-396
- 442 Hubbe MA (2014) Prospects for maintaining strength of paper and paperboard products while using less
443 forest resources: A review. *BioResources* 9:1634–1763.
- 444 Isogai A, Saito T, Fukuzumi H (2011) TEMPO-oxidized cellulose nanofibers. *Nanoscale* 3:71–85. doi:
445 10.1039/c0nr00583e
- 446 Lavoine N, Desloges I, Dufresne A, Bras J (2012) Microfibrillated cellulose - Its barrier properties and
447 applications in cellulosic materials: A review. *Carbohydr Polym* 90:735–764. doi:
448 10.1016/j.carbpol.2012.05.026
- 449 Lavoine N, Desloges I, Khelifi B, Bras J (2014) Impact of different coating processes of microfibrillated
450 cellulose on the mechanical and barrier properties of paper. *J Mater Sci* 49:2879–2893. doi:
451 10.1007/s10853-013-7995-0
- 452 Li X, Tian J, Shen W (2010) Progress in patterned paper sizing for fabrication of paper-based
453 microfluidic sensors. *Cellulose* 17:649–659. doi: 10.1007/s10570-010-9401-2
- 454 Lindström T, Larsson PT (2008) Alkyl ketene dimer (AKD) sizing: a review. *Nord Pulp Pap Res J*
455 23:202–209.
- 456 Lizundia E, Delgado-Aguilar M, Mutjé P, et al (2016) Cu-coated cellulose nanopaper for green and low-
457 cost electronics. *Cellulose* 23:1997–2010. doi: 10.1007/s10570-016-0920-3
- 458 Moral A, Aguado R, Tijero A, et al (2017) High-Yield Pulp from Brassica napus to Manufacture
459 Packaging Paper. *BioResource* 12:2792–2804.
- 460 Saito T, Isogai A (2004) TEMPO-mediated oxidation of native cellulose. The effect of oxidation
461 conditions on chemical and crystal structures of the water-insoluble fractions. *Biomacromolecules*

- 462 5:1983–1989. doi: 10.1021/bm0497769
- 463 Shinoda R, Saito T, Okita Y, Isogai A (2012) Relationship between Length and Degree of Polymerization
464 of TEMPO-Oxidized Cellulose Nanofibrils. *Biomacromolecules* 13:842–849.
- 465 Tarrés Q, Delgado-Aguilar M, Pèlach MA, et al (2016a) Remarkable increase of paper strength by
466 combining enzymatic cellulose nanofibers in bulk and TEMPO-oxidized nanofibers as coating.
467 *Cellulose* 23:3939–3950. doi: 10.1007/s10570-016-1073-0
- 468 Tarrés Q, Oliver-Ortega H, Llop M, et al (2016b) Effective and simple methodology to produce
469 nanocellulose-based aerogels for selective oil removal. *Cellulose* 23:3077–3088. doi:
470 10.1007/s10570-016-1017-8
- 471 Tarrés Q, Pèlach MÀ, Alcalà M, Delgado-Aguilar M (2017) Cardboard boxes as raw material for high-
472 performance papers through the implementation of alternative technologies: More than closing the
473 loop. *J Ind Eng Chem* 54:52–58. doi: 10.1016/j.jiec.2017.05.016
- 474 Tarrés Q, Saguer E, Pèlach MA, et al (2016c) The feasibility of incorporating cellulose micro/nanofibers
475 in papermaking processes: the relevance of enzymatic hydrolysis. *Cellulose* 23:1433–1445. doi:
476 10.1007/s10570-016-0889-y
- 477 Vaswani S, Koskinen J, Hess DW (2005) Surface modification of paper and cellulose by plasma-assisted
478 deposition of fluorocarbon films. *Surf Coatings Technol* 195:121–129. doi:
479 10.1016/j.surfcoat.2004.10.013
- 480 Zimmermann T, Bordeanu N, Strub E (2010) Properties of nanofibrillated cellulose from different raw
481 materials and its reinforcement potential. *Carbohydr Polym* 79:1086–1093. doi:
482 10.1016/j.carbpol.2009.10.045
- 483