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**Abstract**

All-cellulose composites (ACCs) in which both matrices and reinforcing fibers are made from lignocellulose were successfully obtained from alfa *(Stipa tenacissima L)* and wood (*Genus Betula*) fibers. Matrices were prepared either from alfa or wood pulps that were dissolved in 8 wt% NaOH-water, while reinforcing fibers were alfa in both matrices. Prior to the dissolution, alfa and wood pulps were acid hydrolyzed in order to decrease cellulose degree of polymerization to 149 and 145, respectively. The degree of cellulose dissolution was 95-96 % for both alfa and wood dissolving pulps. X-ray diffraction (XRD) analysis confirmed the coexistence of cellulose I and II. The adhesion between the reinforcing fibers and both matrices was investigated using Scanning Electron Microscopy (SEM) and was found to be excellent. The density of ACCs decreased with the increase of the reinforcing fiber content for both types of matrices and ranged from 0.6 to 1.0 g.cm$^{-3}$ leading to remarkably low-density ACCs. Young's modulus reached 3.8 and 4.2 GPa for the composites based on alfa and wood dissolving pulps, respectively, while yield stress reached 16 and 13.9 MPa, respectively.

**Keywords:** All-cellulose composite; Alfa fiber; Stipa Tenacissima; Wood fiber; Density; Mechanical properties;

## 1. Introduction

Bio-composites are defined as materials where the resin and the fibrous reinforcement are made entirely from renewable resources. Recently, they have attracted a lot of interest due to their eco-friendly aspect and potential to compete with composites that are made from petroleum based matrices (Väisänen et al., 2017).

Cellulose is the main component of plant and wood fibers and is the most abundant polymer found in nature. All-cellulose composites (ACCs) are bio-composites in which the matrix and reinforcing fibers are made exclusively from lignocellulose (Nishino et al., 2004). Their preparation is inspired by all-polymer composites principle in which the matrix and the fibers are based on the same thermoplastic polymer (Capiati and Porter, 1975). Due to the fact that both components that form the composite are made from the same material, problems related to adhesion are minimized. Because cellulose does not melt, the matrix is made via cellulose dissolution followed by solvent removal (coagulation and washing) and drying.

All-cellulose composites can be obtained following two different approaches. In the first one, cellulose is dissolved and then coagulated in the presence of short reinforcing fibers. In the second approach, fibers form the major phase: they are partially dissolved upon the addition of solvent and "glued together" by cellulose that comes from the dissolved fraction. The properties of ACCs vary as a function of the processing approach and parameters along with the origin of cellulose used for the matrix and the reinforcing fibers. For example, using the first approach, Qi et al. obtained ACCs by dissolving cotton fibers in 7 wt% sodium hydroxide (NaOH)-12 wt% urea-water and reported Young's modulus of 112-124 MPa and tensile strength of 3.9-5.8 GPa (Qi et al., 2009). However, an ACC that was obtained with the second approach from aligned ramie fibers impregnated by pre-treated ramie dissolved in lithium chloride-N,N-dimethylacetamide (LiCl-DMAc) had much higher mechanical

properties: dynamic storage modulus of 45 GPa and tensile strength of 480 MPa (Nishino et al., 2004). A detailed review that summarizes the preparation and properties of ACCs was published by Huber et al. (Huber et al., 2012).

Different solvents are known to dissolve cellulose (Liebert, 2010). The most common ones are N-methylmorpholine-N-oxyde monohydrate (NMMO), lithium chloride-N,N-dimethyleacetamide (LiCl-DMAc), ionic liquids (ILs) and (6-10) wt% aqueous sodium hydroxide (NaOH). The dissolution of cellulose in NaOH-based solvents dates from 1930,and is still attracting a lot of interest due to its cheapness and easy recovery (Budtova and Navard, 2016). However, several drawbacks of (6-10) wt% NaOH-water have to be taken into account if using this solvent: for example, cellulose solutions are gelling with time and temperature increase, and it is not possible to dissolve cellulose of high molecular weight neither at high concentrations.

Cellulose from different sources can be used to make all-cellulose composites, both for matrix and as reinforcing fibers. Within this scope, the most common fibers that were used to make ACCs were extracted from wood (Shibata et al., 2013) and cotton (Duchemin et al., 2016).

Alfa grass (called also Esparto grass) grows in semi-arid regions located Lybia, Tunisia, Algeria, Morocco and Spain. In Tunisia, surface covered by alfa plants is approximatively 600000 ha (Belkhir et al., 2013). Nowadays, the annual production of alfa in Tunisia is about 40000 tons and it is exclusively used for making pulp and high quality paper (SNCPA). Thermoplastic composites with alfa reinforcing fibers have been reported in several studies and improvements in their Young's modulus were achieved, for example in (Mechakra et al., 2015). However, to the best of our knowledge, ACCs made from alfa fibers have not been reported.

In this work, we used alfa fibers to open new ways of applications of this plant, in particular for making all-cellulose composites. Two sets of ACCs were manufactured: the matrices were based on wood and alfa pulps and the solvent was 8 wt% NaOH-water in order to keep all-cellulose composites truly environmentally friendly while reinforcing fibers were extracted from alfa stems and used for both types of matrices. Morphology, density, crystallinity and mechanical properties of composites were investigated and compared.

**2. Materials and methods**

**2.1. Materials**

Alfa stems (Figure 1) were harvested from Kasserine region in Tunisia and wood pulp was kindly supplied by Stora Enso Oyj as sheets. Sodium hydroxide (purity>98 %) was supplied by VWR International while sulfuric acid, lithium chloride and DMAc were supplied by Sigma-Aldrich. Deionized water was used to make cellulose solvent.

**2.2. Methods**

Alfa stems were used to prepare the reinforcing fibers and alfa pulp. The latter, along with wood pulp, was used to make the dissolving pulp by reducing cellulose degree of polymerization using acid hydrolysis. Then, alfa fibers were used to reinforce matrices that were made from both alfa and wood dissolving pulps. Each step and fibers' treatment is detailed below, and the schematic presentation of all-cellulose composites' preparation is given in Figure 1.

**2.2.1. Preparation of alfa reinforcing fibers**

To prepare the alfa reinforcing fibers (AF), alfa stems were subjected to alkali treatments using 3.25 M NaOH-water for 2.5 hours at 100 °C, with stems/NaOH-water ratio of 1g/20 mL. The fibers were then washed with tap water and dried in an oven at 105 °C for 1 hour.

**2.2.2. Preparation of alfa pulp**

To prepare alfa pulp which will be used for making dissolving pulp (Figure 1), six

different treatments of alfa stems were performed in order to select one which gives the

highest cellulose content and the best yield. Stems were treated in an air bath digester

consisting of six tube-like reactors with a total volume of 2.5 dm$^3$. These reactors were filled

by NaOH 11 wt%-water with stems/NaOH-water ratio of 1g/20 mL and stems were treated

for20, 40 and 60 minutes at 150 °C and for 90, 120 and 150 minutes at 100 °C.

**2.2.3. Preparation of alfa and wood dissolving pulps (acid hydrolysis)**

The degree of polymerization (DP) of both alfa pulp and wood pulp needed to be reduced

in order to enhance the dissolution. The reduction of DP of each type of pulp was performed

with a combined process using mild milling with a Wiley Mill model N°2 followed by

hydrolysis in 0.6 M sulfuric acid-water at 88 °C for 1 hour under mild mechanical stirring.

**2.2.4. Manufacturing of the ACCs**

A 8 wt% NaOH-water solution was pre-cooled to -7 °C using a Thermomix® UB bath

and5wt% of the dissolving pulp, either from wood or from alfa, was introduced. The

dissolution time was 2 hours and the mixing speed was 300 rpm. The reinforcing alfa fibers

were added to solution and mixed for a few minutes. It is to be mentioned that for high

concentrations of reinforcing AFs, some 8 wt% NaOH-water was added in order to wet them

and help their incorporation into the solution of dissolving pulp. The mixtures were then cast

into Petri dishes and introduced into coagulation water baths for 3 days to wash out NaOH.

Water was renewed 5 to 6 times until neutral pH was reached. Finally, wet samples were cold

pressed using a Lorentzen & Wettre sheet press using 3.7 bars for 2 minutes and then hot

pressed using a Carver hydraulic laboratory press at 39.2 bars and 100 °C for 2 hours. ACCs

with 17 wt% of reinforcing AFs were pressed at 80 °C for 90 minutes because samples were

fragile. The final concentrations (weight percentage) of the reinforcing AFs in the dry

composite ranged from 17 to 75 wt%. The obtained ACCs will be named "MAy" where "M"

143 is the dissolving pulp type used for matrix ("A" for alfa and "W" for wood) and "Ay" means

144 that the reinforcing fibers were alfa of "y" concentration in the dry composite. Also, ACCs

145 that are based on alfa pulp will be named alfa ACCs and those made from wood pulp will be

146 named wood ACCs.

**2.2.5. Characterization of the fibers and pulps**

148 Cellulose, hemicellulose and lignin contents was determined according to the NREL/TP-

149 510-42618 standard (Sluiter et al., 2012). Briefly, the fibers were mild milled and then treated

150 with 72 wt% sulfuric acid to dissolve cellulose, hemicellulose and acid soluble lignin (ASL).

151 The latter component was analyzed by Shimadzu UV-2550 spectrophotometer within the

152 wavelength range from 200 nm to 300 nm. ASL adsorption coefficient at the wave length

153 equal to 240 nm was 110 $L.g^{-1}.cm^{-1}$ for wood fibers and 25 $L.g^{-1}.cm^{-1}$ for alfa fibers. The acid

154 insoluble lignin (Klason lignin) content was determined gravimetrically after overnight

155 drying. The monosaccharides from cellulose and hemicellulose were analyzed by high

156 performance anion exchange chromatography equipped with pulse amperometric detection

157 (HPAEC-PAD) in a Dionex ICS-3000 column. The monosaccharides were converted into

158 polysaccharides content using correction factors based on birch fibers data (Janson, 1970).

159 Mineral content was determined using ISO 1762 (2001) standard by burning the organic

160 material at 525 °C for 5 hours and then measuring the weight of residue. For all chemical

161 composition determinations, duplicates were made and the average was considered; the

162 difference was within 5 %.

163 The yield after alfa stems' treatment in the air bath digester was calculated using Equation

164 1.

165 $$Yield\ (\%) = (weight\ of\ extracted\ pulp\ /\ weight\ of\ raw\ stems) \times 100 \qquad (1)$$

166 The number average molecular weight $M_n$ and the weighted average molecular weight $M_w$

167 of cellulose were determined using Gel Permeation Chromatography (GPC), Dionex Ultimate

168    3000 system (measurements were performed in duplicate). Cellulose was dissolved using a

169    90 g.L$^{-1}$ LiCl-DMAc solvent (Ma et al., 2016). Prior to analysis, samples were activated in

170    water, acetone and pure DMAc, respectively.

171    The polymerization degree (DP) was calculated using Equation 2.

$$DP = M_n / M_{glucose} \hspace{4cm} (2)$$

173    The dissolution degree of alfa and wood dissolving pulps in 8 wt% NaOH-water was

174    determined according to the following method. The solution of the dissolved pulp was

175    filtered using a filter with pore size 5 μm. The residue on the top of the filter was flashed with

176    8 wt% NaOH-water to remove the residual dissolved cellulose, then washed with tap water,

177    filtered and dried at 60 °C for 24 hours; it was considered as non-dissolved cellulose.

178    Cellulose from solution that passed the filter was coagulated using 1 M sulfuric acid-water,

179    washed with tap water, collected on 10-12 μm filter paper and then dried at 60 °C for 24

180    hours; it was considered as dissolved cellulose. The dissolution degree (DD) was calculated

181    according to the Equation 3 (Kihlman et al., 2011; Wang, 2008):

$$DD = W_d / (W_d + W_u) \hspace{4cm} (3)$$

183    where $W_d$ and $W_u$ are the weights of dissolved and non-dissolved cellulose, respectively.

184    **2.2.6. Characterization of the ACCs**

185    A Zeiss Sigma VP scanning electron microscope was used to study ACC morphology.

186    Samples were placed on the top a carbon tape and then a thin platinum layer was sputtered

187    using Leica EM ACE600 to ensure conductivity.

188    Density was calculated by drying composites overnight at 105 °C and measuring their

189    weight and volume (three samples per each ACC).

190    Reinforcing AFs and ACCs were studied by X-ray diffraction (XRD). A Bruker D8

191    advance XRD diffractometer with Cu Kα radiation (λ=1,54Å) was used and samples were

192    analyzed for 2θ between 5 and 40°. The obtained curves were simulated using a Gaussian

193 mathematical function (Ma et al., 2011; Qi et al., 2009) and the baseline was subtracted. To

194 take into account the presence of the cellulose amorphous fraction, we followed a method

195 that was described by Piltonen et al. (Piltonen et al., 2016): a Gaussian curve that is centered

196 at 18.6° was added and peaks' full width at half maximum (FWHM) was adjusted to 2θ=7°

197 for reinforcing AFs and to 2θ=10° for ACCs . The crystallinity determinations were

198 conducted by dividing the integrated area of cellulose crystalline peaks by the total area (Qi

199 et al., 2009) as shown in Equations 4-5:

$$Cr = (A_{cell\ I} + A_{Cell\ II}) / (A_{cell\ I} + A_{Cell\ II} + A_{amorph}) \qquad (4)$$

$$Amorph = A_{amorph} / (A_{cell\ I} + A_{Cell\ II} + A_{amorph}) \qquad (5)$$

202 where Cr, A and Amoprh are crystallinity, integrated area and amorphous fraction,

203 respectively.

204   The mechanical properties of composites were investigated using a MTS 400device using

205 a 200 N cell load. Tensile tests were performed according to ISO 1924-2 (2008).Samples

206 were cut into dog bone-like specimens and conditioned for 24 hours at 50 % relative

207 humidity (RH) and 23 °C. The displacement speed was 0.5 mm.min$^{-1}$. For each set of ACCs,

208 a minimum of 5 measurements were conducted. The yield stress ($\sigma_{0.2}$) was recorded at 0.2 %

209 of strain.

210 **3. Results and discussions**

211 **3.1. Production of alfa pulp**

212   Various treatments of alfa stems were used to select the best pulp in terms of highest

213 cellulose content and yield. Table 1 shows the composition of the obtained pulps as a

214 function of the treatment used. Cellulose content was significantly higher for the treatments

215 performed at 150 °C as compared to those at 100 °C. This was expected since the removal of

216 non-cellulosic components is enhanced by increasing the temperature (Kihlman et al., 2011).

217 These results are also consistent with the work done by Borrega et al. where an increase of

218    extraction temperature led to an increase of cellulose percentage in birch wood (Borrega et

219    al., 2013). A slight increase in cellulose content can be seen with the increase in treatment

220    duration, as expected. Hemicellulose and lignin content was significantly lower for all

221    treatments at 150 °C as compared to those at 100 °C. Moreover, lignin content decreased by

222    almost half with increasing the treatment's duration from 20 to 60 minutes at 150 °C, but

223    remained almost the same for the treatments at 100 °C. These results are in agreement with

224    those reported by Borchani et al. where alkaline treatment decreased the amount of

225    hemicellulose and lignin in alfa fibers (Borchani et al., 2015).

226        The yield for all applied treatments was low, especially for fibers treated at 150 °C. This

227    was considered to be normal due to the relatively low content of cellulose in the raw stems.

228    For instance, Hanana et al. (Hanana et al., 2015) found that weight loss of alfa fibers treated

229    in autoclave was around 45 % after treatment with a 4 wt% NaOH-water solution at 120 °C

230    for 20 minutes.

231        In order to select which treatment to apply in order to obtain alfa pulp that will be used for

232    making the matrix, cellulose content and the treatment's yield were considered as the most

233    significant parameters because cellulose is the component that brings the mechanical strength

234    to the composite and the yield should be acceptable to make the process viable. However,

235    higher cellulose contents were obtained with the treatments leading to the lowest yield. As a

236    compromise, the treatment at 150 °C during 20 min was selected.

237    **3.2. Production of alfa and wood dissolving pulps**

238        It is known that cellulose of high molecular weight cannot be well dissolved in (7-9) wt%

239    NaOH-water solvent (Budtova and Navard, 2016). Thus the DP of each pulp, from wood and

240    from alfa, was decreased using acid hydrolysis. Table 2 shows the effect of acid hydrolysis

241    on the DP of alfa and wood pulps. The reduction of DP was calculated towards the initial

242    value. For both types of pulps, acid hydrolysis had a significant effect: for alfa pulp, the DP

243   was reduced by 84 % and for wood by 67 %. After the treatment, the DP of both wood and

244   alfa was almost the same.

245       The composition of the dissolving wood and alfa pulps is presented in Table 2 as well.

246   Wood dissolving pulp was richer in cellulose and poorer in lignin and ash as compared to

247   alfa.

248   **3.3. Dissolution of alfa and wood dissolving pulps in 8 wt% NaOH-water**

249       The degree of dissolution was around 95-96 % for alfa and wood dissolving pulps most

250   probably because their DP were almost the same, as shown in Table 2. These results are in

251   agreement with those reported by Kihlman et al. who dissolved a commercial grade wood

252   pulp in a NaOH-urea-thiourea system after reducing its DP with steam-explosion and reached

253   the degree of dissolution of 94 % (Kihlman et al., 2011). Although some small "particles"

254   corresponding to the non-dissolved fractions were present after the dissolution, they were not

255   considered as a part of the reinforcing fibers as their reinforcing action is minor and their

256   amount and size are low (<5 wt%).

257       We also checked the dissolution of milled alfa pulp before acid hydrolysis and no sign of

258   dissolution was recorded. In addition, mild milled wood pulp before hydrolysis had a

259   dissolution degree equal to 23 % which was considered to be too low for making the matrix.

260   Hence, the acid hydrolysis was mandatory in order to achieve a high DD.

261   **3.4. ACCs morphology and density**

262       Figure 2 shows representative examples of the morphology of the obtained ACCs and of

263   their fractured counterparts. The reinforcing fibers were very well embedded in both types of

264   matrices giving an excellent interfacial adhesion (Figure 2a, b). In fact, the latter parameter is

265   crucial for composites since the interface quality directly affects the final mechanical

266   properties (Mechakra et al., 2015).

267    However, voids appear in the bulk of both types of composites. The presence of voids may

268    be attributed to the high amount of reinforcing AFs that reached 75 wt% in the dry

269    composite: in other words, there was "not enough" matrix to "glue together" the reinforcing

270    fibers. It should be mentioned that this fiber concentration is far beyond the usual fiber load

271    that a traditional polymer matrix can handle (Pai and Jagtap, 2015). As it will be shown

272    further, the presence of voids significantly influences the properties of ACCs.

273    The bulk density of ACCs as a function of the amount of reinforcing fibers in both types

274    of matrices is presented in Figure 3. The two sets of ACCs showed a very similar behavior:

275    the density decreased from 0.9-1 $g.cm^{-3}$ for composites with 17 wt% of reinforcing fibers to

276    0.6-0.7 $g.cm^{-3}$ for composites with 58 wt% of reinforcing fibers and no significant change in

277    the bulk density was observed for the reinforcing fiber content above 58 %. In fact, the latter

278    values of ACCs density are twice lower than the skeletal density of cellulose itself (1.5 $g.cm^{-3}$

279    ) meaning that porosity of composites, calculated according to Equation 6, vary from around

280    30 % to around 60 %.

281    *Porosity (%) = 1 - (bulk density/cellulose skeletal density) × 100*        (6)

282    Overall, the bulk density was decreasing with the increase of reinforcing AFs' content which

283    means that the number of voids increased with the addition of reinforcing fibers. This will

284    have an important effect on the mechanical properties of composites.

285    **3.5. ACCs structural properties**

286    Figures 4a and 4b present the XRD curves for reinforcing AFs along with alfa and wood

287    ACCs, respectively. It is known that  cellulose I crystalline peaks are located around 2θ=14.8,

288    16.3 and 22.6 and correspond to the planes ($1\overline{1}0$), (110) and (200), respectively, while peaks

289    related to cellulose II are located around 2θ=12.1, 19.8 and 22.0 and correspond to the planes

290    ($1\overline{1}0$), (110) and (200), respectively (Ma et al., 2011; Qi et al., 2009).

291     Reinforcing AFs showed the three common cellulose I peaks that were located around

292 15.1, 16.7 and 22.9° together with a fourth peak around 34.6° that is rarely observed (Nam et

293 al., 2016) and that can be present both cellulose I and II. For the crystallinity calculations, we

294 supposed that latter peak represents only the contribution of cellulose I. The peak that

295 corresponds to the (200) plane of cellulose I was slightly shifted towards 22.5° for the two

296 sets of ACCs probably due to residual stress resulting from composites manufacturing. The

297 two sets of ACCs showed the coexistence of cellulose I and cellulose II, as expected, with

298 cellulose II peaks around 12.0 and 19.9°.

299     ACCs' crystalline and amorphous percentages are listed in Table 3 and an example of

300 peaks' deconvolution and fitting for AA67 is shown in Figure 5. Reinforcing fibers

301 crystallinity (Cr) was high as a result of the removal of amorphous non cellulosic materials.

302 Borchani et al. (Borchani et al., 2015) reported Cr values in the same range for alfa fibers that

303 were treated using NaOH. Moreover, ACCs crystallinity was surprisingly higher than that of

304 reinforcing fibers for most AFs' concentrations. To explain this increase of the crystallinity,

305 we supposed that a strong orientation of cellulose chains was induced as a result of the

306 compression step during the preparation of ACCs (Nam et al., 2016). The orientation was less

307 marked when the reinforcing AFs' concentration increased from 16-75 wt% with a decrease

308 of the crystallinity by 10-15 %. This could be due to the role of obstacles that reinforcing

309 fibers played, hindering the formation of crystalline regions inside the matrices under high

310 pressure.

311 **3.6. ACCs mechanical properties**

312     Within the studied ACCs,  reinforcing AFs and the matrix are made from the same matter

313 (lignocellulose), giving rise to two reinforcing mechanisms i) on one hand, the adhesion

314 between fibers and the matrix is extremely good (Nishino and Arimoto, 2007) and ii) on the

315 other hand, alfa fibers are characterized by a Young's modulus E=22 GPa and a tensile

breaking strength $\sigma_b$=565 MPa (Bessadok et al., 2009) that are significantly higher than those of the pure cellulose II having a Young's modulus E ~few GPa and a tensile strength $\sigma$<130 MPa (Budtova and Navard, 2016).

Figure 6a shows the Young's modulus of the prepared ACCs as a function of reinforcing AFs' concentration. The best value was 3.8 GPa for alfa ACCs and 4.2 GPa for wood ACCs, with 38 and 50 wt% of reinforcing AFs, respectively. A strong drop of Young's modulus with the increase of reinforcing fibers was observed for both sets of ACCs; this was not expected since it is widely known that increasing reinforcing fibers' concentration in polymer composites usually increases the modulus. The reason of this decrease can be explained by the decrease of composites' bulk density: the higher the amount of reinforcing fibers is, the lower is ACCs' density, as shown in Figure 3. Therefore, when volume fractions of ACCs that are filled with the matrix decreased with the increase of reinforcing AFs' concentration, the cross section area of tensile samples receiving the mechanical load was reduced leading to mechanically weak ACCs. A similar but much weaker phenomenon was reported for ACC laminates prepared using NaOH-urea-water solvent (Dormanns et al., 2016).

Figure 6b illustrates the relationship between the Young's modulus of the alfa and wood ACCs and their bulk density: as expected, the modulus increased with density increase. Slightly higher modulus values of wood ACCs were obtained; this can be attributed to the difference in composition of the dissolving pulps, as illustrated in Table 2.

A phenomenon similar to Young's modulus dependence was recorded for the yield stress of ACCs: first it decreases with the addition of fibers but then decreases (Figure 7a). The maximum values of yield stress were 16 and 13.9 MPa for alfa and wood ACCs, respectively, corresponding to 38 and 50 wt% of reinforcing AFs, respectively. The maximum obtained for the yield stress reflects two counterbalancing phenomena: the reinforcing effect due to the increase of reinforcing AFs' concentration and the "weakening" effect due to the amount of

341    voids that increased with the increase of alfa fiber content. Yield stress - density dependence

342    also showed a maximum which corresponds to a composites' density around 0.8 g.cm$^{-3}$

343    (Figure 7b).

344        In order to have an insight on the failure mechanism of ACCs, an example of their

345    microstructure after fracture is given in Figure 2c-d. For all the SEM images that have been

346    analyzed, there was no evidence of cracks that would have initiated inside the reinforcing

347    AFs. Moreover, these fibers were not pulled out from the cellulosic matrix as can be seen

348    form Figure 2d where the interface between the fibers and the matrix did not contain any

349    voids. It is well known that in traditional thermoplastic polymer-natural fiber based

350    composites, the pull-out of fibers under mechanical load is a typical phenomenon and occurs

351    when the adhesion between hydrophilic natural fibers and hydrophobic matrix is poor

352    (Mechakra et al., 2015). However, for ACCs, this is not the case since both reinforcing fibers

353    and matrices are made from the same material. Hence, it can be suggested that the main cause

354    for composites failure under tensile loading was the breakdown of the matrices. This failure

355    was an expected consequence of two weakening sources: the first is that they are both made

356    from cellulose II of low molecular weight and the second is the presence of a significant

357    amount of voids.

358

359    **4. Conclusions**

360        ACCs were successfully manufactured using alfa as reinforcing fibers with two types of

361    matrices made from wood and alfa dissolving pulps. Alfa fibers were extracted from alfa

362    stems while dissolving pulps were made by a sequence of treatments. XRD analysis of ACCs

363    showed that native cellulose I and regenerated cellulose II coexisted. Moreover, SEM

364    analysis showed that the adhesion between the reinforcing AFs and both matrices was

365    excellent. However, at high concentrations of reinforcing fibers there was "not enough"

366  matrix to "glue" them together, leading to the presence of voids. This was reflected by the

367  decrease of composite density with the increase of reinforcing AFs' concentration. As a

368  consequence, Young's modulus decreased and yield stress showed a maximum as a function

369  of reinforcing AFs' concentration. The best values, around 4 GPa for Young's modulus and

370  around 14-16 MPa for yield stress, were obtained with 38-50 wt% of reinforcing AFs in the

371  dry composite. Finally, this study confers an added value to alfa fibers as a potential resource

372  for making new ecological materials that combine low density and good mechanical

373  properties.

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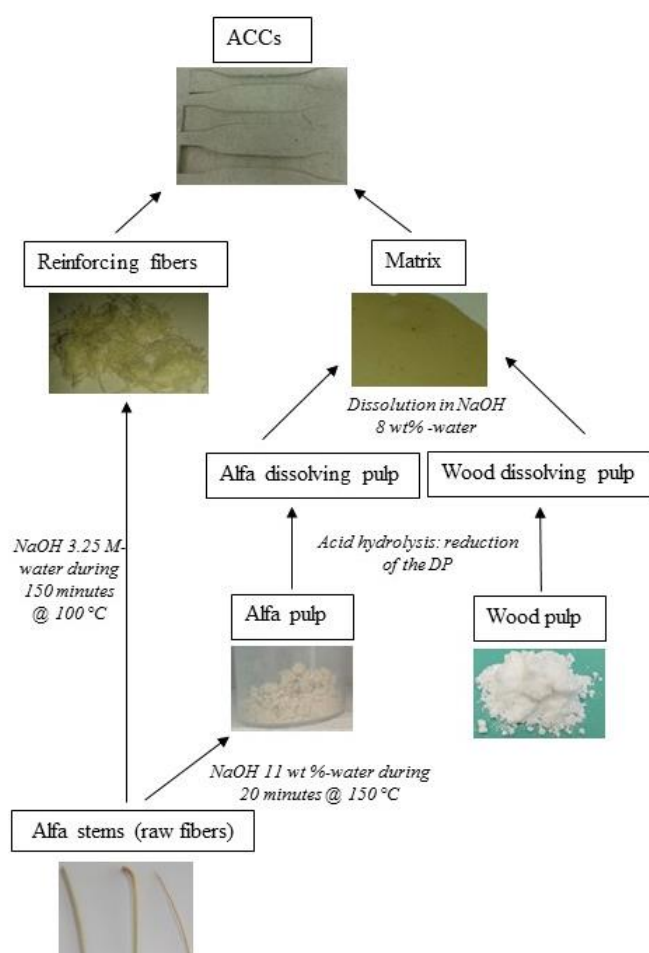
467

468 **Figures**

469



470       Figure 1. Schematic representation of the different steps of ACCs' processing
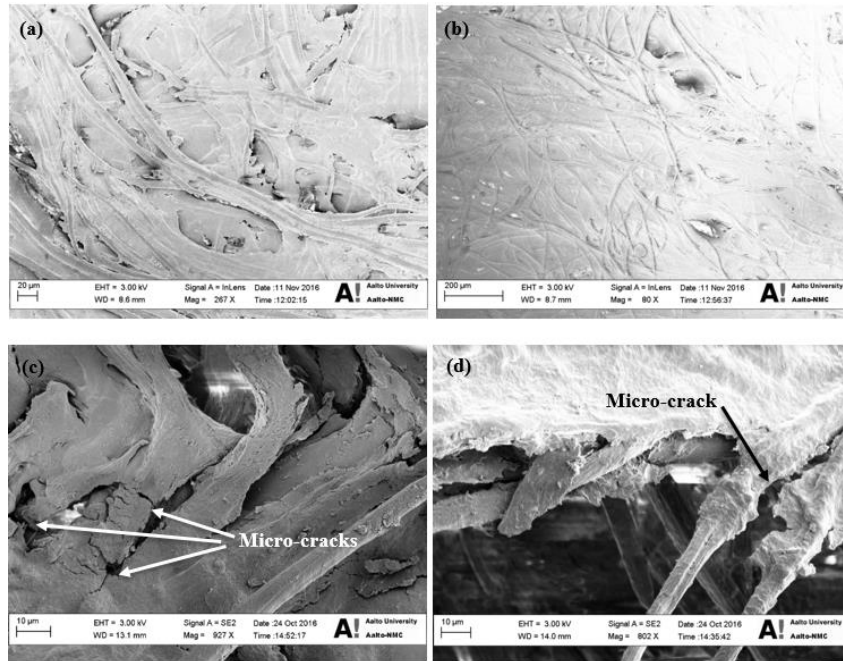
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472    Figure 2. SEM micrographs from the surface of: (a) AA67and (b) WA67 and near the

473    fracture plane of (c) AA50 and (d) WA50
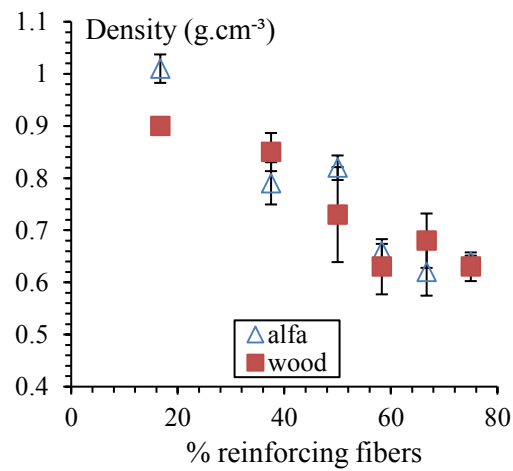
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476    Figure 3. Densities of ACCs as a function of reinforcing AFs' concentration
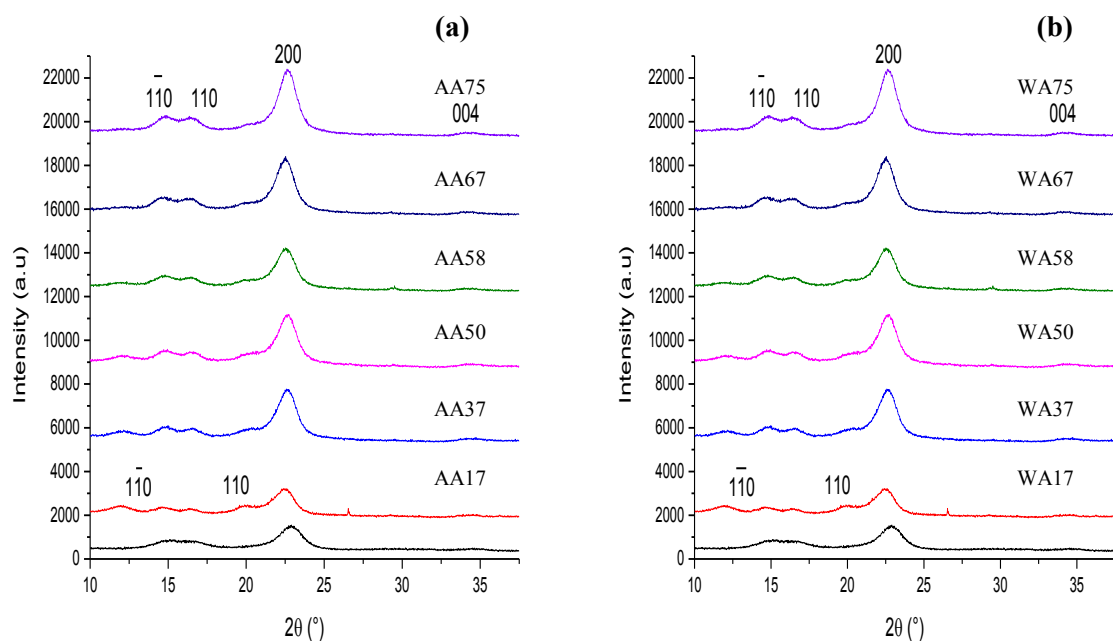
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Figure 4. XRD patterns of reinforcing fibers (curves in the bottom) together with: (a) alfa and
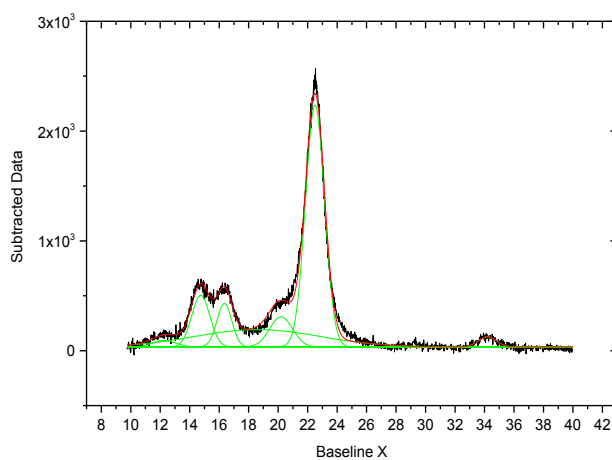
(b) wood ACCs



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Figure 5. XRD curve fitting of AA67 with the correlation coefficient R²=0.9911
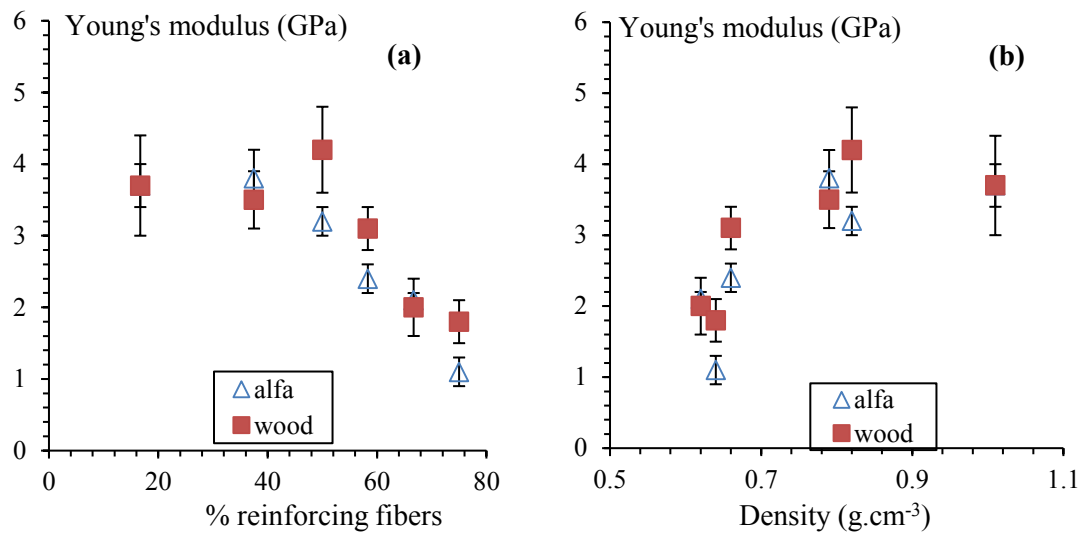
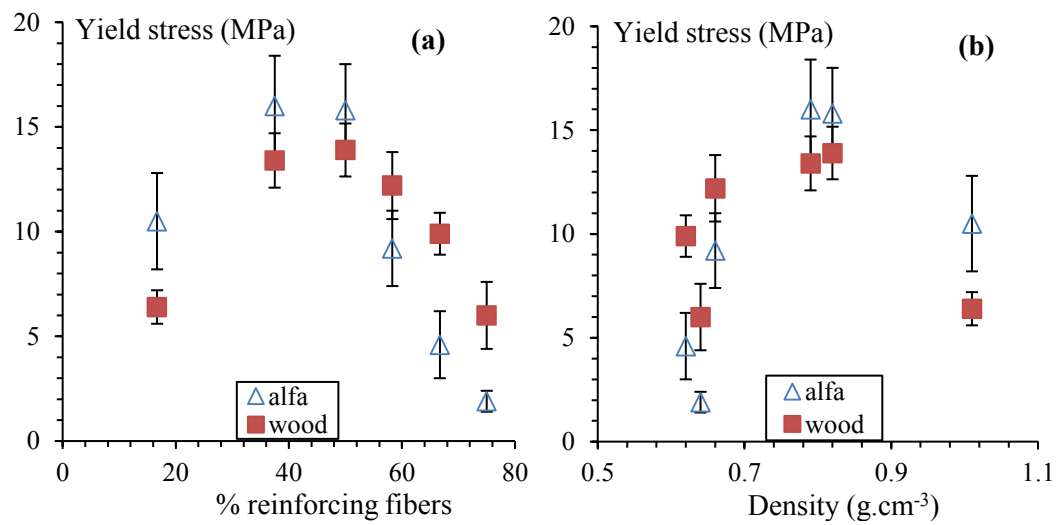Figure 6. Young's modulus of ACCs as a function of: (a) reinforcing AFs' concentration and (b) composites' density



Figure 7. Yield stress of ACCs as a function of: (a) reinforcing AFs' concentration and (b) composites' density

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Table 1. Alfa pulp composition as a function of the applied treatments

| | Initial alfa stems | Alfa pulps | | | | | |
|---|---|---|---|---|---|---|---|
| NaOH (wt%) | - | 11 | 11 | 11 | 11 | 11 | 11 |
| Temperature (° C) | - | 150 | 150 | 150 | 100 | 100 | 100 |
| Time (min) | - | 20 | 40 | 60 | 90 | 120 | 150 |
| Cellulose (wt%) | 44.2 | 81.2 | 83.6 | 83.4 | 76.4 | 78.3 | 77.3 |
| Hemicellulose (wt%) | 23.0 | 3.1 | 2.3 | 1.9 | 4.9 | 4.1 | 4.0 |
| Lignin (wt%) | 25.4 | 5.1 | 3.2 | 2.7 | 8.6 | 7.3 | 8.5 |
| Ash content (wt%) | 2.4 | 1.5 | N.A | N.A | N.A | N.A | N.A |
| Yield (%) | - | 21 | 14.4 | 15.7 | 30 | 32.1 | 31.3 |

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497 Table 2. Evolution of DPs for alfa and wood pulps after treatments together with the

498 dissolving pulps' final composition

| Pulp type | Initial DP | DP after acid hydrolysis | DP reduction (%) | Cellulose (wt%) | Hemicellulose (wt%) | Lignin (wt%) | Ash (wt%) |
|---|---|---|---|---|---|---|---|
| Alfa | 916 | 149 | 84 | 88.2 | 1.2 | 3.7 | 1.5 |
| Wood | 437 | 145 | 67 | 92.9 | 6.7 | 0.4 | 0.0 |

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505 Table 3. The crystallinity of ACC as a function of reinforcing AFs' concentration

| | Alfa ACCs | | | | | | Wood ACCs | | | | | | AFs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AFs (wt%) | 16.7 | 37.5 | 50 | 58.3 | 66.7 | 75 | 16.7 | 37.5 | 50 | 58.3 | 66.7 | 75 | 100 |
| Cr (%) | 93 | 91 | 82 | 78 | 77 | 78 | 91 | 88 | 84 | 87 | 82 | 81 | 80 |
| Amorph (%) | 7 | 9 | 18 | 22 | 23 | 22 | 9 | 12 | 16 | 13 | 18 | 19 | 20 |
| $R^2$ ($10^{-2}$) | 98.91 | 98.66 | 98.65 | 98.88 | 99.11 | 99.08 | 97.46 | 98.09 | 98.47 | 98.85 | 98.74 | 98.87 | 97.95 |

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