

EFFECT OF CHEMICAL TREATMENT OF ALFA NATURAL FIBERS ON THE MECHANICAL PROPERTIES OF POLYETHYLENE MATRIX COMPOSITES

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This study investigated the effects of chemical treatment of fiber Alfa on the mechanical behaviour of high-density polyethylene/plant fiber composites. The Alfa fibers are used as reinforcement after being treated by aqueous NaOH (caustic soda) at 1% and 5% for 24 and 48 hours at 25°C. It is found that the stiffness (Young's modulus) and the tensile strength properties of composites with treated fibers were significantly improved compared to those elaborated without fiber treatments. However, these mechanical properties decline in the case of composites with fibers treated for 48 hours by aqueous caustic soda at 5% concentration. This decrease is attributed to the alteration of the fibers under chemical treatment time prolongation effect.

Keywords: chemical treatment, Alfa natural fibers, high-density polyethylene, composite, material stiffness and strength

1. Introduction

Considerable scientific and technological efforts have been done to reduce the environmental impacts associated with the use of polymeric materials. This is why attention is increasingly focused on biodegradable composite materials such as composites based on thermoplastic polymers with natural fillers such as cellulose, starch and natural fibers. The use of natural fibers as reinforcements in composite materials presents many advantages due to their biodegradability, their low cost and their generally good mechanical properties. The incorporation of natural fibers like fibers of the bamboo, hemp, jute, flax, silk, or the Alfa fibers in polymer materials is very common nowadays in the field of scientific research [1-9]. Some of studies have concluded that these composites present a problem at the interface between the natural fibers hydrophilic surface and the polymer hydrophobic surface. To solve this problem one has often recourse to treat either the matrix or the natural fibers with different techniques like alkali treatment, acetylation, methylation, etc. [10-16]. Alkaline treatment is the most used procedure for treating natural fibers and brings outstanding performance of composite [16]. This treatment is applied to extract the lignin, the hemicelluloses and the impurities (wax, fats). Rokbi and al. [17] have studied the influence of the

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alkali solution concentration and the treatment time of Alfa fibers on the composite's polyester-Alfa mechanical properties. According to their results it was found that the treatment by 10% aqueous solution of sodium hydroxide (caustic soda) during 24 hours at room temperature improves efficiently the quality of Alfa fibers-matrix interface and does not degrade the Alfa fibers during treatment process compared to those treated with 5% NaOH during 48 hours. Arrakhiz and al. [18] have examined the effect of alkali treatment, etherification and esterification treatments on the Alfa fibers surface and their impact on thermal and mechanical properties of polypropylene composites reinforced by Alfa fibers. They found that the esterified fibers improve Young's modulus by 35%. Also, thermal stability is considerably enhanced using etherification-treated fibers with elevation in the temperature reaching 80 °C. Their study shows that fibers treatment is crucial to improving the mechanical properties of composites based on natural fibers.

The main objective of this work is to study the mechanical properties of high-density polyethylene (HDPE) composites reinforced by Alfa natural fibers obtained from Alfa stalks. Alfa fibers have been chemically modified with sodium hydroxide solution in order to enhance their affinity and adhesion with the polyethylene matrix. This treatment would allow creating an innovative and biodegradable composite material, which is completely harmless to the environment. To optimize the Alfa fibers-matrix interface, the influences of aqueous sodium hydroxide concentration and the treatment time have been studied. In this work, we are interested in the evolution of the properties of composites obtained by using HDPE as matrix and treated and untreated natural Alfa fibers. The experimental program includes a set of texture and X-ray diffraction analysis, scanning electron microscopy (SEM) observations and mechanical tests. In the introduction to the paper, the author(s) will specify the present stage of the branch researches (by quoting the adequate bibliography) and will specify the purpose of the paper.

2. Experimental

2.1 Materials

The polyethylene used in this study is high-density polyethylene, as translucent granules. Its fluidity index is higher than 5.5 g/10 min with 190 °C/ 2.16 kg (ISO 1133). The Alfa fibers were obtained from Alfa stalks, which are shrubs about 1 m in high. Alfa fibers were collected from Djelfa region (Algeria). The Alfa fibers are composed of 41.9 to 47.6% cellulose, 24.2 to 38.5% hemicellulose, 11.8 to 24.3% lignin, 2 to 5 % of wax and 1.8 to 5.1% of ash [19, 20]. The Alfa stalks were first dried for 3 days under the sun. This operation will eliminate most of the moisture. After that, they were manually cut to 1-2 cm in length.

Fibers pretreatment is crucial to eliminate a maximum of non-cellulosic components in order to enhance the fibers interface. According to the literature, the Alfa fibers were soaked in a saltwater (35 g/L) at a temperature of 60 °C for 24 hours, in order to eliminate sand and dust that exist on fibers surface. Then, Alfa fibers were soaked in sodium hydroxide solution at 1% and 5% for 24 and 48 hours at 25 °C. After treatment, Alfa fibers were washed with distilled water and neutralized by a solution of 2% acetic acid for 10 minutes to eliminate aqueous caustic soda traces. Finally, the Alfa fibers were stored for 6 hours at 60 °C in order to dry them before using as reinforcement for the preparation of the composite.

2.2 Preparation of composites

To elaborate composite specimens, the various concentrations (5, 10, 15, 20, 25, 30 wt%) of Alfa fibers untreated and treated were mechanically blended with high-density polyethylene using a single screw extruder at 130, 150, 170 and 180 °C temperatures and then injected in the mould to give plates. The specimens for the tensile tests were moulded on cold using a manual press.

2.3 Characterization methods

The texture of the Alfa fibers untreated and treated by NaOH was observed using infrared spectroscopy. The spectra were recorded in ATR mode using a Vertex 70 Fourier transformed infrared spectrophotometer (FTIR, Platinum Diamond). The structure of the Alfa fibers treated or not by NaOH was determined by X-ray diffraction (XRD) using a standard diffractometer XPERT PRO with CuK α radiation ($\lambda = 1.54056$ nm). The scan was carried out at an angle (2θ) between 10 and 120° and a voltage of 45 kV. The use of XRD provides an ease of evaluating the crystallinity index (CI) of the fibers using following equation:

$$CI(\%) = 100 \left[\frac{I_{002} - I_{am}}{I_{002}} \right] \quad (1)$$

Where I_{002} is the maximum diffraction intensity for the angle 2θ of 22.32° representing the plane 002 and I_{am} is the intensity of the diffraction at the angle 2θ of 14.86° representing the amorphous part of the material.

The morphology of the treated and untreated fibers by NaOH is observed by the Philips ESEM XL (tungsten filament) scanning electron microscope coupled to a complete energy dispersive microanalysis (EDS X) system.

The mechanical properties of composites are determined by means of tensile tests carried out using standardized plate specimens. The geometry of the sample is cut according to the standard (ISO 527-4 type 1B). All the tests are carried out at a crosshead speed of 3 mm/min at room temperature using a universal IBERTEST test *machine* having a maximum loading capacity of ± 100

kN with electronic command. Reliability and accuracy of the experimental tests should be considered. Each test is repeated, at least three times under the same experimental conditions of applied load speed and room temperature. If the contrasts between the three responses exceed 5%, then another test should be performed.

3. Results and discussions

3.1 Analysis by Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of alkali-treated and untreated Alfa fibers are presented in Fig. 1. The broad absorption band observed in the 3321 cm^{-1} was related to the hydrogen bonding (OH) stretching vibration present in cellulose and hemicellulose [21]. It was reduced by reason of the hemicelluloses component elimination after NaOH treatment and the peak around 1033 cm^{-1} is associated with the vibration of the C-O bond of hemicelluloses. The intensity of this peak decreases as the concentration of aqueous caustic soda increases.

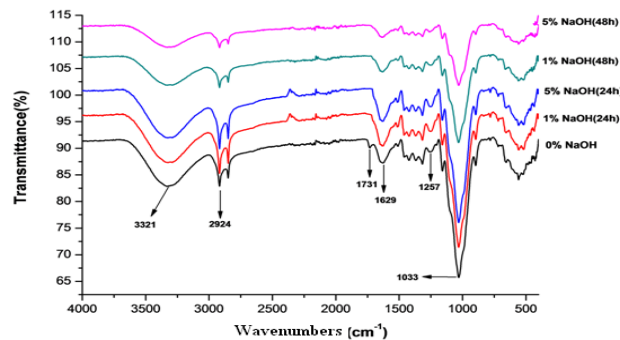


Fig.1. FTIR spectrum of original Alfa fibers and alkali Alfa fibers treated with different concentration of NaOH (1% and 5%) solution for 24 h and 48 h at $25\text{ }^{\circ}\text{C}$.

This decrease is most likely associated with the elimination of the hemicellulose during the treatment. Similarly, the peak at 1257 cm^{-1} corresponding to the vibration of the acetyl group ($\text{C}=\text{O}$) of the lignin also decreases. This was due to the partial removal of lignin from the fiber surface [22]. The band around 1735 cm^{-1} was disappeared with the treatment. It corresponds to the $\text{C}=\text{O}$ carbonyl groups due to the partial hydrolysis of hemicelluloses in alkali medium [23]. It is characterized by the rupture of the C-O-C bonds between two monomers. The band at 2924 cm^{-1} , corresponding to the C-H bonds of the $(-\text{CH}_2)$ groups of the cellulose and lignin segments was affected by the treatment. The peak at 1629 cm^{-1} is assigned to the O-H band deformation, due to the hydrophilic character of the Alfa fibers [24]. All these results help to show that the treatment is essential to eliminate hemicelluloses and lignin.

3.2 X-ray diffraction analysis (XRD)

X-ray diffraction was used to attest the elimination of the amorphous non-cellulosic part (lignin, hemicelluloses, etc.), which indicates the effectiveness of the chemical treatment and therefore the degree of crystallinity. In Fig. 2 the diffraction patterns of the treated and untreated Alfa fibers are presented. All the diffractograms have an intense crystalline peak at a diffraction angle of $2\theta = 22.32^\circ$. It corresponds to the crystallographic plane (002) of cellulose I. The other peak at $2\theta = 14.86^\circ$ corresponds to the crystallographic plane (110) [25, 26].

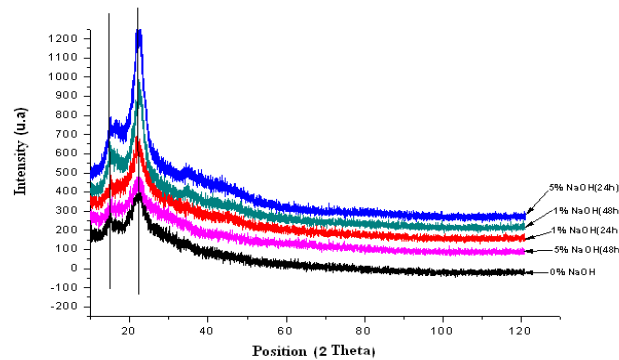


Fig.2. X-Ray diffractograms of treated and untreated Alfa fibers

Table 1 shows the crystallinity index (CI) obtained using the Segal method. It is observed that the crystallinity index evolves with the fiber treatment. For a 5% aqueous caustic soda and more than 24 hours treatment time the crystallinity index decreases due to the conversion of cellulose I into amorphous cellulose II. According to Baley et al. [27], the high concentrations of NaOH solution lead to a reduction of fibers crystallinity.

Table 1

The intensity values of the I_{am} and I_{002} lines, as well as the values of the crystallinity index

Alfa Fibers	I_{002} ($2\theta=22.32^\circ$)	I_{am} ($2\theta= 14.86^\circ$)	CI (%)
Untreated	329.92	232.42	29.55
Treated in 1% NaOH for 24 h	631.07	438.25	30.55
Treated in 1% NaOH for 48 h	914.18	600.02	34.36
Treated in 5% NaOH for 24 h	1214.61	744.46	38.70
Treated in 5% NaOH for 48 h	431.03	319.09	25.97

3.3 Scanning Electron Microscopy (SEM)

Changes in the morphology of Alfa fibers during alkali treatment are very important. Fig. 3 shows the micrographs of fibers surface before and after treatment in different concentration of aqueous caustic soda, and at different treatment time. We observe that the surface of untreated Alfa fibers surface is rough (Fig. 3(a)). This can be referred to non-cellulosic components (waxy

substances, oils and impurities) contained in these fibers [17]. The change in fiber morphology with NaOH concentration and different time of treatment is also noted. The Alfa fibers surface becomes smooth after removal of the non-cellulosic components (Fig. 3(b)) under the aqueous caustic soda concentration of 5% and 24 hours treatment time. Poor consolidation between the fibrils leads to the separation of the fibers (Fig. 3(c)). Rokbi and al. [17] have shown that treatment of Alfa fibers with 5% NaOH for 48 hours results in the alteration of the fibers.

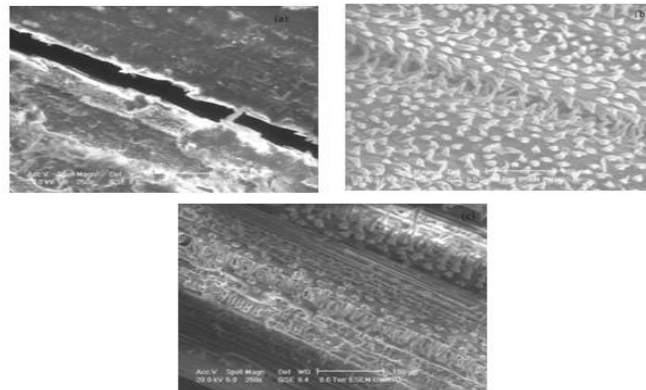


Fig.3. Different morphology of fiber Alfa: (a) untreated, (b) treated (5% NaOH in 24h), and (c) treated (5% NaOH in 48 h).

3.4 Tensile testing

Figs. 4 and 5 show the evolution of the mechanical properties of the HDPE / Alfa fiber composites as a function of Alfa fibers / matrix ratio for treated and untreated specimens.

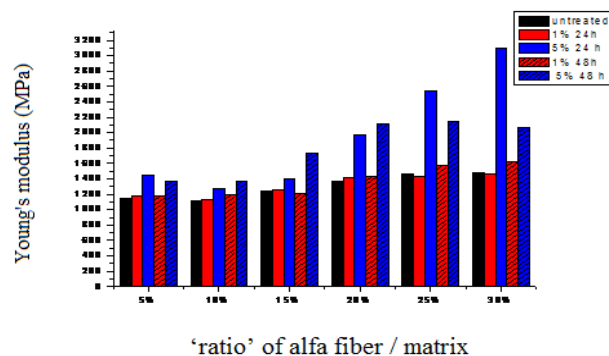


Fig.4. Young's modulus of PE / untreated Alfa fibers and PE / treated Alfa fibers in 1 % and 5% NaOH for 24 h and 48 h at 25 °C

Different treatments with 1% and 5% of aqueous caustic soda for 24 and 48 hours at 25 °C were performed. Regardless of NaOH concentration and treatment time, Young's modulus of the treated specimens is always higher than

the untreated Alfa fibers composites (Fig. 4). This may be due to the bonding of the fibers with the polyethylene matrix thereby improving the fibers-matrix interaction [28]. We also note that Young's modulus of composites with 5% NaOH for 48 h is lower than those obtained by other treatments. This decrease can be due to the prolongation of the alkali treatment time which can be harmful and lead to the alteration of the fibers [28].

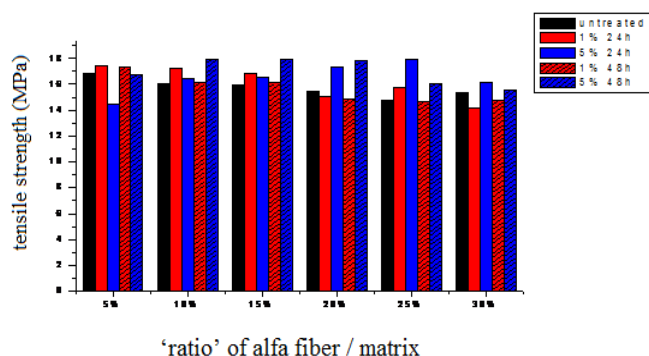


Fig. 5. Tensile strength of PE / untreated Alfa fibers and PE / treated Alfa fiber in 1% and 5% NaOH for 24 h and 48 h at 25 °C

The fibers can act as defects or points of weakness, which reduce the resistance of the composite [29]. This is why the tensile strength of composites with fibers treated by NaOH is almost similar to those of composites with untreated Alfa fibers, except specimens containing 20% and 25% of fibers treated by 5% caustic soda for 24 hours, where we observed a slight progress in tensile strength (Fig. 5).

4. Conclusions

In this work, mechanical behavior of composites based on high-density polyethylene reinforced by Alfa fibers was studied. The Alfa fibers used as reinforcement were submitted to chemical treatment using aqueous caustic soda with two different concentrations (1% and 5%) during 24 and 48 hours at the temperature of 25 °C. The influence of the chemical treatment by NaOH on the mechanical properties of composites revealed the following main points:

- 1) XRD tests had shown the positive effect of the chemical treatment by aqueous caustic soda. Thus, the crystallinity index of fibers treated by 5% NaOH for 24 hours had improved by 38.7% compared to that of untreated fibers.
- 2) The chemical treatment of natural fibers by aqueous caustic soda improves the mechanical properties of composites. The best case is obtained following a treatment by NaOH with a concentration of 5% for 24h.
- 3) Treatment extension, as shown in the case of 5% NaOH for 48 hours, makes

fibers more rigid and weakened, which affects the mechanical properties of composites. These results are confirmed by the XRD and SEM analysis of the Alfa fibers.

As perspective to this work, we plan the formulation of a constitutive model capable of describing the non-linear behavior of the HDPE/Alfa fiber composites. This model will be implemented into a finite element commercial code in order to perform simulations on composites structures.

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