Alfa fiber/polypropylene composites: influence of fiber extraction method and chemical

treatments

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Abstract

Alfa fiber/polypropylene composites were manufactured using twin-screw extrusion. Fibers were

extracted following alkaline and steam explosion methods. Three chemical treatments were also

applied to alkaline extracted fibers namely, stearic acid (SA), potassium permanganate that was

dissolved in water (KW) and in acetone (KA). Finally, a thermal annealing was applied to composites.

It has been shown that composites with steam-exploded fibers had significantly higher melt flow index

than composites with alkaline extracted fibers. Moreover, the incorporation of fibers into the matrix

increased Young's modulus where the optimum result was obtained with alkaline extracted fibers.

Besides, both extraction methods significantly decreased the water uptake especially the steam

explosion. The three chemical treatments increased the melt flow index and conversely decreased the

tensile strength and Young's modulus. In addition, KW treatment decreased the water uptake. Finally,

the thermal annealing increased the tensile strength and Young's modulus of composites with SA-

treated fibers.

1. Introduction

Polymer based composites are defined as materials where reinforcing fibers are incorporated into a polymer matrix in order to enhance its mechanical performance and to replace, in part, that polymer which comes traditionally from fossil resources. These composites have attracted a lot of attention and are being widely used in different applications including but not limited to aeronautical and automotive applications. Conventional composites are made from carbon¹ or glass² fibers thanks to their superior mechanical properties. However, the manufacturing of these fibers requires lot of energy^{3,4} and therefore is harmful to the environment. Thanks to environmental awareness, natural cellulosic fiber composites (NFC) have attracted interest and are widely used in both the academic and industrial fields. The fibers that are used to make these NFC composites come from wood or different plants like flax⁵, hemp⁶, banana⁷ or Alfa⁸. Many extraction methods are used to obtain fibers from plants like alkaline extraction⁹, steam explosion¹⁰ or enzymatic extraction¹¹. The interface between reinforcing fibers and polymeric matrix is an important part in composites since incompatibility between hydrophilic fibers and hydrophobic matrices may lead to poor interfacial adhesion¹². In order to promote the adhesion between fibers and matrix, different surface treatments can be applied and can be either physical i.e corona discharge¹³, chemical i.e using silane coupling agents¹⁴ or mechanical i.e surface micro-fibrillation¹⁵. Among chemical treatments of natural fibers, potassium permanganate (KMnO₄)^{16–18}, stearic acid (CH₃(CH₂)₁₆COOH)^{19,20} and sodium hydroxide (NaOH)⁸ have been successfully applied and improvement in mechanical properties of composites were achieved. Those treatments are applied in order to reduce the hydrophilic feature of natural fibers components by removing hydroxyl groups (OH).

Alfa grass grows in semi-arid regions located Lybia, Tunisia, Algeria, Morocco and Spain. In Tunisia, the surface covered by Alfa plants measures approximatively $600,000 \text{ ha}^{21}$. This plant annual production in Tunisia is about 40,000 tons and is exclusively exploited by the National Company of Cellulose and Alfa Paper for making pulp and high quality paper²². Alfa stems are characterized by a density d=0.89, a Young's modulus E=22 GPa and a strength at break σ_b =565 MPa²³. Alfa fibers have been used to enhance mechanical properties of polymeric composites^{8,24,25}. However, to our knowledge, composites with steam-exploded Alfa fibers where fiber extraction works with water only and composites with stearic acid-treated Alfa fibers have not yet been reported in the literature. Also, the solvents of the stearic acid that were reported in the processing of composites with other types of

fibers were always toluene-based^{19,20} and are then extremely dangerous. Besides, KMnO₄ treatment of Alfa fibers was only applied to make polyester-based composites¹⁶ making this treatment not yet reported for recyclable thermoplastic Alfa fiber composites.

The ultimate aim of the current study was the valorization of Tunisian Alfa fibers in thermoplastic polypropylene (PP) composites that can be used in applications like packaging, furniture or automotive and following methods that reduce the processing environmental impact. The key points of this study were to improve of the surface quality of fibers and to enhance the adhesion between those fibers and PP. This study was divided into 4 sections, namely: (1) the extraction of fibers using alkaline and steam explosion methods and the surface treatment of the alkaline extracted Alfa fibers with stearic acid-isopropanol, KMnO₄-acetone and KMnO₄-water (2) the processing of Alfa fiber/polypropylene composites following twin-screw extrusion (3) the study of the effect of fiber extraction methods and chemical treatments on density, melt flow index (MFI), mechanical properties, morphology and water uptake, (4) the thermal annealing of composites in order to reduce the residual stresses subsequent to extrusion^{26,27} and the study of its impact on mechanical properties.

2. Materials and methods

2.1. Materials

Alfa stems were harvested from Kasserine region in Tunisia, this region is characterized by a semi-arid climate. Stems have a cylindrical shape with two tips: one is thick while the other is thin (Figure 1a). Polypropylene granules (PP 100) were supplied by Eltex® MED. NaOH (purity ≥98 %) was supplied by Honeywell International Inc. Potassium permanganate (KMnO₄), acetone and stearic acid (SA) (CH₃(CH₂)₁6COOH) were supplied by Sigma Aldrich (Ireland). Isopropanol was supplied by Lab-Scan Analytical Sciences.

2.2. Extraction of fibers from stems

2.2.1. Alkaline extraction

Alfa stems were subjected to alkaline treatments using 3.25 M sodium hydroxide (NaOH) solution for 2.5 hours at 100 °C. For each experiment, 30g of raw fibers were used and fibers to solution ratio was 1g:20ml. We selected these treatment parameters based on efficiency on fiber bundle breakdown that was assessed visually. This assessment was done after a series of experiments for NaOH concentrations ranging from 0.25 to 7 M, temperatures from room temperature to 110 °C and

durations from 1.5 to 48 hours. After alkaline assays and washing with tap water until pH reached 7, treated stems were pressed using a pestle and a mortar to give a pulp consisting mainly of single fibers. Then fibers were washed, filtered and dried in an oven at 105 °C for 1 hour. A representative image of alkaline extracted fibers is shown in Figure 1a. The reaction between NaOH molecules and fibers is presented in Scheme 1.

2.2.2.Steam explosion extraction

An E070 Autoclave that was supplied by Matex S.p.A was used to steam-explode the Alfa stems. Tap water was used to generate the vapour and no chemicals were used in order to reduce the environmental impact. According to the manufacturer descriptions, water was filled up to 4 cm height inside the autoclave chamber. Treatments were carried out at 180 °C for 20 minutes after which the chamber was suddenly decompressed until pressure in the vessel equalled normal atmospheric pressure. The above treatment parameters were selected based on efficiency on fiber bundle breakdown. The extraction efficiency was assessed visually after a series of experiments conducted with temperatures ranging from 120 to 200 °C and durations from 10 to 40 minutes. For each test, 30g of raw fibers were used. After steam explosion tests, stems were washed and then pressed using a pestle and a mortar to give a pulp consisting mainly of single fibers. Finally, fibers were washed, filtered and dried in an oven at 105 °C for 1 hour. A representative image of steam-exploded fibers is shown in Figure 1a. In the results and discussions, steam-exploded and autoclave-treated fibers mean the same thing.

2.3. Chemical treatments

2.3.1.Stearic acid (SA)

A 4 % based on fibers weight²⁸ solution of stearic acid in isopropanol²⁹ was prepared. Then alkaline extracted fibers were soaked in that solution for 2 hours at room temperature and respecting a fibers to solution ratio of 3g:100ml. Subsequently, fibers were rinsed with water, filtered and dried for 48 hours in an air oven at 40 °C. The reaction between SA molecules and fibers is presented in Scheme 2.

2.3.2.Potassium permanganate (KMnO₄)

Two 0.055 % wt:wt KMnO₄ solutions¹⁷ were prepared where KMnO₄ was dissolved in acetone (KA treatment) and in water (KW treatment). Fibers to solution ratio was 3g:100ml and each treatment was conducted for 1 minute^{17,18} under manual stirring and at room temperature. Subsequently, treated fibers were rinsed with water, filtered and dried for 48 hours in an air oven at 40 °C. Representative images of the chemically treated fibers are given in Figure 1b. The reaction between KMnO₄ molecules and fibers is presented in Scheme 3.

2.4. Composites manufacturing

Fibers were first dried in an air oven at 50 °C for 24 hours³⁰. Alfa fibers were blended to the PP matrix using a PRISM TSE26 twin-screw extruder that is supplied by Thermo Fisher Scientific. The extrusion temperature was 190 °C and the screw speed was 110 rpm. All batches of composites were prepared in 100g weight batch sizes. Prior to the extrusion, PP granules were distributed evenly in the feeder and fibers were added on the top and evenly in order to have a good fiber consistency.

Composites with 5 % wt:wt (5g of fibers and 95g of PP) were manufactured for raw, alkaline extracted, steam-exploded, KA, KW and SA-treated fibers. In order to get samples for characterizations, the extruded composite strands passed through two rotating rollers and different composite films were then prepared. Those films were subsequently cooled in air and stored at room temperature. After finishing the manufacturing of each composite batch, the screws were purged with virgin PP to remove contaminations.

2.5. Thermal annealing

PP and Alfa/PP composites were thermal-annealed in an oven at 105°C for 1 hour³¹ and subsequently cooled in air at room temperature.

2.6. Characterizations

2.6.1. Fourier Transform Infra Red spectroscopy (FTIR)

Alfa fibers were tested with Perkin Elmer One FTIR spectrometer to study the effect of extraction method and chemical treatments. Baseline was corrected and all graphs were smoothed respecting a factor of 20 and using PerkinElmer software. For each test, 4 scans were done between 650 and 4000 cm⁻¹. In order to have reliable results, the comparison between the different treatments was made according to the ratio of the studied band intensity of that particular group in the sample divided by the intensity of an arbitrarily chosen reference band³². For our study, the reference band is centred at 1024 cm⁻¹ and corresponds to the aromatic deformation vibration of the C-H group and the C-O stretching vibration of lignin³³.

2.6.2.Melt Flow Index (MFI)

The MFI was determined experimentally using Ceast Melt Flow Rate supplied by Engelmann Buckham Limited. Tests were conducted according to ASTM D1238. Granules were packed inside the equipment's cylinder for 1 minute and then heated at 190 °C for 5 minutes under a 2.16 Kg load. Then extrudates were cut-off every 30 seconds and were subsequently weighted. For each test, 10 determinations were done and the average weight was considered. MFI in grams per 10 minutes was calculated using the following Equation 1:

MFI = average weight of cut-off x20

(Equation 1)

2.6.3. Density

Specimens were tested using a Rolbatch RBDT-01 densimeter. For each test, 10 determinations were done and the average was considered. ASTM D702-08 method B was applied to determine the densities. Each specimen was weighed in air then in distilled water at 21 °C using a sinker and a wire to hold the specimen completely submerged in water, ensuring that no air bubbles were trapped before each measurement.

2.6.4. Tensile Tests

Tensile properties were determined using a Lloyd LRX machine according to ASTM D3039. Prior to tests, specimens were conditioned at room temperature for 24 hours and were cut using a

dumbbell cutting tool and for each batch of samples, 10 determinations were carried out. The testing displacement speed was 50 mm/min.

2.6.5. Morphology

A Mira FE scanning electron microscope (SEM) was used to study the morphology and a freeze-fracture method was applied in order to have a high quality fracture surface. Prior to observations, composites were immersed in liquid nitrogen for 10 minutes and then fractured manually. After returning to room temperature, samples were coated with gold using a Baltec SCD 005 vapour deposition device in order to increase the electrical conductivity. The acceleration voltage was 15 kV.

2.6.6.Water uptake

Specimens were weighted and then placed in tap water. For each set of measurements, test specimens were first removed from water and then wiped carefully with a blotting paper to eliminate water on their surface, 10 measurements were taken at the following time points: the 3rd, 7th, 10th and 13th days.

2.6.7. Statistical analysis

A statistical analysis was done on density, MFI, tensile strength, Young's modulus and water absorption results. Following assessment of normality of distribution and homogeneity of variance, treatments were compared using a one way ANOVA with a Tukey's Honesty Significant Difference Post hoc test to determine differences between specimens' results. An IBM SPSS statistics version 19 software was used and differences were considered significant when $p \le 0.05$.

3. Results and discussions

3.1. FTIR spectroscopy analysis

3.1.1. Effect of extraction methods

Figures 2a and 2b shows the FTIR graphs for raw and alkaline extracted fibers, respectively. For alkaline extracted fibers, the bands that are at 1053.2, 1104.5 and 1159.5 cm⁻¹ and that correspond to the C-OH stretching vibration, the C-O-C stretching vibration and to the C-C of cellulose^{34,35}, respectively either appeared or strongly increased. The bands located at 2858.8 and 2922.4 cm⁻¹ that are linked to the C-H stretching vibration of wax^{36,37} completely disappeared showing the removal of this component. This may explain why the peaks related to the cellulose have appeared; in fact, Alfa

stems have a waxy cuticle layer³⁸ and then when this layer is removed, cellulose groups became more available to FTIR analysis. The band centred at 1731.2 cm⁻¹ that corresponds to the C=O stretching vibration of pectin³⁸ disappeared. This confirms the breaking down of fiber bundles into single fibers since pectin is the main component that binds fibers to each other in plant fibers³⁹. Hence it can be concluded that the alkaline extraction was very efficient regarding the removal of non-cellulosic components.

Figure 2c shows the FTIR graph for steam-exploded fibers. The bands that correspond to wax and pectin were decreased but not removed like the alkaline extracted fibers. This indicates that alkaline extraction is more efficient than the steam explosion in removing non-cellulosic materials.

3.2. Effect of surface treatments

Figure 2d shows the FTIR graphs for SA-treated fibers. The band centred at 1587.3 cm⁻¹ that is linked to the carboxylic acid group COOH increased. Cao et al. reported that the presence of this latter group is a sign of SA grafting⁴⁰. Also, two bands centred at 2846.7 and 2920 cm⁻¹ corresponding to the C-H stretching vibration of the CH₂ group have appeared. The bands at 2846.7 and 2920 cm⁻¹ were also observed elsewhere and were linked to the grafting of SA^{40,41}. This indicates that SA was successfully grafted on the surface of Alfa fibers.

Figure 2e shows the FTIR graph for KA-treated fibers. The band centred at 1053.2 cm⁻¹ that corresponds to the C-OH stretching vibration of cellulose³⁸ decreased in agreement with previous findings where this decrease was explained by the formation of a new complex on the surface of fibers which is in this case related to the KMnO₄ treatment. There was no evidence of surface chemical etching as reported by many authors, for instance in⁴². This might be due to the effectiveness of the previous alkaline extraction removal of non-cellulosic components.

Figure 2f shows the FTIR graph for KW-treated fibers. Compared to results from KA-treated fibers, KW-treated fibers presented a new band appeared at 1000 cm⁻¹. In fact, the dissolved KMnO₄ molecules act as oxidizing agents for natural fibers unless the used solvent is acetone⁴³. The appearance of this band indicates the presence of oxidation product from one or many fiber components. This is supported by the strong change in the colour of the KW-treated fibers.

3.3. Density

Thanks to their inferior density compared to mineral fillers, natural fibers confer a lightweighting feature to polymer-based composites and present therefore good candidates to compete with or replace these fillers in structural composites⁴⁴. Figure 3 shows the density of the different tested composites. The only decrease in density was observed for composites with raw fibers. This is probably due to the existence of relatively high void content as a result of a poor adhesion between fibers and the matrix or simply because the stems' density, which equals to 0.89³⁸, is lower than that of the matrix.

In the other hand, the steam-exploded fibers increased the density of composites (p=0.016) probably thanks to a lower void content in the interface leading to the highest adhesion between fibers and the matrix. The density increase after the incorporation of natural fibers into polymers was reported elsewhere, for instance by Placet where incorporating hemp fiber into the PP matrix increased its density⁴⁵. Cao et al. found similar results with high density polyethylene peat ash composites⁴⁰.

Besides, the alkaline extraction together with the three chemical treatments did not have any significant influence in the density.

3.4. MFI

Polymers MFI can be used predict changes in the processability of polymers and a high MFI means that polymer is easy to process. Figure 4 shows the MFI values for the studied composites. The fibers incorporation into the PP matrix reduced the melt flow rate for all sets of composites. This is consistent with results reported by Nekkaa et al. and Li et al. where they found that adding Spartium Jenceus Broom fibers to PP and flax fibers to high density polyethylene reduced their MFIs^{20,46}. This decrease is probably due to the fact that fibers hinder the mobility of PP chains making their movement slower.

The maximum recorded value was obtained for composites with raw fibers. A possible explanation is that, due to the greatly larger bundle size compared to the composites with treated fibers where fiber bundles broke down giving smaller bundles and single fibers, the PP chains had significantly more free space to flow.

Composites with alkaline extracted fibers had the lowest MFI. Tayfun et al. found that the alkaline treatment applied to their flax fibers decreased the MFI of thermoplastic polyurethane matrix⁴⁷. The steam explosion increased the MFI by 64 % compared to alkaline extraction (p≤0.001). This increase was probably because they have a smoother surface due to less removal of non-cellulosic component from their surface as shown by our FTIR analysis leading then to easier PP chain mobility. This can also explain why composites with raw fibers had the highest MFI among tested composites.

All surface treatments significantly increased the MFI compared with alkaline extraction (p≤0.001) especially for composites with SA-treated fibers where the MFI reached 2.5 g/10 minutes. Kiattipanich et al.⁴⁸ found similar results with LDPE/sisal fiber composites treated with SA and correlated this increase of the MFI with the ability of SA to act as a lubricant. Moreover, the composites with KMnO₄-treated fibers had lower MFI than composites with SA-treated fibers (p≤0.001).

3.5. Mechanical properties of non thermal-annealed composites

3.5.1.Tensile strength

The maximum tensile strength was obtained for neat PP and was 30 MPa as shown in Figure 5. Composites with raw fibers exhibited a sharp drop with 31 % decrease. Arrakhiz et al. found that the incorporation of raw Alfa fibers into the PP matrix resulted in a lower tensile strength⁴⁹ and this decrease was attributed to the poor adhesion between fibers and matrix.

However, composites with alkaline extracted fibers did not show any significant decrease (p=0.485) while composites with steam-exploded fibers showed a 19% decrease (p≤0.001). In fact, the latter decrease is expected since at such steam explosion treatment temperature (180 °C), fibers thermal degradation is likely to happen⁵.

Regarding the effect of chemical treatments, only composites with KA-treated fibers showed a significant decrease compared to composites with alkaline extracted fibers (p=0.001). In fact, Rashid et al.¹⁸ reported a decrease of tensile strength for KA-treated banana fibers /PP composites and this reduction was attributed to an excess removal of lignin during that surface treatment. A possible cause of the reduction of tensile strength for the composites with chemically treated fibers can be the degradation of fibers due to the treatments conditions as previously shown for KW-treated fibers. In addition, a visual examination of composites with chemically treated fibers showed a significantly higher fiber agglomeration compared to composites with alkaline extracted fibers where fiber

aggregates were absent. We can then conclude that these chemical treatments have significantly increased fiber-fiber interaction leading to a poorer matrix to fiber stress transfer. Moreover, when fibers are agglomerated, they are not anymore embedded with the PP matrix and are directly in touch with each other and hence their weak interface can promote crack initiation and propagation.

3.5.2. Young's modulus

In contrast to tensile strength, the incorporation of fibers led to significantly higher Young's modulus values (p≤0.001) thanks to the higher stiffness of fibers compared to the PP matrix⁴⁹ (Figure 6).

The optimum result was obtained for alkaline extracted fibers composites where the modulus reached 1696 MPa, which means an important increase by 69 % compared to neat PP. El-abbassi et al.⁹ found similar results and the improvement was attributed to the removal of non cellulosic components and the breakdown of fiber bundles into thinner bundles increasing then the effective surface of stress transfer between the matrix and fibers. This was the case for our fibers as concluded from previous results. Composites with steam-exploded fibers showed an increase by 37 % but their Young's modulus remains significantly lower than the observed increase with of composites with alkaline extracted fibers (p≤0.001). This can be explained by two reasons: the higher amount of fibers non-cellulosic components as previously shown and the partial degradation of fibers due to elevated treatment's temperature.

Regarding the effect of chemical treatments, the Young's modulus strongly decreased for all three chemical treatments (p≤0.001) and the lowest decrease was observed for composites with KW-treated fibers. Moreover, there was no significant difference between results from composites with SA and KA- treated fibers. Bulut et al.⁴² reported a decrease of Young's modulus for KA-treated jute fibers/PP composite, they explained this decrease by the opening of pyranose ring of cellulose due to the oxidation of primary and secondary alcohol and by the reduction of the cellulose polymerization degree.

3.6. Effect of the thermal annealing on mechanical properties

3.6.1. Tensile strength

The thermal annealing increased the tensile strength of neat PP and composites with SA-treated fibers where tensile strength jumped respectively from 30 to 37.3 MPa and from 26.5 to 35.4 MPa (Figure 5). However, for the other composites, the increase was not significant. The tensile strength's improvement was expected since the thermal annealing gives PP chains more mobility as a result of less energy arrangements⁵⁰. Hence, the interface between fibers and matrix was more energetically stable hindering crack initiation and propagation. Our results are consistent with results from a study done by Xiang and Frey where thermal annealing increased the tensile strength of carbon fiber nylon composites⁵¹.

3.6.2. Young's modulus

Young's modulus increased for neat PP (Figure 6). Conversely, it decreased for composites with raw and alkaline extracted fibers by18 and 26 % respectively while it did not significantly change for composites with steam-exploded fibers. This drop of Young's modulus can be attributed to an increased chain mobility due to the annealing⁵² making the deformation of composites easier.

However and surprisingly, Young's modulus of composites with SA fibers showed a meaningful increase by 32 % reaching 1568 MPa. In addition, the annealing did not significantly change Young's modulus for composites with KW-treated fibers while a decrease was observed for composites with KA-treated fibers.

3.7. Morphology

Figure 7 shows SEM photomicrographs from the fracture surfaces of composites with raw, alkaline extracted, steam-exploded and KW-treated fibers composites. The raw fibers composite (Figure 7a) showed a significant amount of fiber pullout with few fiber breaks evidencing weak fiber to matrix adhesion⁵³. Conversely, the alkaline extraction gave a lower fiber pullout and a higher amount of fiber breaks leading to a stronger interface (Figure 7b). This finding is supported by the improvement of the tensile strength after the alkaline extraction. Our results are in agreement with results found by Paul et al. who studied the morphology of the fracture surface for banana fiber/PP composite and reported that NaOH-extraction significantly reduced fiber pullout⁵⁴. Composites with steam-exploded fibers (Figure 7c) showed a similar behavior to composites with alkaline extracted fibers. The only difference between the two extraction methods is that alkaline extracted fibers surface looked cleaner. This is

due to the removal of non-cellulosic components like waxes that are still present in fibers after the stem-explosion.

The fracture surface from a KW-treated fibers composite is presented in Figure 7d. A significant amount of voids appear in the surface. This can be a possible cause that stands behind the drop in mechanical performance of composites with KW-treated fibers.

3.8. Water uptake

Moisture content should be taken into account as it can affect the mechanical behavior of natural fibers composites. In fact, several studies have shown that the immersion of composites in water resulted in lower tensile strength, flexural strength, impact strength and Young's modulus^{9,55,56}.

Figure 8 presents the water uptake behavior of the different composites. Composites with raw fibers showed significantly higher water uptake than composites with extracted fibers. This increase in the water uptake can be attributed to two reasons: a higher amount of non-cellulosic materials of raw fibers and a poorer adhesion between fibers and matrix since the interface accommodates water molecules9. Hence, it can be concluded that both fiber extraction methods reduced the water uptake. In fact, El-abbassi et al. found that their alkaline treatment decreased the water absorption of Alfa fiber/PP composites thanks to the improved adhesion between fibers and the matrix9. The best result was seen for composites with steam-exploded fibers that showed a significant decrease in the water uptake ranging from 46 to 53 % compared to composites with alkaline extracted fibers. This can be related to the better adhesion between fibers and the matrix as concluded from previous findings.

Besides, the KW treatment did not induce any improvement probably due to the presence of voids. However, the KA treatment decreased the water uptake by 22-36 % compared to composites with alkaline extracted fibers. Moreover, composites with SA-treated fibers had a similar behavior probably thanks to an improved interface between fibers and the matrix¹⁹.

4. Conclusion

In the present study, the properties of composites with raw and extracted fibers were compared and the effect of the three chemical treatments was investigated. Also, the different composites were thermal-annealed and their mechanical properties were studied. A particular attention was paid to use treatments that reduce the environmental impact of composites processing.

The experimental study showed that the incorporation of fibers increased the Young's modulus of PP composites with both raw and extracted fibers. That increase was explained by the improvement of the interface quality as a result of the elimination of non-cellulosic impurities and the reduction of fibers dimensions. There were no improvement regarding the tensile strength probably because the increase of the creation of a weak interfacial area. In addition, raw fibers decreased the density and the reason behind could be the significant amount of voids as shown in the SEM analysis. That analysis was also used to explain the reduction of the water uptake which showed composites with extracted fibers. The major drawback of composites with extracted fibers was the decrease of the MFI compared to neat PP and composites with raw fibers leading to a slower processing. Nevertheless, the three applied surface treatments increased the MFI but in the other hand resulted in a significant drop of composites mechanical performance. Regarding the thermal annealing, it can be applied to restore a part of the loss in tensile strength as a result of the incorporation of fibers in the matrix. Conversely, that annealing reduced the Young's modulus of composites except those where the reinforcing fibers were treated with SA.

Finally, our Alfa fiber/PP composites can compete with or replace neat PP as they can present a higher mechanical performance and in the same time, contribute to the preservation of environment by limiting the used amount of that fossil-based polymer.

Declarations of interest

None

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References

- 1. Na, W.; Lee, G.; Sung, M.; Han, H. N.; Yu, W. Compos. Struct. 2017, 168, 92.
- 2. Drummer, D.; Zhai, Z.; Gr, C. Polym. Test. 2016, 54, 126.
- 3. Suzuki, T.; Takahashi, J. In *The Ninth Japan International SAMPE symposium*; **2005**; pp 14.
- 4. Dai, Q.; Kelly, J.; Sullivan, J.; Elgowainy, A.; Group, S. A.; Division, E. S. Life-Cycle Analysis

- Update of Glass and Glass Fiber for the GreetTM Model; 2015.
- 5. Baley, C.; Morvan, C.; Grohens, Y. Macromol. Symp. 2005, 222, 195.
- Le Troedec, M.; Sedan, D.; Peyratout, C.; Bonnet, J. P.; Smith, A.; Guinebretiere, R.;
 Gloaguen, V.; Krausz, P. Compos. Part A Appl. Sci. Manuf. 2008, 39, 514.
- 7. Prasad, N.; Kumar, V.; Shishir, A. *Iran. Polym. J.* **2016**, *25*, 229.
- 8. Elfehri Borchani, K.; Carrot, C.; Jaziri, M. Compos. Part A Appl. Sci. Manuf. 2015, 78, 371.
- 9. El-Abbassi, F. E.; Assarar, M.; Ayad, R.; Lamdouar, N. Compos. Struct. 2015, 133, 451.
- 10. Karlsson, J.; Blachot, J.; Peguy, A.; Gatenholm, P. Polym. Compos. 1996, 17, 300.
- 11. Hanana, S.; Elloumi, A.; Placet, V.; Tounsi, H.; Belghith, H.; Bradai, C. *Ind. Crops Prod.* **2015**, 70, 190.
- 12. Mechakra, H.; Nour, A.; Lecheb, S.; Chellil, A. Compos. Struct. 2015, 124, 152.
- Ragoubi, M.; George, B.; Molina, S.; Bienaimé, D.; Merlin, A.; Hiver, J. M.; Dahoun, A.
 Compos. Part A Appl. Sci. Manuf. 2012, 43, 675.
- 14. Xie, Y.; Hill, C. A. S.; Xiao, Z.; Militz, H.; Mai, C. Compos. Part A Appl. Sci. Manuf. 2010, 41, 806.
- Zhong, L. X.; Fu, S. Y.; Zhou, X. S.; Zhan, H. Y. Compos. Part A Appl. Sci. Manuf. 2011, 42,
 244.
- 16. Benyahia, A.; Redjem, A.; Rahmouni, Z. E. A.; Merrouche, A. Rom. J. Mater. 2016, 46, 25.
- 17. Joseph, K.; Thomast, S. Polymer (Guildf). 1996, 37, 5139.
- Rashid, M.; Samad, S. A.; Gafur, M. A.; Chowdhury, A. M. S. Int. J. Sci. Eng. Res. 2015, 6,
 1870.
- 19. Zaman, H. U.; Beg, M. D. H. Fibers Polym. 2014, 15, 831.
- 20. Nekkaa, S.; Chebira, F.; Haddaoui, N. J. Eng. Appl. Sci. 2006, 1, 278.
- 21. Belkhir, S.; Koubaa, A.; Khadhri, A.; Ksontini, M.; Nadji, H.; Smiti, S.; Stevanovic, T. Ind. Crops

- Prod. 2013, 44, 56.
- SNCPA National Company of Cellulose and Esparto Paper.
 http://www.sncpa.com.tn/accueileng.php (accessed July 20, 2017).
- 23. Bessadok, A.; Roudesli, S.; Marais, S.; Follain, N.; Lebrun, L. Compos. Part A Appl. Sci. Manuf. 2009, 40, 184.
- 24. Zrida, M.; Laurent, H.; Rio, G. J. Compos. Mater. 2015, 1.
- 25. Espinach, F. X.; Delgado-Aguilar, M.; Puig, J.; Julian, F.; Boufi, S.; Mutjé, P. *Compos. Part B Eng.* **2015**, *81*, 98.
- 26. Väisänen, T.; Das, O.; Tomppo, L. J. Clean. Prod. 2017, 149, 582.
- 27. Maxwell, T. Residual stress in plastics; 2003.
- 28. Kalaprasad, G.; Francis, B.; Thomas, S.; Kumar, C. R.; Pavithran, C.; Groeninckx, G.; Thomas, S. *Polym. Int.* **2004**, *1638*, 1624.
- 29. Arrakhiz, F. Z.; Elachaby, M.; Bouhfid, R.; Vaudreuil, S.; Essassi, M.; Qaiss, A. *Mater. Des.* **2012**, *35*, 318.
- 30. Martin, N.; Mouret, N.; Davies, P.; Baley, C. Ind. Crops Prod. 2013, 49, 755.
- 31. Perez-Fonseca, A. A.; Robledo-Ortiz, J. R.; Gonzalez-Nunez, R.; Rodrigue, D. *J. Appl. Polym.* Sci. 2016, 133, 1.
- 32. Yuen, S. N.; Choi, S. M.; Phillips, D. L.; Ma, C. Y. Food Chem. 2009, 114, 1091.
- 33. Kabir, M. M.; Wang, H.; Lau, K. T.; Cardona, F. Appl. Surf. Sci. 2013, 276, 13.
- 34. Dallel, M. Evaluation du potentiel textile des fibres d'Alfa (Stipa Tenacissima L.): caractérisation physico-chimique de la fibre au fil, Haute Alsace University, **2012**.
- 35. Bessadok, A.; Marais, S.; Gouanvé, F.; Colasse, L.; Zimmerlin, I.; Roudesli, S.; Métayer, M. Compos. Sci. Technol. **2007**, *67*, 685.
- 36. Patra, A.; Bisoyi, D. K.; Manda, P. K.; Singh, A. K. *J. Appl. Polym. Sci.* **2012**, 1.
- 37. Huo, S.; Thapa, a.; Ulven, C. a. Adv. Compos. Mater. 2013, 22, 109.

- 38. Bessadok, A. Compos. Sci. Technol. 2007, 67, 685.
- 39. Baley, C. Compos. Part A Appl. Sci. Manuf. 2002, 33, 939.
- 40. Cao, Z.; Daly, M.; Geever, L. M.; Major, I.; Higginbotham, C. L.; Devine, D. M. *Compos. Part B* **2016**, *94*, 312.
- 41. Lu, Z. Appl. Surf. Sci. 2015, 353, 735.
- 42. Bulut, Y.; Aksit, A. Cellulose 2013, 20, 3155.
- 43. Khan, J. A.; Khan, M. A.; Islam, R. *J. Reinf. Plast. Compos.* **2012**, 1.
- 44. Holbery, J.; Houston, D. J. Miner. Met. Mater. Soc. 2006, 58, 80.
- 45. Placet, V. Compos. Part A 2009, 40, 1111.
- 46. Li, X.; Tabil, L. G.; Panigrahi, S.; Crerar, W. J. In *The Canadian society for engineering in agricultural, food, and biological systems*; **2016**; pp 1.
- 47. Tayfun, U.; Dogan, M.; Bayramli, E. J. Nat. Fibers 2016, 13, 309.
- 48. Kiattipanich, N.; Kreua-Ongarjnukool, N.; Pongpayoon, T.; Phalakornkule, C. *J. Polym. Eng.* **2007**, *27*, 411.
- 49. Arrakhiz, F. Z.; Malha, M.; Bouhfid, R.; Benmoussa, K.; Qaiss, A. Compos. Part B Eng. 2013, 47, 35.
- 50. Karian, H. Handbook of Polypropylene and Polypropylene Composites, Revised and Expanded; **2003**.
- 51. Xiang, C.; Frey, M. W. Materials (Basel). 2016, 9, 1.
- 52. Yeh, G. S. .; Germany, W. Polymer (Guildf). 1976, 17, 309.
- 53. Prasad, N.; Agarwal, V. K.; Sinha, S. Korean J. Chem. Eng. 2015, 32, 2534.
- 54. Paul, S. A.; Joseph, K.; Mathew, G. D. G.; Pothen, L. A.; Thomas, S. *Compos. Part A Appl. Sci. Manuf.* **2010**, *41*, 1380.
- 55. Deo, C.; Acharya, S. K. J. Reinf. Plast. Compos. 2010, 29, 2513.

Figures

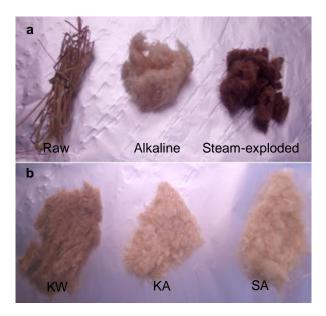
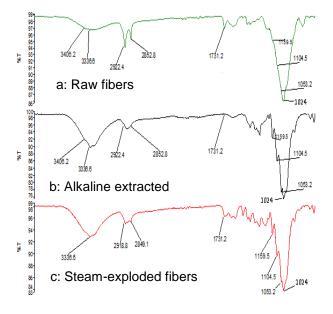


Figure 1. L to R: (a) raw; alkaline extracted and steam-exploded fibers (b) KW; KA and SA chemically-treated fibers



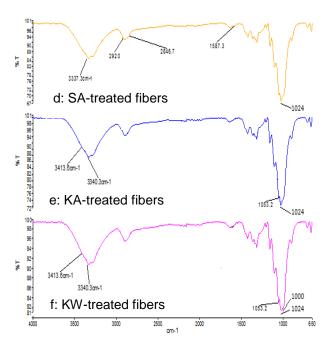


Figure 2. FTIR graphs of: (a) raw (b) alkaline extracted (c) steam-exploded (d) SA-treated (e) KA-treated and (f) KW-treated fibers

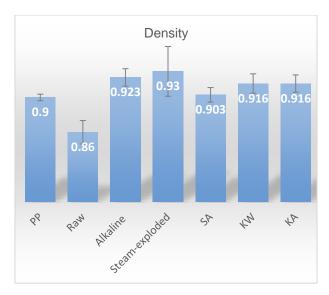


Figure 3. Density

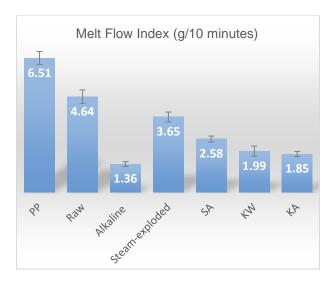


Figure 4. MFI

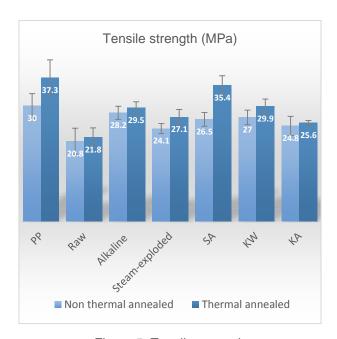


Figure 5. Tensile strength

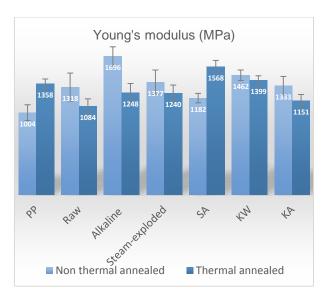


Figure 6. Young's modulus

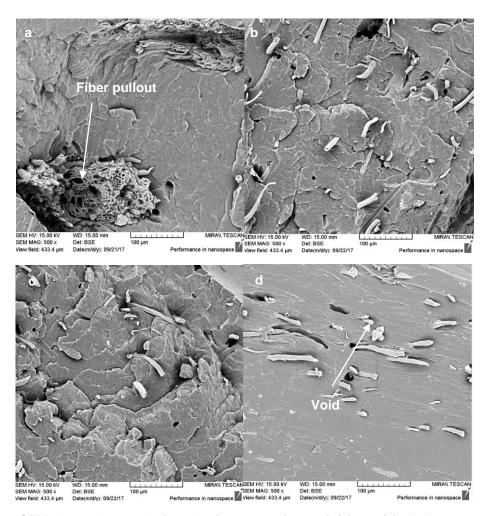


Figure 7. SEM photomicrographs from the fracture surfaces of: (a) raw (b) alkaline extracted (c) steam-exploded and (d) KW-treated fiber composites

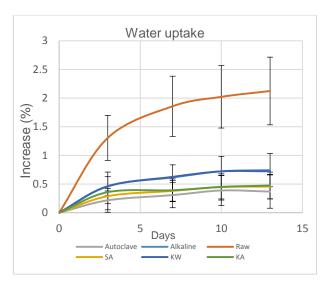


Figure 8. Water uptake behaviour

Graphical abstract

