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Effect of olive husk flour silanization on the mechanical and thermal properties of high-density polyethylene composites

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Abstract

The present paper summarizes an experimental study on the mechanical and thermal behavior of olive husk flour (OHF) reinforced high-density polyethylene (HDPE) composites. Several formulations of PE filled with 10, 20 and 30 % by weight of untreated olive husk and that treated with vinyltriacetoxy-silane (VTAS) were prepared. Fourier transform infrared (FTIR) spectroscopy was used to analyse involved silanization reactions. Scanning electron microscopy (SEM) was used to show the morphology of the flour surface. Furthermore, the mechanical and thermal characteristics of the various composite samples were investigated as a function of both loading contents and chemical treatment. The results showed that the properties of the composite materials are positively affected by silanization treatment of OHF.

Keywords: *composites, high-density poly(ethylene) (HDPE), olive husk flour, surface treatments, silanization.*

I. Introduction

Interest in the development of new composite materials derived from natural fibers and thermoplastic polymer matrices has grown markedly in the last years because there are environmental and economic advantages to produce wood flour thermoplastic composites. These composites are being used in a large number of applications, including automotive, interiors, building industry and many other furnitures [1,2].

Wood fillers can be combined with both thermosets and thermoplastics such as high density polyethylene (HDPE), which is one of the most important thermoplastics due to its good properties, i.e. fluidity, flexibility, electrical insulation, etc [3].

Olive husk is an agricultural residue produced as industrial by-products of olive milling. Every year, thousands of tons of this product are incinerated or rejected in the wild by causing major inconvenience to the environment, despite the fact that this product has significant advantages as a wood filler compared to mineral fillers, such as lightness, high stiffness, low cost, and renewable materials. However, their association with plastics, in particular polyolefins however, presents a major inconvenience. They have a strong affinity with water which creates incompatibility at interfaces between wood particles and hydrophobic thermoplastic causing swelling inside the material and subsequently, a deterioration of all mechanical properties [4,5] To solve the problem of incompatibility, it appears necessary to develop solutions through the use of chemical treatments. The chemical treatment of wood filler or the functionalization of the polymer usually requires the use of reagents, which contain functional groups that are capable of reacting and form chemical bonds with the hydroxyl groups of the lignocellulosic material [6-8]. A lot of research was devoted to composites based on HDPE and lignocellulosic fillers, but only few works ware published on polymer composites loaded with olive husk flour. In this work, composites based on HDPE and olive husk flour before and after treatment with vinyltriacetoxy-silane was studied. Moreover, the effects of the treatment on the mechanical, morphological and thermal properties of the composites were also investigated.

II. Experimental

a. Materials

High-density polyethylene used is “POLYMED 6030”, (MFI= 2-3 g/10 min, 190°C/2.16Kg). Sigma Aldrich Company (Germany) produced the vinyltriacetoxy-silane (VTAS). The main characteristics of the product are: density = 1.167g/cm^3, melting point = 76°C and boiling point = 126 – 128°C. Olive husk flour (< 100 µm) from Béjaïa, Algeria

b. Flour treatment

10 g of olive husk flour were added into a mixture of methanol/water (90/10, w/w) and stirred for 12 h at room temperature. The flour was then filtered and dried in an oven at 80 °C for 12 h. For the flour surface treatment, 5% (wt/wt) of vinyl triacetoxy silane was dissolved in a methanol/water mixture at room temperature and the pH of the solution adjusted to 4 with the addition of acetic acid. After the continuous stirring of the solution for 10 min, the dried olive husk flour was immersed in the solution and stirred for 24 h at room temperature. The olive husk flour was then filtered and dried at 80°C for 12h [9].

Various formulations based on high-density polyethylene (HDPE), olive husk flour before (UTOHF) and after treatment with vinyl-triacetoxy-silane (OHFTS), were prepared, whose codes (UT: untreated, TS: treated with silane) and compositions are reported in table 1.

c. Preparation of Composites

Films were prepared by twin-roll milling process, using a rotating speed of 28.5 rpm for the back cylinder and 29.8 rpm for the front cylinder at 160°C and a residence time of 8 min. The gap in between the rolls is roughly 1 mm. The films were then granulated and pressed into plates of 2 mm thick by using a hydraulic press model FONTUME HOLAND at 180°C and 50 KN during 5 min. The plates obtained were used for testing.

d. Spectroscopic analysis (FTIR)

The reaction product was qualitatively characterized by FTIR, using KBr pellet technique. Spectra were recorded using an infrared spectrophotometer Fourier transform (FTIR) model *SHIMADZU FTIR-8400* with a resolution of 4 cm^{-1} within the region 4000 - 400 $cm^{-1.}$

e. Tensile test

The tensile test is carried out using a tensile machine of the type *BTC-FR 2,5 TN.D09,* according to the standard ISO 527, June 1993. The speed of deformation is maintained constant at 50 mm/min. The curves strength-deformation are plotted, each value obtained represents the average of six samples.

f. Thermogravimetric analysis

Thermogravimetric analysis aims to assess the loss of mass that undergoes a sample during a heat treatment as a function of temperature. The apparatus used is type *SETARAM TGA 92* ", consisting of a TGA / DTG / ATD coupled and driven by a microcomputer. The experiments were conducted on samples of mass from 10 to 20 mg, which are built in a crucible and heated in platin in an inert nitrogen with a heating rate of about 10 °C/min and in a temperature range from 20 to 700 ° C.

g. Test of water absorption

Composite samples were used for measuring water absorption according to the following procedure: after being oven-dried at 70°C for 24 h, the specimens were kept in the desiccators at room temperature. Then, the specimens were weighted before immersion in distilled water and the corresponding mass was recorded as (M_0). The specimens were periodically removed from the water bath, surface dried with absorbent paper, and weighed again. The corresponding mass was defined as (M). Three specimens were tested for each compound and the average readings were recorded. Water absorption was calculated according to standard NF 51-002.

h. Scanning electron microscopy

Scanning electron microscopy (SEM) was performed with a ***FEI CONTA 200*** microscope. Before the fracture, the specimens were frozen into liquid nitrogen to impede the plastic deformation of the matrix and to get well defined fiber–matrix interface. The objective was to get some information regarding the filler dispersion and bonding quality between filler and matrix and to detect the presence of microdefects.

Table I. Mass composition of the various PE formulations

Components	F0	F10 UT	F20 UT	F30 UT	F10 TS	F20 TS	F30 TS
HDPE [% wt]	100	90	80	70	90	80	70
UTOHF [% wt]	0	10	20	30	0	0	0
OUFTS [% wt]	0	0	0	0	10	20	30

III. Results and discussion

a. Fourier transform infrared spectroscopy

FTIR spectra of both untreated and silanized olive husk flour are presented in figure 1. In the silanized olive husk flour, it is clearly observed the appearance of the same peaks as for untreated OHF. The only difference noted is related to the absorption band located in the range 3700 and 3050 cm^{-1}, which corresponds to the elongation vibrations of hydroxyl groups (-OH), for which there is a decrease in intensity compared to the untreated olive husk flour (UTOHF). This decrease as reported by Kaci and Bengtsson [10,11] was attributed mainly to the diminution of the hydrophilic character of the olive husk flour after treatment.

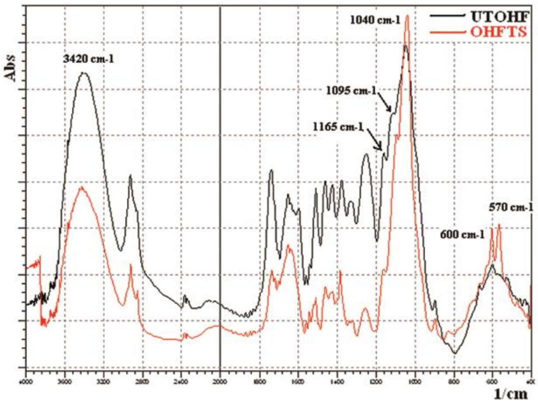


Figure 1: Spectra (FTIR) of the olive husk flour untreated and treated

It was also noticed an absorption band at 1165 cm-^{1} which can be assigned to Si-O-cell or Si-O-Si groups, the first confirms the grafting of silane on fibers and the second is an indication that the intermolecular condensation is produced between adjacent silanols groups. There are also one absorption band centred at 1095 cm^{-1}, characteristic of Si-O-Si vibration; this could be attributed to the substitution of OH groups from olive husk flour by silanol groups (obtained during hydrolysis of silanes) by condensation reaction, indicating the occurrence of silanisation reaction [12]. The peak near 1039 cm-^{1} of the treated flour is related to the residual unhydrolyzed Si–O–CH_3 groups; the weak intensity suggests that most of the silane was hydrolyzed. We also observe an absorption band in the region of 1625 cm $^{-1}$ attributed to connection (C=C) of the vinyl groups of the coupling agent. FTIR analysis confirms that the reaction of silanisation took place, which makes it possible is to propose a suitable reactional mechanism for this modification (See Scheme 1) [13].

b. Mechanical properties

The evolution of the elongation at break and Young's modulus of untreated and treated PE composites as a function of wood filler loadings is presented in figure 2 and 3, respectively. It is observed that the deformation of the untreated HDPE/ OHF composites decrease linearly with increasing the flour loading up to 30%. These results are expected and are in agreement with literature. Kaci and Kim [10, 14] have attributed this decline to the decrease of the strength of connection between the filler and the matrix that blocks the spread of effort. This decline increases as the flour loading becomes higher; this can be explained by the tendency of particles of olive husk flour to form agglomerates which induce heterogeneities within the matrix. The addition of untreated OHF in the polyethylene matrix increases the Young's modulus of the composite and this becomes stronger with increasing the flour content. This behaviour can be explained by the rigid nature of OHF.

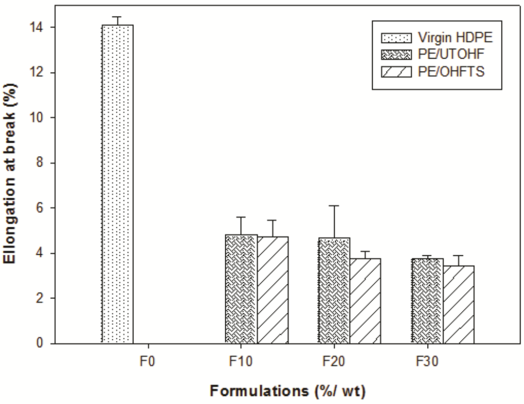


Figure 2: Evolution of elongation at break of composites PE/OHF

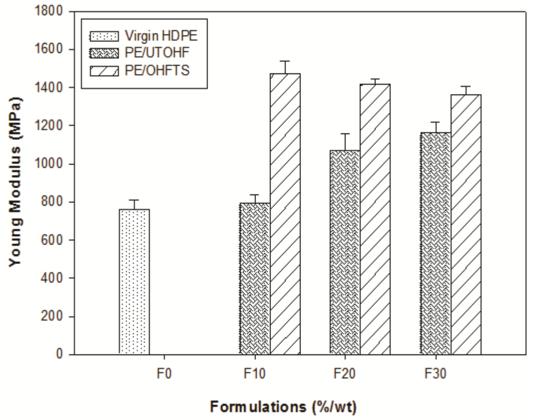
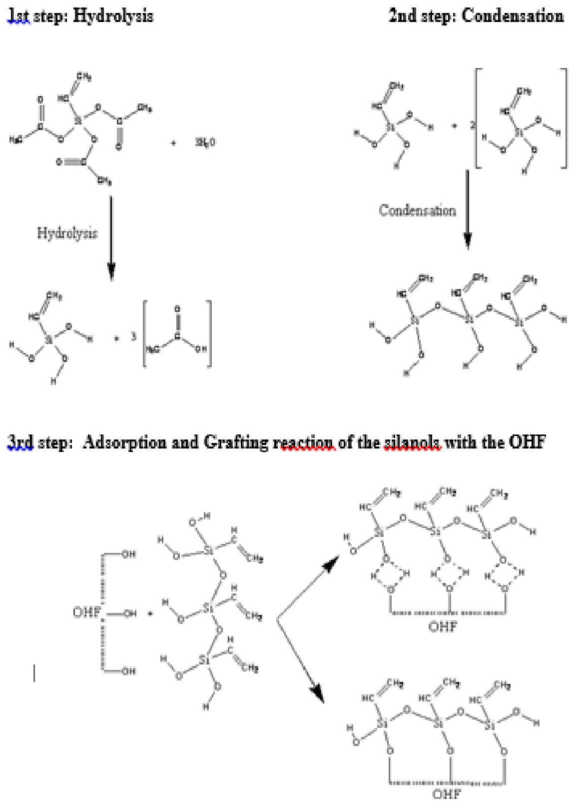


Figure 3: Evolution of Young modulus of composites PE/OHF

After chemical treatment, the elongation at break decrease compared to the untreated composites, but not in terms of overall deformation compared to virgin PE. This decrease is attributed to the good dispersion of the flour by adding the modifying agent which gives stiffness to the material [15, 16] Furthermore, we notice that the addition of treated flour with vinyl-silane induces a drastic increase in the Young's modulus. This increase is mainly due to greater interfacial adhesion matrix/filler due to the good dispersion of the treated filler in the PE matrix [17].

c. Thermal characterizations of composites

Figures 4, 5 and 6 show the TG and DTG thermograms of different composites prepared with untreated and treated loadings at 10, 20 and 30%, respectively. We notice that the addition of untreated olive husk flour in the PE matrix decreases the onset decomposition temperature and this decrease becomes higher with the flour content. This decrease can be attributed to the presence of three main components (cellulose, hemicellulose and lignin) in OHF as confirmed by Ersan Putun [18]. The cellulosic filler is degraded between 200 and 350°C, whereas PE is degraded at higher temperatures (400°C). Therefore, the thermal behaviour of the composite is the sum of the individual constituents of both filler and matrix. Around 460°C, there is a level of stability, attributed to the formation of a residue.



Scheme 1: Mechanism between the olive husk flour and the vinyltriacetoxysilane

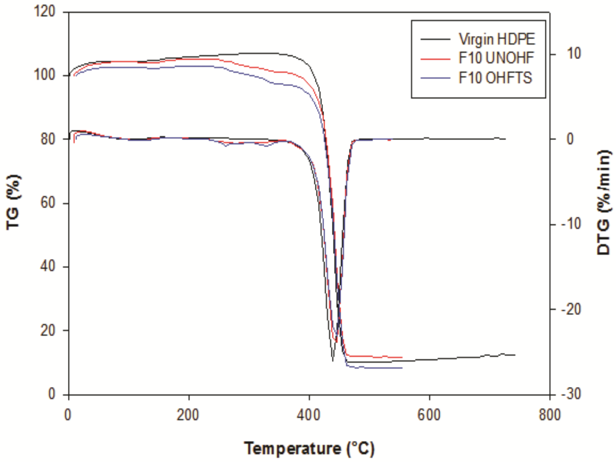


Figure 4: TG and DTG thermograms of different composites prepared with untreated and treated loadings at 20%.

For the DTG thermograms of untreated and treated composites, we see the formation of different endothermic peaks. A first peak appearing around 100°C, corresponds to the evaporation of water physically adsorbed on the surface of particles of untreated olive flour composites. The peaks areas is more important when the rate of untreated flour is higher, this phenomenon can be attributed to the hydrophilic nature of untreated flour, which has the capacity to absorb more water. However, at the same temperature interval, polyethylene does not show any peak due to its hydrophobic character. A second peak corresponds to the thermal degradation of hemicellulose and cellulose and it is located between 200 and 300°C. More specifically, the thermal decomposition of cellulose occurs mainly by depolymerisation from 300°C [19, 20] Hemicellulose is less thermally stable than cellulose, and degrades between 200 and 260°C. In a study of jute fiber and its components by Bhaduri [21], they attributed this process to pyrolysis of the hemicellulose fraction. At approximately 350 ° C, a third peak appears, it corresponds to the decomposition of lignin. This process can be explained by the cleavage of carbon-carbon bond between the structural units of lignin and dehydration reactions between 380-470°C [14], a broader peak with high intensity appears and it corresponds to the polyethylene matrix decomposition. Beyond 500°C, there is stability due to the formation of residue. The effect of treatment in F10 formulation improves the thermal stability of the composite materials. On the contrary, to the treated formulations based on F20 and F30, the results show an increase in the onset decomposition temperature compared to untreated composites.

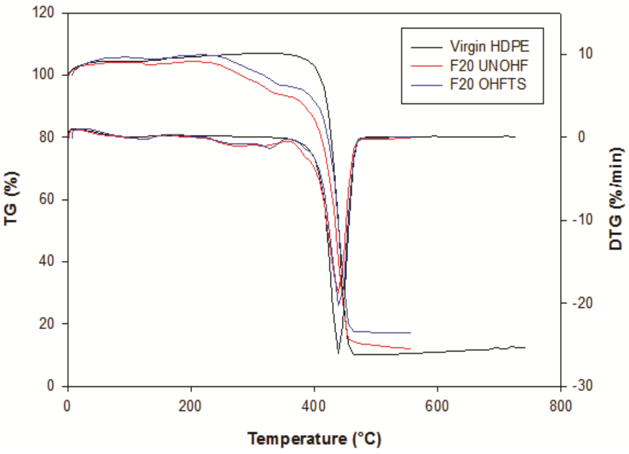


Figure 5: TG and DTG thermograms of different composites prepared with untreated and treated loadings at 10%.

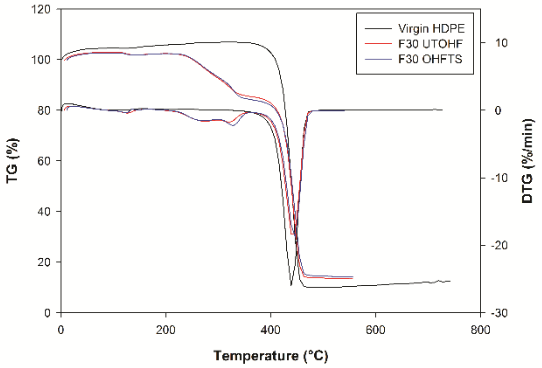


Figure 6: TG and DTG thermograms of different composites prepared with untreated and treated loadings at 30%.

d. Water absorption test

The evolution of water absorption of the composites HDPE/OHF as a function of time is shown in figure 7. We can clearly see an increase in the absorption rate of water with immersion time for the untreated olive husk flour, which is quite expected. Boufi and Dufresne [12, 22] reported the same result and they explained that the olive husk flour is highly rich in hydroxyl groups; they form hydrogen bonds with water molecules. For the virgin PE, there is very low water absorption due to apolar nature of this polymer, and its hydrophobic character. After silane-treatment of OHF, the rate of water absorption decreases. This result can be attributed to a diminution of the concentration of -OH groups of the cellulosic filler. However, the hydrophilic character is more pronounced for the untreated composites compared to the composites treated with modifying agent (vinyltriacetoxy-silane) [10,12].

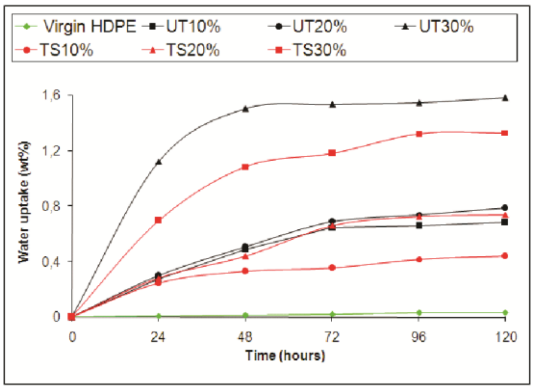


Figure 7: Evolution of the rate of water absorption of HDPE/OHF composites untreated and treated with silane.

e. Scanning electron microscopy

SEM micrographs of the fractured surface of HDPE-based composite reinforced with 20 wt% are shown in figure 8. For the untreated composites (figure.8a), we can see the presence of many voids and cavities on the surface, indicating that the particles of olive husk flour are pulled out from the matrix during fracture. This observation indicates clearly that the interfacial adhesion between the cellulosic filler and the polymer matrix is very weak. The presence of olive husk aggregates provides an evidence of the poor dispersion of the filler within the polymeric matrix [23].

On the other hand, the SEM micrographs of the modified fillers with silane (figure. 8 b) seem to provide better and finer dispersion of the cellulosic fillers in HDPE and subsequently a strong interfacial adhesion has occurred between the olive husk filler and the polymer matrix. This behavior is due to the surface chemical modification, which confers a non-polar character to the surface of the cellulosic fillers [24]. However, the addition of olive hush flour treated with silane seems to enhance better the direct contact between the lignocellulosic fillers and the polymer matrix than the untreated composites.

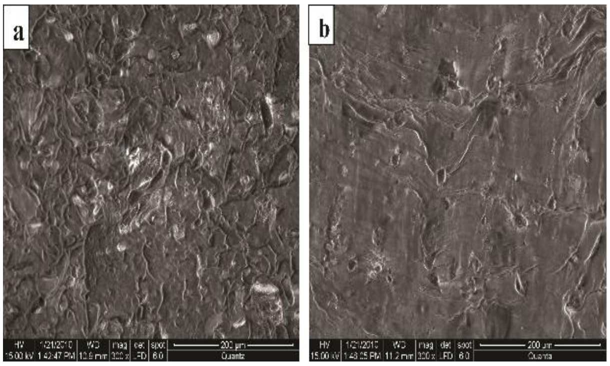


Figure 8: Scanning electron micrographs of fractured surface of HDPE /OHF composite loading at the 20 wt% (*700): (a) composite untreated (b) composite treated with silane

IV. Conclusion

The results of FTIR analysis of the OHF modified with vinyltriacetoxy-silane confirm the reaction of silanization. The results showed that the mechanical properties of the composite materials are positively affected by silanization treatment of OHF, when the untreated olive husk flour increases, the elongation at break decreases, while the Young modulus progressively increases. After chemical modification with the vinyl silane, the elongation at break also decreases and the Young's modulus increases for both composites but more pronounced for the modified ones. The thermal analysis has shown that the incorporation of the untreated olive husk flour in the PE matrix decreases the onset decomposition temperature. The effect of treatment for formulations F10 does a little improvement in thermal stability of composites. However, there is a gain in the temperature of the beginning of decomposition for formulations F20 and F30 compared to the untreated formulation. The rate of water absorption depends on the immersion time and the rate of olive husk flour, which gives a character more or less hydrophobic to the materials. These results are confirmed by scanning electron microscopy (SEM) micrographs.

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