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1 **XYLAN-CELLULOSE FILMS: IMPROVEMENT OF HYDROPHOBICITY,**
2 **THERMAL AND MECHANICAL PROPERTIES**

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11
12 **Abstract**

13 Xylan-rich hemicellulose from corn cob has been used for new material elaboration.
14 Commercial cellulose was used as reinforcement in different percentages to improve
15 properties of the films. Two types of composites were elaborated by solvent casting.
16 *Hydrophilic films*, composed by bleached hemicellulose (BH), unmodified cellulose and
17 glycerol as plasticizer, and *hydrophobic films* formed by acetylated bleached
18 hemicellulose (BAH) and acetylated cellulose. The degree of substitution of BAH was
19 1.8 and acetylated cellulose presented a degree of substitution of 0.54. Thermal and
20 mechanical properties of films were analyzed. A significant improvement was observed
21 in the thermal behaviour of hydrophobic films ($T_{max} \sim 368$ °C) respect to hydrophilic
22 films ($T_{max} \sim 300$ °C). Although the addition of cellulose clearly increase the properties
23 of both type of films, hydrophobic films (Young's Modulus ~ 2300 MPa, strength ~ 44.1
24 MPa, strain at break $\sim 5.7\%$) showed better mechanical properties than hydrophilic films
25 (Young's Modulus ~ 3.3 MPa, strength ~ 3.3 MPa, strain at break $\sim 5.3\%$).

26 **Keywords:** Xylan; Acetylation; Cellulose; Thermal properties; Mechanical properties

27

28 **1. Introduction**

29 Nowadays, most plastics materials produced are from petroleum. Although the
30 development of polymeric materials has a vital importance in the society over the years
31 and has contributed to facilitate our way of life, their use creates many potential
32 problems due to their non-renewable nature and ultimate disposal (Saxena &
33 Ragauskas, 2009). Moreover, the plastics are present in most products consumed and
34 used every day, is a material used in all industrial sectors and for the manufacture of a
35 wide range of products. Therefore, in recent years, the growing environmental concerns
36 have created an urgent need to develop biodegradable materials that have comparable
37 properties to polymeric materials at an equivalent cost. For this purpose, the use of
38 lignocelluloses resources as agricultural wastes, are becoming an attractive alternative
39 due to their renewable origin, the biodegradability of their components and their non-
40 human food application (Mikkonen & Tenkanen, 2012). In addition, agricultural
41 residues are produced in large quantities every year and most of them being discarded
42 and burned with no value. Hemicelluloses, the second most abundant biopolymer on
43 Earth has a great potential as bio-based and biodegradable packaging materials
44 (Mikkonen et al., 2011; Stepan, Höjje, Schols, De Waard, & Gatenholm, 2012),
45 constitute about 20–35% of most plant depending on the particular plant species
46 (Ayoub, Venditti, Pawlak, Sadeghifar, & Salam, 2013; Fang, Sun, Tomkinson, &
47 Fowler, 2000). Its structure is amorphous in nature and can be formed by a wide variety
48 of monosaccharides including: xylose, arabinose, glucose, galactose, mannose, fructose,
49 glucuronic acid and galacturonic acid depending upon the source (Stepan et al., 2012;
50 Ayoub et al., 2013) and used extraction method. Xylans are an important sub-group of
51 hemicelluloses with a $\beta(1 - 4)$ -D-xylopyranose backbone with various ramifications and
52 substitutions. They are found mainly in hardwoods, and agricultural plant species

53 (Hansen, Blomfeldt, Hedenqvist, & Plackett, 2012; Peng, Ren, Zhong, & Sun, 2011).
54 Hemicelluloses are hydrophilic molecules and have good barrier properties against oils
55 and fats, but are less efficient as moisture, and water vapour barriers. Also, oxygen
56 barrier properties are good at low or moderate relative humidities, particularly for
57 xylans (Gröndahl & Gatenholm, 2007; Tharanathan, 2003). However, synthetic
58 polymers are usually hydrophobic, and this significantly limits the use of hemicellulose
59 in industrial applications. However, due to the reactive groups (hydroxyl groups),
60 hemicelluloses properties can be modified by different reactions. Many authors have
61 studied chemical treatments of the hemicelluloses with the aim of substitute the
62 hydroxyl group of hemicellulose to increase material hydrophobicity and thermal
63 stability of modified hemicellulose (Belmokaddem, Pinel, Huber, Petit-Conil, & Da
64 SilvaPerez, 2011; Grace, Fundador, Enomoto-Rogers, Takemura, & Iwata, 2012;
65 Jonoobi et al., 2012). Hemicellulose based composite materials have also been
66 developed in an attempt to improve the hemicellulose material properties because
67 mechanical properties of pure hemicellulose-based films are generally considered being
68 low without additives (Stevanic, Bergstrom, Gatenholm, Berglund, & Salmén, 2012).
69 Therefore, in recent years, incorporation of biodegradable reinforcements such as
70 cellulose into other polymers has already proven to be an important strategy for
71 obtaining composites with high mechanical performance. These biodegradable
72 reinforcements also offer great possibilities for the development of novel hemicellulose-
73 based composite materials and its structure allows surface modification to improve
74 compatibility with hydrophobic matrix. Several publications can be found about the use
75 of hemicelluloses reinforced with cellulose for materials productions (Mikkonen et al.,
76 2012; Stevanic et al., 2011) and the use of modified cellulose as reinforcement in
77 hydrophobic matrix such a poly(lactic acid) in order to improve compatibility between

78 two components in new material (Lin,Huang, Chang, Feng, & Yu, 2011; Tingaut,
79 Zimmermann, & Lopez-Suevos, 2010). The present study was focused on hemicellulose
80 extraction from a renewable resource and purification for elaboration new materials.
81 The main effort has been to evaluate the initial hemicellulose film characteristics and
82 the improvement of its thermal and mechanical properties through the addition of
83 cellulosic reinforcement in different percentages and use acetylation process.
84 Hemicellulose was acetylated in order to obtain hydrophobic matrix and also for greater
85 thermal stability. Commercial cellulose was also acetylated to improve affinity with
86 hydrophobic matrix and so improve mechanical properties of hydrophobic films. The
87 object of this research was to evaluate physical, thermal and mechanical properties of
88 two types of elaborated biocomposite films and the effect of modified cellulose
89 addition.

90 **2. Materials and methods**

91 **2.1. Hemicellulose extraction, purification and acetylation**

92 Hemicelluloses used for composites elaboration has been extracted from corn cob, was
93 purified by ultrafiltration and then subjected to a bleaching process (BH) following the
94 same method described by Egüés et al. (2014). The acetylation treatment was performed
95 with the aim of substitute the hydroxyl group of hemicellulose and increase material
96 hydrophobicity (BAH). Acetylation process was also the same as followed by Egüés et
97 al. (2014).

98 **2.2. Cellulose: Characteristics and acetylation**

99 Commercial cellulose nanofibers used in this work were provided by the University of
100 Maine, Orono, United States. The average size is 100-200 nm lengths and diameters of
101 between 10 and 20 nm. Cellulose acetylation was carried out using similar process to

102 that used to acetylate the hemicellulose but with some modification. 0.5 g of nanofibers
103 was dispersed in 25 mL formamide under vigorous stirring at room temperature until a
104 homogeneous phase was obtained. Then, 40 mL pyridine was added. Every 3 hours, 3.3
105 mL of acetic acid anhydride was added until a total of three additions. 25 hours later, the
106 viscous dark solutions were thrown into 1 L of distilled water. Acetylated cellulose was
107 filtered and washed with acetone, followed by ethanol and distilled water until neutral
108 pH. This washing step allowed the removal of unreacted acetic acid and pyridine from
109 the samples. The acetylated cellulose was dried in an oven at 50 °C for further
110 characterization.

111 **2.3. Films elaboration**

112 Two types of composites have been prepared; one was formed by bleached
113 hemicellulose (BH) reinforced with unmodified cellulose (*hydrophilic films*). In this
114 case, glycerol was used to obtain a continuous film. The second type was formed of
115 acetylated hemicellulose (BAH) as matrix and acetylated cellulose as reinforcement
116 (*hydrophobic film*). Both films have been elaborated by solvent casting. In both cases,
117 three steps were necessary in order to produce homogenous films. For hydrophilic films
118 elaboration; (a) bleached hemicellulose solubilized in 10 mL of water for about 3 h, (b)
119 cellulose was dispersed during 3 h in 10 mL distilled water with magnetic stirring (c)
120 finally, solubilized hemicellulose was added to dispersed cellulose, and last glycerol
121 was added and stirred for 1 h. The total amount of dry substance (hemicellulose and
122 cellulose) in each film was kept constant at 0.5 g. The cellulose content in the composite
123 films was 0, 1, 5, 10 and 20.0 wt% of the total dry mixture, respectively. The glycerol
124 content was kept 40 wt% (based on the total dry mixture). The solutions were poured
125 onto polystyrene dishes (9x9 cm) and allowed to dry at 25 °C and 50% RH in a climate-
126 controlled chamber for 7 days. For hydrophobic film, chloroform was used as solvent

127 for its ability to dissolve acetylated hemicellulose and disperse acetylated cellulose; (a)
128 acetylated cellulose was dispersed at room temperature with magnetic stirring in 10 mL
129 of chloroform for 2-3 h, then sonicated for about 5-10 min, (b) acetylated hemicellulose
130 solubilized in 10 mL of chloroform for about 3 h and finally, (c) solubilized
131 hemicellulose was added to the dispersed cellulose and stirred in order to form a
132 homogeneous solution. The total amount of dry substance (hemicellulose and cellulose,
133 both acetylated) in each film was also kept constantly at 0.5 g. The cellulose content in
134 this case was 0, 1 and 5% of the total dry mixture. After completing the process of
135 obtaining films, the solutions were poured onto polystyrene dishes (9x9 cm) and were
136 dried in a vacuum oven (500 mBa) at 30 °C in order to avoid the occurrence of bubbles
137 in the films. All composites were conditioned prior to analysis at 25 °C and 50%
138 relative humidity in a climate-controlled chamber.

139 **3. Characterization**

140 The weight-average (M_w) and number-average (M_n) molecular weights and
141 polydispersity ($IP = M_w/M_n$) of the bleached hemicellulose was determined by gel
142 permeation chromatography (GPC) in a GPC Jasco LC-Net II/ADC equipped with a
143 photodiode array detector and refractive index detector. The column was PL aquagel-
144 OH MIXED. The mobile phase was constituted by 0.005 N H_2SO_4 prepared with 100%
145 deionised and degassed water (0.6 mL/min flow, 40 °C and injection volume of 40 μ L).
146 Calibration curve was made using Pullulan polysaccharides (Calibration kit SAC-10,
147 Varian) with different molecular weights (between 180 and 805,000 Da).

148 Sugars monomers quantification was carried out in a high performance liquid
149 chromatography (HPLC) Jasco LC Net II/ADC equipped with a refractive index
150 detector and a photodiode array detector. A Phenomenex Rezex ROA HPLC column
151 with 0.005 N H_2SO_4 prepared with HPLC grade degassed water was used as mobile

152 phase (0.35 mL/min flow, 40 °C and injection volume 40 µL). High purity standards of
153 D (+) glucose, D (+) xylose, D (-) arabinose, galacturonic acid, and acetic acid (supplied
154 by Sigma Aldrich), were used for the calibration curves. For monomeric sugars
155 quantifications, bleached hemicellulose (BH) samples were subject to post-hydrolysis
156 process, using sulphuric acid at a concentration of 4% (w/w) for 60 min.

157 The FT-IR analysis of dried samples of acetylated and nonacetylated cellulose
158 was performed on a NICOLET MODEL NEXUS 670 FT-IR spectrophotometer.
159 Acetylated and bleached hemicellulose was also analyzed. All samples were analyzed in
160 order to confirm that the acetylation reaction has been occurred successfully. A total of
161 20 scans were accumulated in transmission mode with a resolution of 4 cm⁻¹. The
162 spectrum was obtained from a range of 4000 to 650 cm⁻¹.

163 The degree of acetylation of acetylated hemicellulose (BAH) was calculated by
164 ¹H-NMR spectrometry, using a Bruker 500 MHz spectrometer at a frequency of 250
165 MHz with an acquisition time of 0.011 s, at room temperature. The spectrum was
166 recorded over 32 scans and DMSO-d₆ was used as solvent for acetylated bleached
167 hemicellulose (BAH).

168 The chemical degree of substitution (DS) is the average value of -COCH₃ groups
169 that replace hydroxyls in every glucose cycle. The DS of the acetylated samples were
170 determined through a saponification reaction (ASTM D 871-96). Approximately 0.5 g
171 of dry acetylated cellulose was placed in a flask, and 8 mL of 75% ethanol was added.
172 Then, the mixture was heated for 30 min at 60 °C. Following this, 8 mL of a 0.5 N
173 sodium hydroxide (NaOH) solution was added, and the mixture was heated at 60 °C for
174 15 min. The flask was stoppered tightly and left to stand at room temperature for 72h.
175 Then, the NaOH was titrated with 0.5 N hydrochloric acid (HCl) with phenolphthalein
176 as an indicator. At the point where the indicating pink color disappeared, an excess 1

177 mL of 0.5 N HCl was added, and the mixture was allowed to stand overnight. The small
178 excess of acid was then back-titrated with a 0.5 N NaOH solution to the phenolphthalein
179 end point (when the pink color reappeared). Blank titration was also performed with
180 unmodified MFC, and the data was used as a reference. The acetyl content was
181 calculated with the following equation:

$$182 \quad \text{Acetyl content(\%)} = [(D-C)N_a + (A-B)N_b] \times \left(\frac{4.035}{W} \right) \quad (1)$$

183 where A is the volume of NaOH added to the sample (mL), B is the volume of NaOH
184 added to the blank (mL), C is the volume of HCl added to the sample (mL), D is the
185 volume of HCl added to the blank (mL), W is the weight of the sample (g), and N_a and
186 N_b are the normality of the HCl and NaOH solutions, respectively. The average number
187 of acetyl groups per anhydro-D-glucose unit of cellulose (DS) could be calculated from
188 the following equation:

$$189 \quad DS = \frac{[3.86 \times \text{Acetyl content (\%)}]}{[102.4 - \text{Acetyl content (\%)}]} \quad (2)$$

190 The X-ray powder diffraction patterns were collected by using a PHILIPS X'PERT
191 PRO automatic diffractometer operating at 40 kV and 40 mA, in theta-theta
192 configuration, secondary monochromator with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a
193 PIXcel solid state detector (active length in 2θ 3.347°). The samples were mounted on a
194 zero background silicon wafer fixed in a generic sample holder. Data was collected
195 from 5 to $32^\circ 2\theta$ (step size = 0.026 and time per step = 80 s) at RT. A fixed divergence
196 and antiscattering slit giving a constant volume of sample illumination were used. The
197 crystalline index of cellulose, C_{I_r} , was calculated based on the empirical method
198 proposed by Segal, Creely, Martin and Conrad (1959) where I_{200} is the peak intensity
199 corresponding to cellulose I, and I_{am} is the peak intensity of the amorphous fraction.

200
$$CIr(\%) = (I_{200} - I_{am}) / I_{200} \times 100 \quad (3)$$

201 Contact angle measurements were also carried out with water using a
202 Dataphysics Contact angle system OCA 20, in order to determine changes in the
203 hydrophilic character of cellulose after acetylation treatment. The average value of five
204 measurements was calculated.

205 Thermogravimetric analyses were carried out with TGA/SDTA 851 METTLER
206 TOLEDO. Cellulose, bleached hemicellulose and acetylated samples were analyzed to
207 determinate their thermal stability. Samples about 5-10 mg were tested under nitrogen
208 atmosphere at heating rate of 10 °C/min from 25 °C to 600 °C. Both types of composites
209 were also analyzed to determinate their thermal stability.

210 Samples with 6 cm long were prepared, with thicknesses between 80-120 µm,
211 and width of 5 mm, were mechanically tested by MTS Insight 10 equipment provided
212 with pneumatic clamps (Advantage Pneumatic Grips) and with a loading cell of 250 N
213 with a speed of 5 mm/min. The stress/strain measurements were performed using a
214 video extensometer with digital video camera connected to a PC. The starting distance
215 between the clamps was 25 mm. The values quoted are the average of eight
216 measurements.

217 **4. Results and discussion**

218 **4.1. Composition and GPC results of bleached hemicellulose**

219 The composition of the bleached hemicellulose obtained after 60 min of post-hydrolysis
220 and the average molecular weights are shown in Table 1. Obtained hemicellulose is
221 composed mainly for xylose, galacturonic and small amount of arabinose and glucose.
222 On the other hand, this sample had a high polydispersity because it has two fractions,

223 one fraction with low molecular weight, about 20% of $M_w = 3800$ g/mol and the other
224 80% $M_w = 67300$ g/mol.

225 **Table 1.** Sugar monomeric characterization and weight average (M_w), number average (M_n) and
226 polydispersity index (M_w/M_n) of bleached hemicellulose.

	Xylose	Galacturonic Acid	Arabinose	Glucose	Ara/Xyl ratio	Mn	Mw	IP
BH	52.8	34.6	6.8	1.4	0.13	12300	54000	4.4

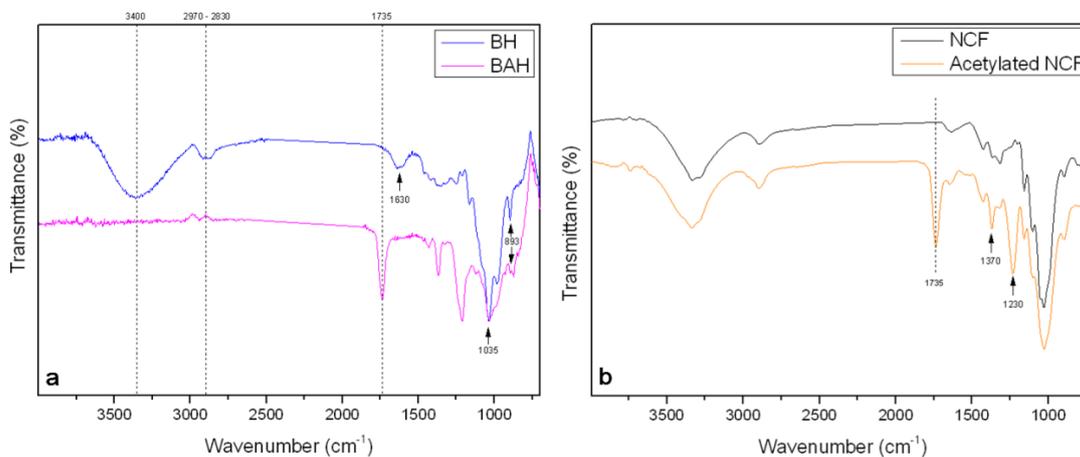
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228 4.2. FTIR

229 Fourier transform infrared spectra of different samples are shown in Fig. 1. Both figures
230 confirm that the acetylation reaction was successful. In the case of bleached
231 hemicellulose (BH) (Fig. 1a) the bands found around 3400 and 2970-2830 cm^{-1}
232 indicated the OH stretching and CH bond deformation of CH_2 and CH_3 groups,
233 respectively. The other band found at 1630 cm^{-1} corresponds with water absorption
234 (Ayoub et al., 2013). The absorbance between 1460-893 cm^{-1} seen in the spectrum are
235 associated with native hemicelluloses (Sun, Fang, Tomkinson, & Jones, 1999). The
236 presence of xylan was observed at 1035 cm^{-1} and the domain of β -glycosidic bonds
237 between sugars units was demonstrated at 893 cm^{-1} . The evidence of acetylation was
238 observed clearly in BAH, showed by the presence of three important ester bands (Ren,
239 Peng, Zhong, Peng, & Sun, 2007; Sun et al., 1999) at 1735 cm^{-1} (C=O ester), at 1370
240 cm^{-1} ($-\text{C}-\text{CH}_3$) and at 1210 cm^{-1} ($-\text{C}-\text{O}-$ stretching band). On the other hand, this
241 analysis provides information about the chemical modification of cellulose fibers.
242 Spectra in Fig. 1b showed the differences between bands before and after fibers
243 acetylation. The main change of treated fibers in comparison to untreated fibers spectra
244 is related to the appearing of band at 1735 cm^{-1} , this band is proceeding from wide C=O
245 carbonyl peak from bonded acetyl group. In addition, a new absorption bands at 1370
246 cm^{-1} associated (C-H) the methyl in-plane bending and at 1230 cm^{-1} (C-O) was assigned

247 to the carbonyl C–O stretch vibration Lin, Huang, Chang, Feng, & Yu, 2011; Tingaut et
248 al., 2010; Tomé et al., 2011).

249 **Fig. 1.** Fourier transform infrared spectroscopy: (a) spectra of bleached hemicellulose (BH), bleached
250 acetylated hemicellulose (BAH) and (b) spectra of nanocellulose fibers (NCF) and acetylated
251 nanocellulose fibers.



252
253

254 4.3. Degree of substitution

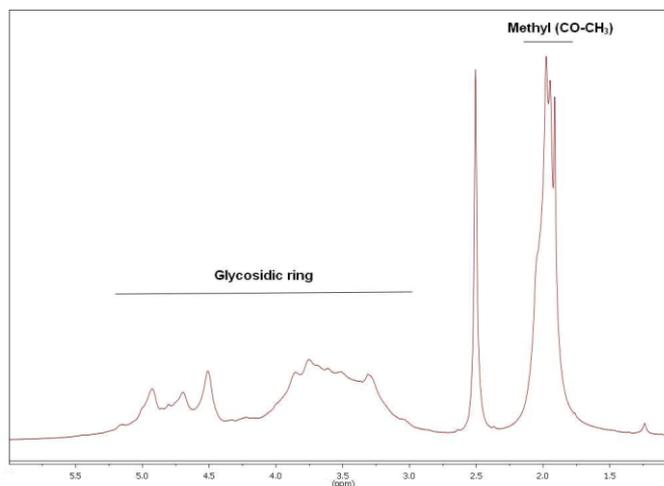
255 The degree of substitution (DS) of the acetylation reaction was determined by ¹H NMR
256 following the method used by Belmokaddem et al., (2011). The area of methyl protons
257 of ester chains at 1.9–2.0 ppm (*I_{methyl}*) and the area of anomeric proton of xylan at 4.5
258 ppm (*I_{anomericXylan}*) were compared as shown in Eq. (4):

$$259 \quad DS = I_{methyl} / (3 \times I_{anomericXylan}) \quad (4)$$

260 The spectrum in fig. 2 showed the presence of an intense signal at 2.0 ppm, which was
261 attributed to the acetyl moiety in the product, indicating that the acetyl groups were
262 introduced into the hemicellulose molecules (Ayoub et al., 2013; Belmokaddem et al.,
263 2011). In this study, the value of DS for bleached acetylated hemicellulose (BAH) was
264 DS = 1.8. Taking into account that the average number of available OH groups per
265 sugar unit is DS = 2, the degree obtained can be considered an acceptable value. In the
266 case of cellulose, the acetyl contents determined by saponification were 12.6% after 30
267 h of reaction time. When eq. (2) was applied, this could be translated to a (DS) of 0.54.

268 Although the degree of substitution was not very high, it was adequate for correct
269 dispersion of the fibers in chloroform. Similar results were reported by other authors
270 (Hu,Chen, Xu, & Wang, 2011; Tingaut et al., 2010).

271 **Fig. 2.** ^1H NMR spectrum of bleached acetylated hemicellulose (BAH) (dissolved in DMSO-d₆).



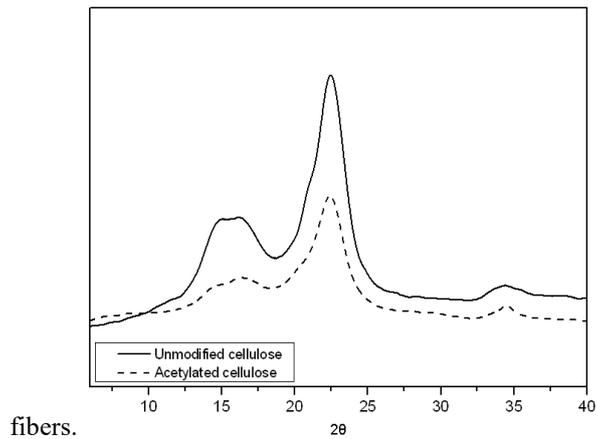
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273 4.4. X-Ray

274 The impact of chemical modification on the fiber crystal structure was evaluated using
275 X-ray diffraction in order to determine how crystallinity was affected by the chemical
276 modification performed in this study. The X-ray diffraction profiles of the cellulose
277 before and after acetylation are given in Fig. 3. Unmodified cellulose display the typical
278 XRD pattern of the native cellulose, with the main diffraction signals at around 2θ 14.9,
279 16.2, 22.5 and 34.3°. The acetylated cellulose also presented this diffraction pattern
280 which indicates that the original structure of cellulose was maintained. Besides, the
281 crystallinity index has remained constant around 0.7 after acetylation process which
282 suggested that the modification has been limited to the surface of fibers or more
283 accessible amorphous domains into the cellulose and did not affect crystalline regions in
284 the cellulose. These results demonstrated that the fibers mantain reinforcement
285 potential. Similar results were found by other authors for acetylated cellulose used to
286 reinforce PLA (Tingaut et al., 2010; Tomé et al., 2011).

287

Fig. 3. XRD spectra of unmodified an acetylated cellulose



288

289

4.5. Films appearance

290

Bleached hemicellulose used to prepare composites was not able to form film without plasticizer. It was necessary to use 40% of plasticizer to form a film without cracks.

291

292

However, acetylated hemicellulose was able to form film without the addition of any kind of additional substance. In both cases, the addition of cellulose (unmodified and

293

294

acetylated) as reinforcement enhanced the formation of the film. All films were homogeneous without any visible particles presence as inspected by eyes. However,

295

296

optical microscope showed the presence of some irregularly shaped agglomerates that could have been originated from less soluble fractions of used hemicellulose. Addition

297

298

of cellulose did not cause a remarkable change in the films appearance. They did not lose their transparency with the addition of cellulose, but in the case of hydrophilic

299

300

films showed a slight colour change, being somewhat more yellowish at high percentages of cellulose in the composite. The hydrophobic films showed completely

301

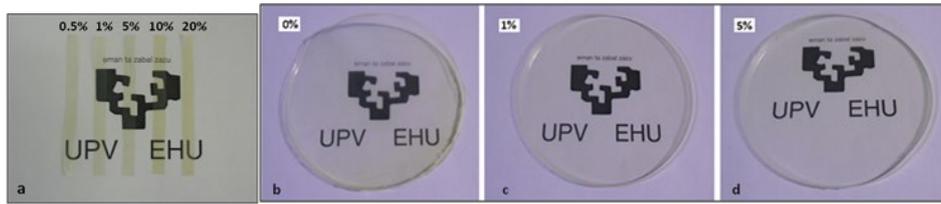
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transparent appearance, no yellowish. The thickness of the films varied between 40 and 120 μm . (fig. 5)

303

304

305 **Fig. 4.** Optical images of films: (a) Test specimens of hydrophilic films with different percentages of
306 nanofiber, (b) Hydrophobic films without reinforcement, (c) Hydrophobic films with 1% of acetylated
307 cellulose and (d) Hydrophobic films with 5% of acetylated cellulose.



308

309 **4.6. Contact angle**

310 The acetylation increases the hydrophobicity of the cellulose fibers and their adhesion to
311 the hemicellulose acetylated matrix. The transformation of the surface characteristics of
312 cellulose was further confirmed by the results of the contact angle measurements. As
313 shown in Fig. 5, acetylated cellulose presented a sharp increase in θ_{water} from 48° to 73°
314 due to the replacement of some of the surface hydroxyl groups with non-polar $-\text{COCH}_3$.
315 A similar observation was reported by Lin et al. (2011).

316 **Fig. 5.** Contact angle images: (left) unmodified cellulose, (right) acetylated cellulose.



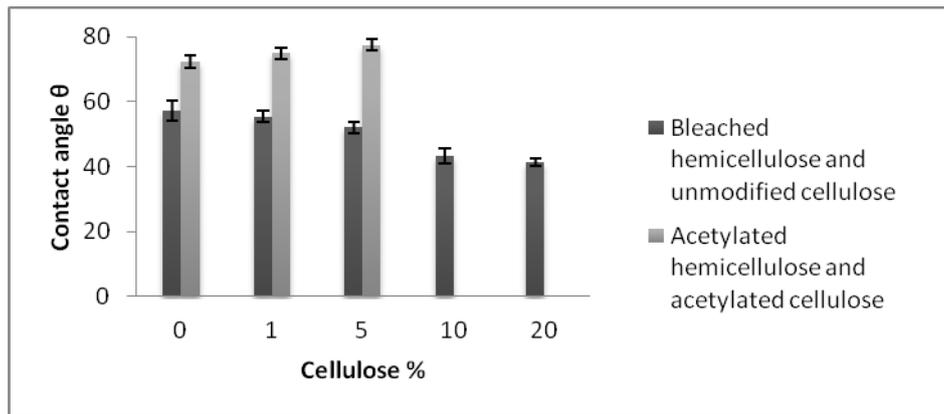
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318

319 Moreover, Fig. 6 proves that the hemicellulose acetylation considerably enhances the
320 hydrophobic character of the obtained films. As can be observed, the film formed by
321 bleached hemicellulose and glycerol (CBH) showed a contact angle around 57° while
322 the film elaborated by acetylated hemicellulose (CBAH) was 72° . Also it demonstrated
323 that increasing cellulose content in hydrophilic composites decreased the contact angle.
324 This can be attributed to increased surface roughness and the introduction of a
325 component more hydrophilic than the matrix. However, in composites formed by
326 acetylated hemicellulose and acetylated cellulose the opposite happened, as it increases
327 content of acetylated cellulose increases contact angle. Besides, during the time
328 maintained hydrophobic behavior because very few degrees reduced the contact angle.

329

Fig. 6. Contact angle of composites.



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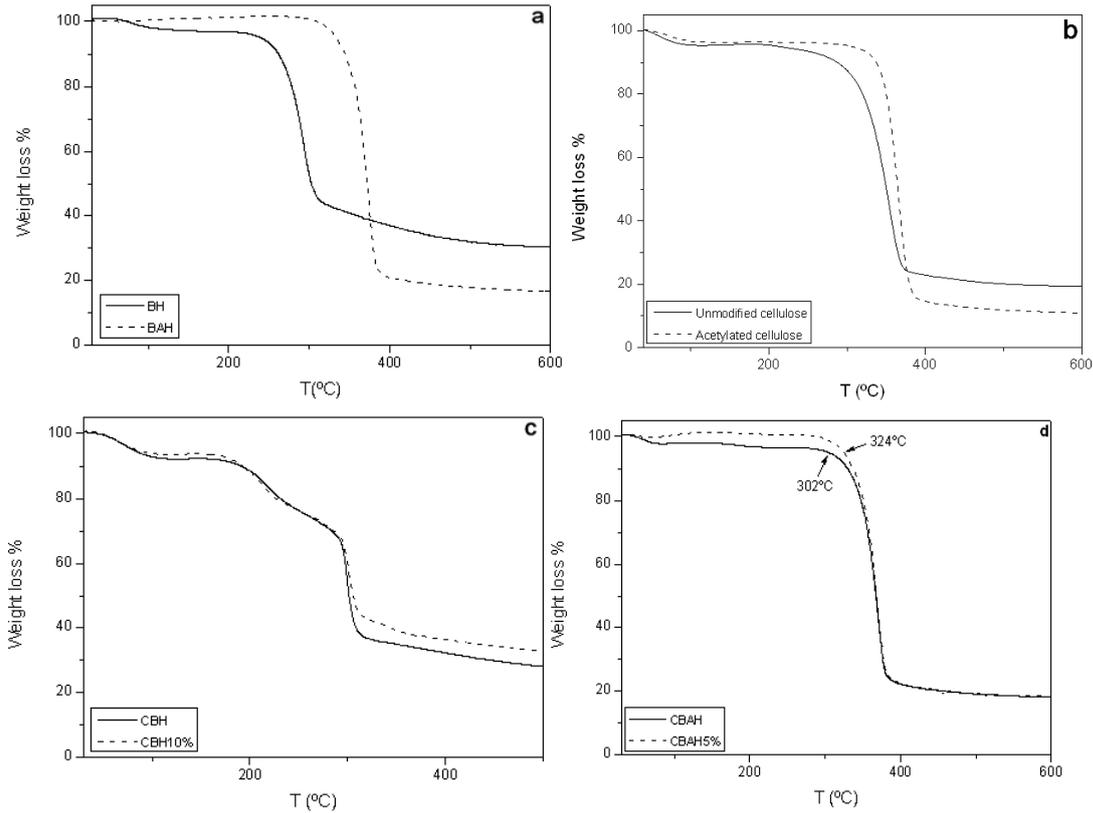
4.7. Thermal analysis

333 The results of the thermal gravimetric analysis under nitrogen atmosphere of the
334 different samples are shown in Fig. 7. The initial degradation temperature ($T_{5\%}$), the
335 maximum weight loss temperature (T_{max}) and char residue at 600 °C have been
336 analyzed. Fig. 7a showed thermal stability of the bleached and acetylated
337 hemicelluloses. As can be seen, acetylated hemicellulose presented higher thermal
338 stability than bleached hemicellulose. The initial degradation temperature corresponding
339 to 5% weight loss ($T_{5\%}$) of acetylated hemicellulose (BAH) is marked higher than
340 bleached hemicellulose (BH) with values of 334 °C and 239 °C respectively. The
341 maximum weight loss rate in acetylated hemicellulose could be observed at 372 °C,
342 while bleached hemicellulose showed a temperature of 303 °C. The solid residue at 600
343 °C for the bleached hemicellulose was 30% and 17% for acetylated hemicellulose.
344 Similar behaviour was found in other studies that modify hemicellulose (Fang et al.,
345 2000; Grace et al., 2012; Jonoobi et al., 2012; Sunet al., 1999). This important
346 improvement achieved after acetylation process, indicates higher thermal resistant
347 behaviour, desired for thermoplastic processing conditions. Furthermore, a change in
348 thermal properties after chemical modification of cellulose was confirmed by TGA
349 analysis. Fig. 7b showed that acetylated cellulose presented higher thermal stability than

350 unmodified one. Similar results were obtained by other authors (Tingaut et al.,
351 2010;Tomé et al., 2011; Urruzola, Serrano, Llano-Ponte, De Andrés, &Labidi, 2013).
352 The initial degradation temperature ($T_{5\%}$) for unmodified cellulose was 212 °C,
353 however, acetylated cellulose begins to degrade at higher temperatures $T_{5\%}= 305$ °C.
354 Besides, the maximum weight loss temperature (T_{max}) of original cellulose and
355 acetylated was 350 °C and 366 °C, respectively. The solid residue at 600 °C for the
356 unmodified cellulose and acetylated cellulose was 19% and 10%, respectively. In the
357 case of the thermal stability of elaborated composites, bleached hemicellulose film with
358 40% glycerol (CBH) and composite with 10% of reinforcement (CBH10%) have been
359 analyzed. In addition, acetylated hemicellulose film without reinforcement (CBAH) and
360 with 5% acetylated reinforcement (CBAH5%) have also been analyzed. A significant
361 improvement was obtained in the thermal behaviour of the composites made from
362 acetylated hemicellulose and acetylated cellulose respect to prepared with bleached
363 hemicellulose and unmodified cellulose. Fig. 7c showed that the hydrophilic films had
364 a small weight loss below 100 °C due to gradual evaporation of moisture followed by
365 another small mass loss around 205 °C because of the presence of glycerol in both
366 samples. As found in literature (Hansen et al., 2012), the content of glycerol in the films
367 affects the thermal stability because it creates a plasticizing effect in the matrix
368 increasing the free volume and generating less force between the two components of the
369 material. The maximum weight loss rate was observed at 299 °C for composite without
370 reinforcement and at 302 °C for film with 10% cellulose content. This demonstrates that
371 the cellulose content increase thermal stability of the material in a few degrees as found
372 in the literature. Composite containing 10% cellulose also presented another drop
373 around 350 °C due to the presence of cellulose. Other type of composites, hydrophobic
374 films, showed that although both films had the same maximum decomposition rate at

375 368 °C, composite film with 5% of acetylated cellulose begins to degrade later, at 324
376 °C, while unreinforced film start at 302 °C. The solid residue at 600 °C for the both
377 composite films was the same around 18.5%.

378 **Fig. 7.** Thermal stability of (a) bleached and acetylated hemicellulose, (b) unmodified and acetylated
379 cellulose, (c) hydrophilic composites films without reinforcement (CBH) and with 10% of cellulose
380 (CBH10%), and (d) hydrophobic composite films without reinforcement (CBAH) and with 5% of
381 acetylated cellulose (CBAH5%).



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4.8. Mechanical properties

385 The Young's modulus, tensile strain at break and tensile strength at break of the
386 biocomposites are shown in the following Table 2. These tests were performed after
387 specimens acclimate at 25 °C and 50% RH. The results demonstrate that the films
388 obtained from bleached hemicellulose had poor properties but were improved with the
389 addition of cellulose as reinforcement and plasticizer. Moreover the acetylation of
390 bleached hemicellulose generated films with better mechanical properties, which were
391 also improved by reinforcing with acetylated cellulose. In the case of hydrophilic films,

392 up to 5% of cellulose as reinforcement had an increased strength and stiffness. The film
393 without reinforcement and with 40% glycerol (CBH) showed a rather poor properties
394 compared with those found in literature (Hansen et al., 2012; Peng et al., 2011). This
395 film had little stiffness and strength but was quite ductile. However, the addition of 1%
396 cellulose greatly enhanced all of the measured properties, exhibited greater stiffness and
397 supported higher stress at break. The strain at break of this film seems to have
398 improved, but it would be expected that the elongation will decrease with the
399 reinforcement. Moreover, introducing 5% of cellulose continues to increase both the
400 Young's modulus and strength, however, in this case the elongation decreases as
401 expected. Although with 10% and 20% of cellulose as reinforcement properties were
402 still better than the unreinforced matrix, these films showed a decrease in the properties
403 compared to films with lower percentage of cellulose. The composite with 10%
404 cellulose has greater stress at break than the others, presents a similar deformation to
405 film with 5% cellulose, but decreases its stiffness. However, reinforcing 20% had a
406 lower strength and stiffness but deformation remains around 12%. This decrease in
407 properties at high percentages could probably be related to agglomerations due to poor
408 dispersion of the reinforcement in the matrix and the use of high percentages. These
409 agglomerations makes that exist a bad stress transfer between the reinforcement and the
410 matrix and could generate weak structure by creating stress concentration points
411 (Zhang, Zhang, Liang, & Lu, 2008). A similar thing happened to Stevanic et al. (2011)
412 who reinforced arabinoxylan films with bacterial cellulose and found that the addition
413 of 15% resulted in a decrease in the material strength by the presence of
414 agglomerations. In general, it was found that the addition of a correct amount of
415 reinforcement enhanced the performance of bleached hemicellulose films. On the other
416 hand, hydrophobic films presented a much better mechanical properties than

417 hydrophilic films. The experimental results indicate that the addition of acetylated
 418 cellulose improves the mechanical properties of the acetylated hemicellulose matrix.
 419 The improvement in mechanical properties has been by the use of an appropriate
 420 amount of reinforcement in the matrix, good dispersion of fibers and compatibility
 421 between the two components (Bulota, Kreitsmann, Hughes, & Paltakari, 2012). Film
 422 without reinforcement (CBAH) had similar properties that obtained by other authors
 423 (Mikkonen et al., 2012; Stepan et al., 2012). The addition of acetylated cellulose as
 424 reinforcement in the matrix generated films that support higher stress at break. This
 425 happened because appropriate amounts of reinforcement were added into the material,
 426 thereby, prevented fibers auto-aggregation and favored the dispersion, thus generating
 427 stress concentration points in the matrix to contribute to the reinforcement (Lin et al.,
 428 2011). The stiffness was also increased with increasing content of acetylated cellulose.
 429 On the other hand, elongation at break decreased with the addition of reinforcement as
 430 expected. Similar behaviors have been found in literature when reinforced material with
 431 acetylated cellulose (Bulota et al., 2012; Jonoobi et al., 2012; Lin et al., 2011).

432 **Table 2.** Average Values of Tensile strength at Break, Strain at Break and Young's Modulus for
 433 Composite Films in Tensile Testing.

Hydrophilic films				Hydrophobic films			
<i>Bleached hemicellulose + cellulose</i>				<i>Acetylated hemicellulose + acetylated cellulose</i>			
	Tensile strength (MPa)	Tensile strain (%)	Young's modulus (MPa)	Tensile strength (MPa)	Tensile strain (%)	Young's modulus (MPa)	
Cellulose content %	0	3.3 ± 0.4	5.3 ± 1.7	3 ± 1	44.1 ± 2.9	5.7 ± 2.1	2300 ± 207
	1	4.8 ± 0.4	19.7 ± 3.2	146 ± 29	48.5 ± 4.3	3.5 ± 1.0	2900 ± 228
	5	5.8 ± 0.8	12.2 ± 4.9	206 ± 3	51.0 ± 1.9	2.9 ± 0.8	3200 ± 408
	10	7.5 ± 1.2	12.4 ± 3.8	170 ± 12	-----	-----	-----
	20	4.5 ± 0.3	12.6 ± 1.4	90 ± 21	-----	-----	-----

434

435 5. Conclusions

436 In this work, two types of composites were elaborated. Hemicellulose was extracted
 437 from corn cob. Ultrafiltration process was used with the aim to concentrate the liquor

438 and retain high molecular weight components, which are more suitable for materials.
439 Bleaching process was used as a purification method to remove the yellow colour of
440 original hemicellulose in order to be used as hydrophilic matrix. Commercial cellulose
441 was used as reinforcement in hydrophilic films. Hemicellulose acetylation was
442 performed to obtain a hydrophobic matrix and commercial cellulose was also acetylated
443 to obtain better interactions between both components, which may be reflected in the
444 improvement of the mechanical properties of the hydrophobic films. Acetylation of
445 cellulose did not change its reinforcing potential. So the acetylation process was
446 successful for obtaining films with greater hydrophobic character, high thermal stability
447 and better mechanical properties than hydrophilic films.

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