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All-cellulose composites from alfa and wood fibers

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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-oxide monohydrate (NMMO), lithium chloride-N,N-dimethylacetamide (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 in Libya, Tunisia, Algeria, Morocco and Spain. In Tunisia, surface covered by alfa plants is approximately 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 dm³. These reactors were filled by NaOH 11 wt%-water with stems/NaOH-water ratio of 1g/20 mL and stems were treated for 20, 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 and 5 wt% 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”

is the dissolving pulp type used for matrix (“A” for alfa and “W” for wood) and “Ay” means that the reinforcing fibers were alfa of “y” concentration in the dry composite. Also, ACCs that are based on alfa pulp will be named alfa ACCs and those made from wood pulp will be named wood ACCs.

2.2.5. Characterization of the fibers and pulps

Cellulose, hemicellulose and lignin contents was determined according to the NREL/TP-510-42618 standard (Sluiter et al., 2012). Briefly, the fibers were mild milled and then treated with 72 wt% sulfuric acid to dissolve cellulose, hemicellulose and acid soluble lignin (ASL). The latter component was analyzed by Shimadzu UV-2550 spectrophotometer within the wavelength range from 200 nm to 300 nm. ASL adsorption coefficient at the wave length equal to 240 nm was $110 \text{ L.g}^{-1}.\text{cm}^{-1}$ for wood fibers and $25 \text{ L.g}^{-1}.\text{cm}^{-1}$ for alfa fibers. The acid insoluble lignin (Klason lignin) content was determined gravimetrically after overnight drying. The monosaccharides from cellulose and hemicellulose were analyzed by high performance anion exchange chromatography equipped with pulse amperometric detection (HPAEC-PAD) in a Dionex ICS-3000 column. The monosaccharides were converted into polysaccharides content using correction factors based on birch fibers data (Janson, 1970). Mineral content was determined using ISO 1762 (2001) standard by burning the organic material at 525 °C for 5 hours and then measuring the weight of residue. For all chemical composition determinations, duplicates were made and the average was considered; the difference was within 5 %.

The yield after alfa stems’ treatment in the air bath digester was calculated using Equation 1.

$$\text{Yield (\%)} = (\text{weight of extracted pulp} / \text{weight of raw stems}) \times 100 \quad (1)$$

The number average molecular weight M_n and the weighted average molecular weight M_w of cellulose were determined using Gel Permeation Chromatography (GPC), Dionex Ultimate

3000 system (measurements were performed in duplicate). Cellulose was dissolved using a 90 g.L⁻¹ LiCl-DMAc solvent (Ma et al., 2016). Prior to analysis, samples were activated in water, acetone and pure DMAc, respectively.

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

$$DP = M_n / M_{glucose} \quad (2)$$

The dissolution degree of alfa and wood dissolving pulps in 8 wt% NaOH-water was determined according to the following method. The solution of the dissolved pulp was filtered using a filter with pore size 5 µm. The residue on the top of the filter was flashed with 8 wt% NaOH-water to remove the residual dissolved cellulose, then washed with tap water, filtered and dried at 60 °C for 24 hours; it was considered as non-dissolved cellulose.

Cellulose from solution that passed the filter was coagulated using 1 M sulfuric acid-water, washed with tap water, collected on 10-12 µm filter paper and then dried at 60 °C for 24 hours; it was considered as dissolved cellulose. The dissolution degree (DD) was calculated according to the Equation 3 (Kihlman et al., 2011; Wang, 2008):

$$DD = W_d / (W_d + W_u) \quad (3)$$

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

2.2.6.Characterization of the ACCs

A Zeiss Sigma VP scanning electron microscope was used to study ACC morphology. Samples were placed on the top a carbon tape and then a thin platinum layer was sputtered using Leica EM ACE600 to ensure conductivity.

Density was calculated by drying composites overnight at 105 °C and measuring their weight and volume (three samples per each ACC).

Reinforcing AFs and ACCs were studied by X-ray diffraction (XRD). A Bruker D8 advance XRD diffractometer with Cu K α radiation ($\lambda=1,54\text{\AA}$) was used and samples were analyzed for 2θ between 5 and 40°. The obtained curves were simulated using a Gaussian

mathematical function (Ma et al., 2011; Qi et al., 2009) and the baseline was subtracted. To take into account the presence of the cellulose amorphous fraction, we followed a method that was described by Piltonen et al. (Piltonen et al., 2016): a Gaussian curve that is centered at 18.6° was added and peaks' full width at half maximum (FWHM) was adjusted to 2θ=7° for reinforcing AFs and to 2θ=10° for ACCs. The crystallinity determinations were conducted by dividing the integrated area of cellulose crystalline peaks by the total area (Qi et al., 2009) as shown in Equations 4-5:

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

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

where Cr, A and Amorph are crystallinity, integrated area and amorphous fraction, respectively.

The mechanical properties of composites were investigated using a MTS 400 device using a 200 N cell load. Tensile tests were performed according to ISO 1924-2 (2008). Samples were cut into dog bone-like specimens and conditioned for 24 hours at 50 % relative humidity (RH) and 23 °C. The displacement speed was 0.5 mm.min⁻¹. For each set of ACCs, a minimum of 5 measurements were conducted. The yield stress (σ_{0.2}) was recorded at 0.2 % of strain.

3. Results and discussions

3.1. Production of alfa pulp

Various treatments of alfa stems were used to select the best pulp in terms of highest cellulose content and yield. Table 1 shows the composition of the obtained pulps as a function of the treatment used. Cellulose content was significantly higher for the treatments performed at 150 °C as compared to those at 100 °C. This was expected since the removal of non-cellulosic components is enhanced by increasing the temperature (Kihlman et al., 2011). These results are also consistent with the work done by Borrega et al. where an increase of

extraction temperature led to an increase of cellulose percentage in birch wood (Borrega et al., 2013). A slight increase in cellulose content can be seen with the increase in treatment duration, as expected. Hemicellulose and lignin content was significantly lower for all treatments at 150 °C as compared to those at 100 °C. Moreover, lignin content decreased by almost half with increasing the treatment's duration from 20 to 60 minutes at 150 °C, but remained almost the same for the treatments at 100 °C. These results are in agreement with those reported by Borchani et al. where alkaline treatment decreased the amount of hemicellulose and lignin in alfa fibers (Borchani et al., 2015).

The yield for all applied treatments was low, especially for fibers treated at 150 °C. This was considered to be normal due to the relatively low content of cellulose in the raw stems. For instance, Hanana et al. (Hanana et al., 2015) found that weight loss of alfa fibers treated in autoclave was around 45 % after treatment with a 4 wt% NaOH-water solution at 120 °C for 20 minutes.

In order to select which treatment to apply in order to obtain alfa pulp that will be used for making the matrix, cellulose content and the treatment's yield were considered as the most significant parameters because cellulose is the component that brings the mechanical strength to the composite and the yield should be acceptable to make the process viable. However, higher cellulose contents were obtained with the treatments leading to the lowest yield. As a compromise, the treatment at 150 °C during 20 min was selected.

3.2. Production of alfa and wood dissolving pulps

It is known that cellulose of high molecular weight cannot be well dissolved in (7-9) wt% NaOH-water solvent (Budtova and Navard, 2016). Thus the DP of each pulp, from wood and from alfa, was decreased using acid hydrolysis. Table 2 shows the effect of acid hydrolysis on the DP of alfa and wood pulps. The reduction of DP was calculated towards the initial value. For both types of pulps, acid hydrolysis had a significant effect: for alfa pulp, the DP

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

The composition of the dissolving wood and alfa pulps is presented in Table 2 as well. Wood dissolving pulp was richer in cellulose and poorer in lignin and ash as compared to alfa.

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

The degree of dissolution was around 95-96 % for alfa and wood dissolving pulps most probably because their DP were almost the same, as shown in Table 2. These results are in agreement with those reported by Kihlman et al. who dissolved a commercial grade wood pulp in a NaOH-urea-thiourea system after reducing its DP with steam-explosion and reached the degree of dissolution of 94 % (Kihlman et al., 2011). Although some small “particles” corresponding to the non-dissolved fractions were present after the dissolution, they were not considered as a part of the reinforcing fibers as their reinforcing action is minor and their amount and size are low (<5 wt%).

We also checked the dissolution of milled alfa pulp before acid hydrolysis and no sign of dissolution was recorded. In addition, mild milled wood pulp before hydrolysis had a dissolution degree equal to 23 % which was considered to be too low for making the matrix. Hence, the acid hydrolysis was mandatory in order to achieve a high DD.

3.4. ACCs morphology and density

Figure 2 shows representative examples of the morphology of the obtained ACCs and of their fractured counterparts. The reinforcing fibers were very well embedded in both types of matrices giving an excellent interfacial adhesion (Figure 2a, b). In fact, the latter parameter is crucial for composites since the interface quality directly affects the final mechanical properties (Mechakra et al., 2015).

However, voids appear in the bulk of both types of composites. The presence of voids may be attributed to the high amount of reinforcing AFs that reached 75 wt% in the dry composite: in other words, there was “not enough” matrix to “glue together” the reinforcing fibers. It should be mentioned that this fiber concentration is far beyond the usual fiber load that a traditional polymer matrix can handle (Pai and Jagtap, 2015). As it will be shown further, the presence of voids significantly influences the properties of ACCs.

The bulk density of ACCs as a function of the amount of reinforcing fibers in both types of matrices is presented in Figure 3. The two sets of ACCs showed a very similar behavior: the density decreased from 0.9-1 g.cm⁻³ for composites with 17 wt% of reinforcing fibers to 0.6-0.7 g.cm⁻³ for composites with 58 wt% of reinforcing fibers and no significant change in the bulk density was observed for the reinforcing fiber content above 58 %. In fact, the latter values of ACCs density are twice lower than the skeletal density of cellulose itself (1.5 g.cm⁻³) meaning that porosity of composites, calculated according to Equation 6, vary from around 30 % to around 60 %.

$$\text{Porosity (\%)} = 1 - (\text{bulk density} / \text{cellulose skeletal density}) \times 100 \quad (6)$$

Overall, the bulk density was decreasing with the increase of reinforcing AFs' content which means that the number of voids increased with the addition of reinforcing fibers. This will have an important effect on the mechanical properties of composites.

3.5. ACCs structural properties

Figures 4a and 4b present the XRD curves for reinforcing AFs along with alfa and wood ACCs, respectively. It is known that cellulose I crystalline peaks are located around $2\theta=14.8$, 16.3 and 22.6 and correspond to the planes $(\bar{1}\bar{1}0)$, (110) and (200) , respectively, while peaks related to cellulose II are located around $2\theta=12.1$, 19.8 and 22.0 and correspond to the planes $(\bar{1}\bar{1}0)$, (110) and (200) , respectively (Ma et al., 2011; Qi et al., 2009).

Reinforcing AFs showed the three common cellulose I peaks that were located around 15.1, 16.7 and 22.9° together with a fourth peak around 34.6° that is rarely observed (Nam et al., 2016) and that can be present both cellulose I and II. For the crystallinity calculations, we supposed that latter peak represents only the contribution of cellulose I. The peak that corresponds to the (200) plane of cellulose I was slightly shifted towards 22.5° for the two sets of ACCs probably due to residual stress resulting from composites manufacturing. The two sets of ACCs showed the coexistence of cellulose I and cellulose II, as expected, with cellulose II peaks around 12.0 and 19.9°.

ACCs' crystalline and amorphous percentages are listed in Table 3 and an example of peaks' deconvolution and fitting for AA67 is shown in Figure 5. Reinforcing fibers crystallinity (Cr) was high as a result of the removal of amorphous non cellulosic materials. Borchani et al. (Borchani et al., 2015) reported Cr values in the same range for alfa fibers that were treated using NaOH. Moreover, ACCs crystallinity was surprisingly higher than that of reinforcing fibers for most AFs' concentrations. To explain this increase of the crystallinity, we supposed that a strong orientation of cellulose chains was induced as a result of the compression step during the preparation of ACCs (Nam et al., 2016). The orientation was less marked when the reinforcing AFs' concentration increased from 16-75 wt% with a decrease of the crystallinity by 10-15 %. This could be due to the role of obstacles that reinforcing fibers played, hindering the formation of crystalline regions inside the matrices under high pressure.

3.6. ACCs mechanical properties

Within the studied ACCs, reinforcing AFs and the matrix are made from the same matter (lignocellulose), giving rise to two reinforcing mechanisms i) on one hand, the adhesion between fibers and the matrix is extremely good (Nishino and Arimoto, 2007) and ii) on the 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 $E \sim \text{few GPa}$ 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

voids that increased with the increase of alfa fiber content. Yield stress - density dependence also showed a maximum which corresponds to a composites' density around 0.8 g.cm^{-3} (Figure 7b).

In order to have an insight on the failure mechanism of ACCs, an example of their microstructure after fracture is given in Figure 2c-d. For all the SEM images that have been analyzed, there was no evidence of cracks that would have initiated inside the reinforcing AFs. Moreover, these fibers were not pulled out from the cellulosic matrix as can be seen from Figure 2d where the interface between the fibers and the matrix did not contain any voids. It is well known that in traditional thermoplastic polymer-natural fiber based composites, the pull-out of fibers under mechanical load is a typical phenomenon and occurs when the adhesion between hydrophilic natural fibers and hydrophobic matrix is poor (Mechakra et al., 2015). However, for ACCs, this is not the case since both reinforcing fibers and matrices are made from the same material. Hence, it can be suggested that the main cause for composites failure under tensile loading was the breakdown of the matrices. This failure was an expected consequence of two weakening sources: the first is that they are both made from cellulose II of low molecular weight and the second is the presence of a significant amount of voids.

4. Conclusions

ACCs were successfully manufactured using alfa as reinforcing fibers with two types of matrices made from wood and alfa dissolving pulps. Alfa fibers were extracted from alfa stems while dissolving pulps were made by a sequence of treatments. XRD analysis of ACCs showed that native cellulose I and regenerated cellulose II coexisted. Moreover, SEM analysis showed that the adhesion between the reinforcing AFs and both matrices was excellent. However, at high concentrations of reinforcing fibers there was “not enough”

matrix to “glue” them together, leading to the presence of voids. This was reflected by the decrease of composite density with the increase of reinforcing AFs’ concentration. As a consequence, Young’s modulus decreased and yield stress showed a maximum as a function of reinforcing AFs’ concentration. The best values, around 4 GPa for Young’s modulus and around 14-16 MPa for yield stress, were obtained with 38-50 wt% of reinforcing AFs in the dry composite. Finally, this study confers an added value to alfa fibers as a potential resource for making new ecological materials that combine low density and good mechanical properties.

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Declaration of interest: none

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Figures

Figure 1. Schematic representation of the different steps of ACCs' processing

Figure 2. SEM micrographs from the surface of: (a) AA67 and (b) WA67 and near the fracture plane of (c) AA50 and (d) WA50

Figure 3. Densities of ACCs as a function of reinforcing AFs' concentration

Figure 4. XRD patterns of reinforcing fibers (curves in the bottom) together with: (a) alfa and (b) wood ACCs

Figure 5. XRD curve fitting of AA67 with the correlation coefficient $R^2=0.9911$

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

Tables

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

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