

Effect of Compatibilizing Agents on the Mechanical Properties of High-Density Polyethylene/Olive Husk Flour Composites

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ABSTRACT: The main objective of this research was to investigate the effect on the thermal and mechanical properties of the addition of two different compatibilizing agents, maleic anhydride-grafted polyethylene (PE) [synthesized in a solution state (MAPE) and commercial (XA255)], to olive husk flour, high-density polyethylene (HDPE) composites. The composites contain 30 wt % of olive husk flour and a variable proportion of compatibilizer (3, 5, and 7 wt %). The grafting reaction was followed by Fourier transform infrared, and the grafting degree was evaluated by means of titration. The effect of grafting on the thermal properties of MAPE was observed by ATG/DTG. The mechanical and thermal properties of the composite were investigated. A morphological study of the composite reveals that there is a positive effect of compatibilizing agent on interfacial bonding. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: composites; compatibilization; fibers

Received 27 June 2012; accepted 1 August 2012; published online

DOI: 10.1002/app.38434

INTRODUCTION

In recent years, the incorporation of lignocellulosic materials as reinforcing agents or as fillers in polymer composites has received an increased attention.^{1,2} Commodity thermoplastics such as polyethylene (PE), polypropylene (PP), and poly(vinyl-chloride) are the polymer matrices mostly used in the manufacture of fibers/thermoplastic composites. Among these thermoplastic, the PE is a ubiquitous material with versatile properties. It is produced and used in greater volume than any other thermoplastic. The olive husk, one among several lignocellulosic materials, is an agricultural residue produced as by-products during the olive milling process in the olive producing countries such as Algeria. Every year, thousands of tons of this product are incinerated or rejected in the nature, causing a major inconvenience to the environment.³

Lignocellulosic materials exhibit a number of attractive features including low density, low processing, abundance, and certainly biodegradability. Despite these advantages, use of wood flour was restricted due to its inherent high-moisture absorption capacity, thermal instability during processing, poor wettability, and poor adhesion toward polyolefins.^{4,5} This incompatibility is due to their different chemical nature. Lignocellulosic fibers are hydrophilic while on the thermoplastic matrix is hydrophobic. To promote the interaction between them, various coupling agents or compatibilizers have been used.^{6,7} Among them,

maleic anhydride (MA)-grafted PE is the most commonly available compatibilizers because of its ability to effectively enhance mechanical properties of the composites.⁸

In this work, high-density polyethylene (HDPE) modified chemically by MA in solution in the presence of benzoyl peroxide (BP) is prepared and incorporated in HDPE/OHF composites and is compared to composites elaborated with a commercial compatibilizing agent (XA255). The thermal and mechanical properties of the composite materials with various types of compatibilizers (synthesized and commercial) and concentrations (0, 3, 5, and 7 wt %) were investigated.

EXPERIMENTAL

Materials

HDPE used was a commercial PE sold under the grade name Hostalen GC7260 (Basell Service Company B.V.). The polymer has a density of 0.960 g/cm³ and a melt flow index of 8.0 g/10 min (190°C/2.16 kg).

Olive husk flour from Béjaïa, Algeria, was used as filler. The size fraction selected after sifting the olive husk has a maximum average diameter of 90 μm.

Two compatibilizers were used: MA-grafted PE (XA225) was obtained from SOLVAY with a grafting degree of 0.18%, and the MA-grafted polyethylene (MAPE) synthesized in the laboratory with a grafting degree of 1.35%.

Grafting Procedure

The grafted HDPE was prepared in solution according to the procedure reported previously by Martinez et al.⁹ About 10 g of PE and 2.5 g of MA have been added in 100 mL of xylene. The mixture was then stirred under inert atmosphere (N₂) at 140°C up to complete dissolution. After adding 0.1 g of BP to the mixture, the reaction took place during 3 h. The grafted polymer was dissolved in 100 mL of refluxing xylene during 1 h and was separated from the rest by precipitation in acetone, then filtered, and washed in acetone three times before drying under vacuum at 80°C for 12 h. Quantitative analysis of grafted polar groups was done by an improved hot-titration method and correlated with Fourier transform infrared (FTIR) spectra results.

Preparation of Composites

All composite samples were prepared with 30 wt % and incorporating 1, 3, and 5 wt % of MAPE and XA255. OHF was oven-dried at 100°C for 24 h. The matrix polymer, HDPE, was blended with the OHF and compatibilizing agents (MAPE and XA255) altogether in co-rotating, twin-screw extruder using three general processes: melt blending, extrusion, and pelletizing. The extruder barrel was divided into eight zones with the temperature in each zone being individually adjustable. The temperature of mixing zone in the barrel was maintained at 180°C. The extruded strand was cooled in a water bath and pelletized. Extruded pellets were dried for 24 h. The material was injected into standard mechanical test specimens using a *BATTENFELD (BA200-CD)* injection-molding machine at 190°C.

Fourier Transform Infrared Spectroscopy

The grafted PE was characterized by FTIR spectroscopy, using KBr pellet technique. Spectra were recorded using a *SHIMADZU FTIR-8400* spectrophotometer with a resolution of 4 cm⁻¹ within the region 4000 cm⁻¹ to 400 cm⁻¹.

Acid–Base Titrations

The quantity of MA grafted onto the HDPE was determined by titration of acid groups derived from the anhydride functions.¹⁰ After dissolution of 1.0 g of MAPE in 100 mL of xylene at boiling temperature, 0.2 mL of water was added to hydrolyze anhydride functions into carboxylic acid functions. Then the solution was refluxed for 1.0 h to complete the hydrolysis. The carboxylic acid concentration was determined by titration with 0.05 *N* alcoholic potassium hydroxide in isopropanol. The indicator used was a solution of 1% phenolphthalein in isopropanol. The graft polymer (MAPE) was completely soluble in xylene at reflux conditions. The titration was stopped at the visual endpoint when the color change was stable. The MA content was then calculated from the titrating agent's volume and its concentration according to the eq. (1):¹¹

$$\text{MA}(\%) = \frac{(V_1 - V_2) \times N}{2W \times 1000} \times 98 \times 100 \quad (1)$$

where *N* is the concentration (mol/L), *V*₁ and *V*₂ (mL) are the volumes used in the blank test and in the test with samples, respectively, and *W* is the weight (g) of the MAPE sample. The molecular weight of MA is 98 g/mol.

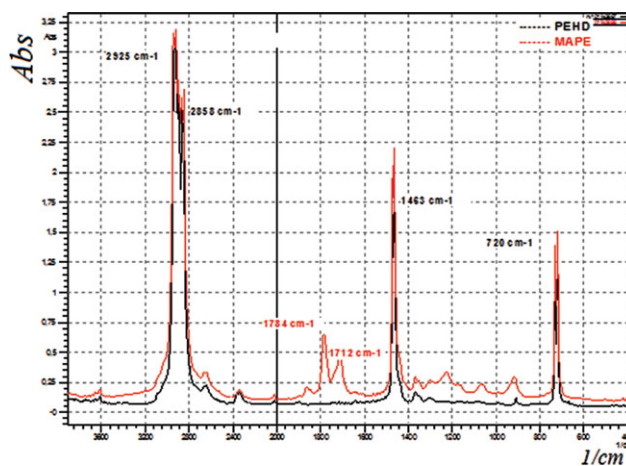


Figure 1. FTIR spectra of virgin PE and MAPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) analysis was carried out using a TA Instrument *TGA Q10* with 5–10 mg of sample. Each sample was scanned from 40 to 240°C at a heating rate of 10°C/min, and the thermal properties were determined from the second scan. *T*_m was defined to be the maximum of the endothermic melting peak from the second heating scan. The specimens' degree of crystallinity, *X*_c, was calculated according to the eq. (2):¹²

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{w} \quad (2)$$

where ΔH_m is the melting enthalpy, ΔH_m^0 is the theoretical melting enthalpy for 100% crystalline PE ($\Delta H_m^0 = 290$ J/g), and *w* is the mass fraction for PE in the composite.

Tensile Tests

The tensile tests were carried out by using a tensile machine *Instron 33 R-4469*. The speed of deformation was fixed at 50 mm/min. Each experiment was repeated on six samples.

Scanning Electron Microscopy

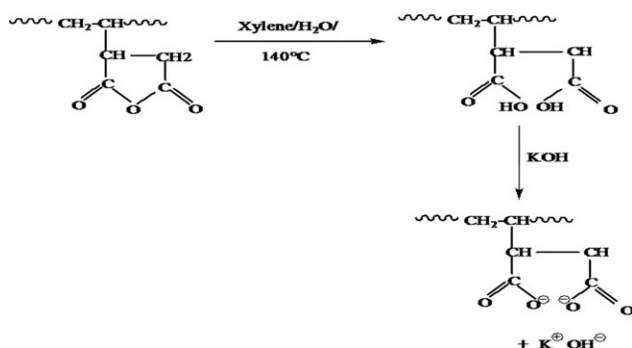
Scanning electron microscopy (SEM) was performed with a *FEI CONTA 200* microscope. Before the fracture, the specimens were cooled down into liquid nitrogen to get well-defined fiber–matrix interface. The objective was to get some information regarding the filler dispersion and filler/matrix interface.

RESULTS AND DISCUSSION

Grafted Polyolefins Characterization

FTIR Spectra. Fourier transform infrared (FTIR) spectra of the virgin HDPE and the MAPE are presented in Figure 1. The virgin HDPE registered several absorption bands characteristic of this polymer. It is observed mainly because:

- The presence of two absorption bands of strong intensity at 2925 cm⁻¹ to 2858 cm⁻¹ and to which corresponded to vibrations Asymmetric and symmetric of the CH-bonded CH₂ group.
- The peak centered at 1463 cm⁻¹ corresponding to bending vibrations of the same group (CH₂).



Scheme 1. Hot titration scheme.

- Another peak of medium intensity located at 720 cm^{-1} that characterizes the stretching vibrations of the C—C group $(\text{CH}_2)_{n-1}$.

This analysis shows clearly that the HDPE used in this study is a pure polymer.

The same peaks can be seen for the MAPE at the exception of the area $1860\text{--}1600\text{ cm}^{-1}$ where we register the appears of two new absorption bands of average intensity around 1784 cm^{-1} and 1712 cm^{-1} , which correspond to the vibrations of elongation of the carbonyls groups $\text{C}=\text{O}$ of MA. The first peak is assigned to the grafted anhydride, which is due to symmetric (strong) and asymmetric (weak) $\text{C}=\text{O}$ stretching vibration of succinic anhydride rings grafted on the PE backbone, respectively.¹³ The second peak is assigned to the grafted maleic acid formed from ring-opening reaction of the succinic anhydride because of moisture.^{3,8} We also note the absence of absorption band between $1600\text{--}1500\text{ cm}^{-1}$, characteristic of double bonds ($\text{C}=\text{C}$), which informs us about the effectiveness of washing to the acetone with an aim of eliminating MA that has not reacted and that grafted MA is the only responsible for the appearance of the band of carbonyls.

Therefore, the formation of graft copolymer of PE and MA was confirmed. These results are in agreement with the result reported by Bengtsson and Oksman.⁸

Acid–Base Titrations

A titration is used to measure the acid number of the MA-grafted polymer. The acid number is a measure of the proportion of MA contained in the polymer. The degree of grafting, calculated from the average of three trials, is 1.35%, slightly higher than that of commercial MAPE, usually used in the literature. The basic potassium alkoxide solution neutralizes one carboxyl group of the MA ring to create a half acid ester (Scheme 1).

Thermogravimetric Analysis

According to Figure 2, we notice that both TGA thermograms have the same shape and show two stages of stability and decay

- The first was recorded in the temperature range $350\text{--}410^\circ\text{C}$, where the sample is thermally stable. The evolution of the curves is almost constant for both the virgin HDPE and the MAPE.
- The second stage is a very significant mass loss. For the virgin PE, onset temperature of decomposition is of the order of 412°C .

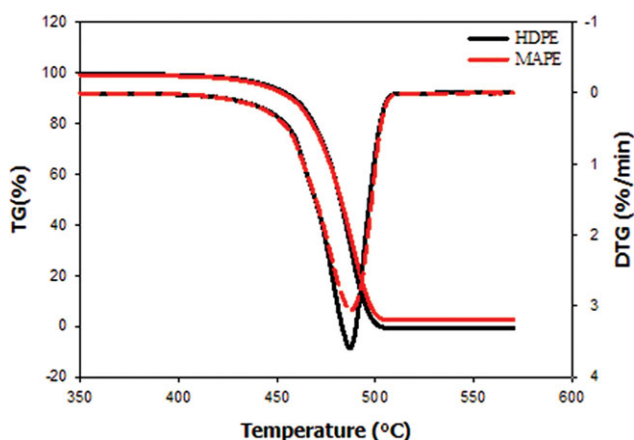


Figure 2. TGA/DTG thermogram of HDPE and MAPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

- The third stage is a level of stability, recorded from 450°C ; it corresponds to the formation of ash. The MAPE record 10.87% ash; however, the PE record only 4.38%.
- DTG thermograms of virgin HDPE and HDPE show a single intense peak localized between 400 and 450°C . Maximum speeds decomposition for virgin PE and MAPE is 3.45%/min and 2.87%/min, respectively. Therefore, the MAPE is more thermally stable.
- We also note the shift of the peak toward higher temperatures for the sample MAPE signature of the better thermal stability.

Characterization of Composites

Tensile Properties. From Figure 3, we notice a decrease in tensile strength of composites loaded with olive husk flour untreated compared to virgin HDPE. These results are predictable and are consistent with many research works. Ma et al.,¹⁴ Djidjelli et al.,¹⁵ and Kim et al.¹⁶ have attributed this decrease to the decrease of the strength of connection between the filler

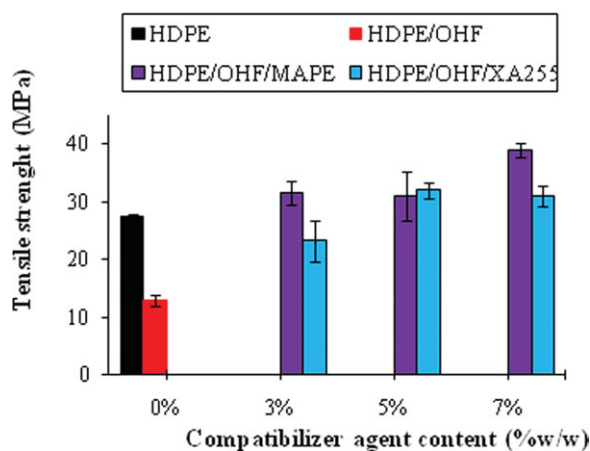


Figure 3. Evolution of the tensile strength for HDPE/OHF composites as a function of the agent compatibilizer type and content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

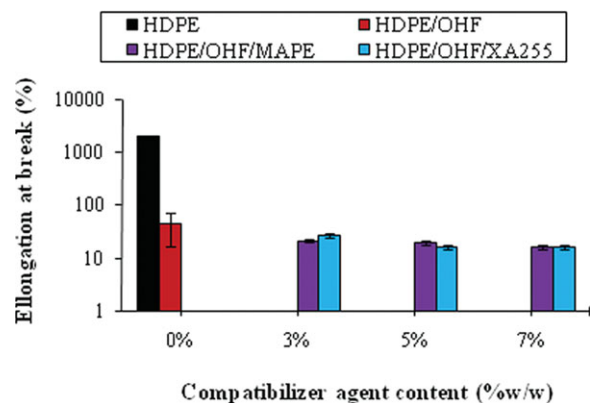


Figure 4. Evolution of the elongation at break for HDPE/OHF composites as a function of the agent compatibilizer type and content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and the matrix that blocks the spread of effort. This decrease increases when the flour loading becomes higher; this phenomenon can be explained by the tendency of OHF particles to form agglomerates that induce heterogeneities and non-uniform stress within the matrix. After adding the compatibilizing agent MAPA and XA255, the tensile strength of composites increased compared to the noncompatibilized composites. This increase is mainly attributed to better dispersion of the fiber and its reinforcing effect.

The evolution of the elongation at break of compatibilized and noncompatibilized composites based on the rate of olive husk flour is illustrated in Figure 4. We note that the trend of all the formulations according to the content of olive husk flour treated and untreated is characterized by a significant decrease in elongation at break. For composites prepared with untreated flour, this decrease could be explained partly by the hydrophilic nature of untreated fibers, which absorb more moisture and cause swelling in the PE matrix, which induces the embrittlement of the material and second because of the increasingly important volume occupied by filler particles, creating defects in the system and reducing the interchain interactions, together with a variation of ductile-brittle material behavior.¹⁷

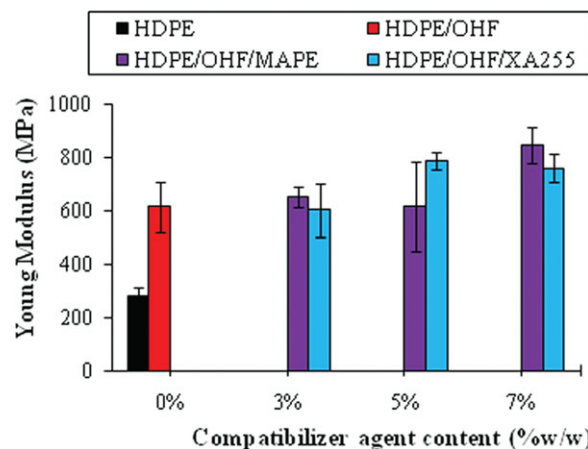


Figure 5. Evolution Young modulus for HDPE/OHF composites as a function of the agent compatibilizer type and content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The addition of compatibilizers (MAPE and XA255) does not improve the elongation at break compared to untreated composite or compared to HDPE virgin.

Figure 5 shows the evolution of Young's modulus of composites compatibilized and noncompatibilized by the content of olive husk flour. The introduction of untreated olive husk flour in the PE matrix increases the stiffness of the material. This can be explained by the rigid nature of the olive husk flour.

After, the addition of PE-grafted MA Young's modulus increases greatly compared to untreated composites. This increase is mainly due to better interfacial adhesion fiber/matrix due to good dispersion of the treated fiber in the PE matrix. The treatment resulted in the formation of chemical bonds between the hydrophobic part of the compatibilizing agent and the matrix surface and the hydrophilic part of compatibilizing agent with the fiber surface.¹⁸

Differential Scanning Calorimetry Analysis. The results of the DSC characterization of composites HDPE/OHF for different compatibilizing agent type and content are shown in Table I. We could not detect the T_g of HDPE/OHF composites with different MAPE and XA255 contents, because they were not

Table I. DSC Characterization of Composites HDPE/OHF at Different Compatibilizing Agent Type and Content

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	X_c (%)
HDPE	132	169.7	114.5	193	58.5
HDPE/OHF	131.2	155.7	114.7	158.2	76.7
HDPE/OHF/MAPE (%)					
3	133	117.9	112.7	128.6	58.1
5	131.6	123.5	115.1	127.2	60.8
7	131.4	127.8	115.1	141.9	62.9
HDPE/OHF/XA255 (%)					
3	131	149.6	115.4	164	73.7
5	130.7	140.3	116.2	144	69.1
7	130.7	120.2	114.8	124.5	59.2

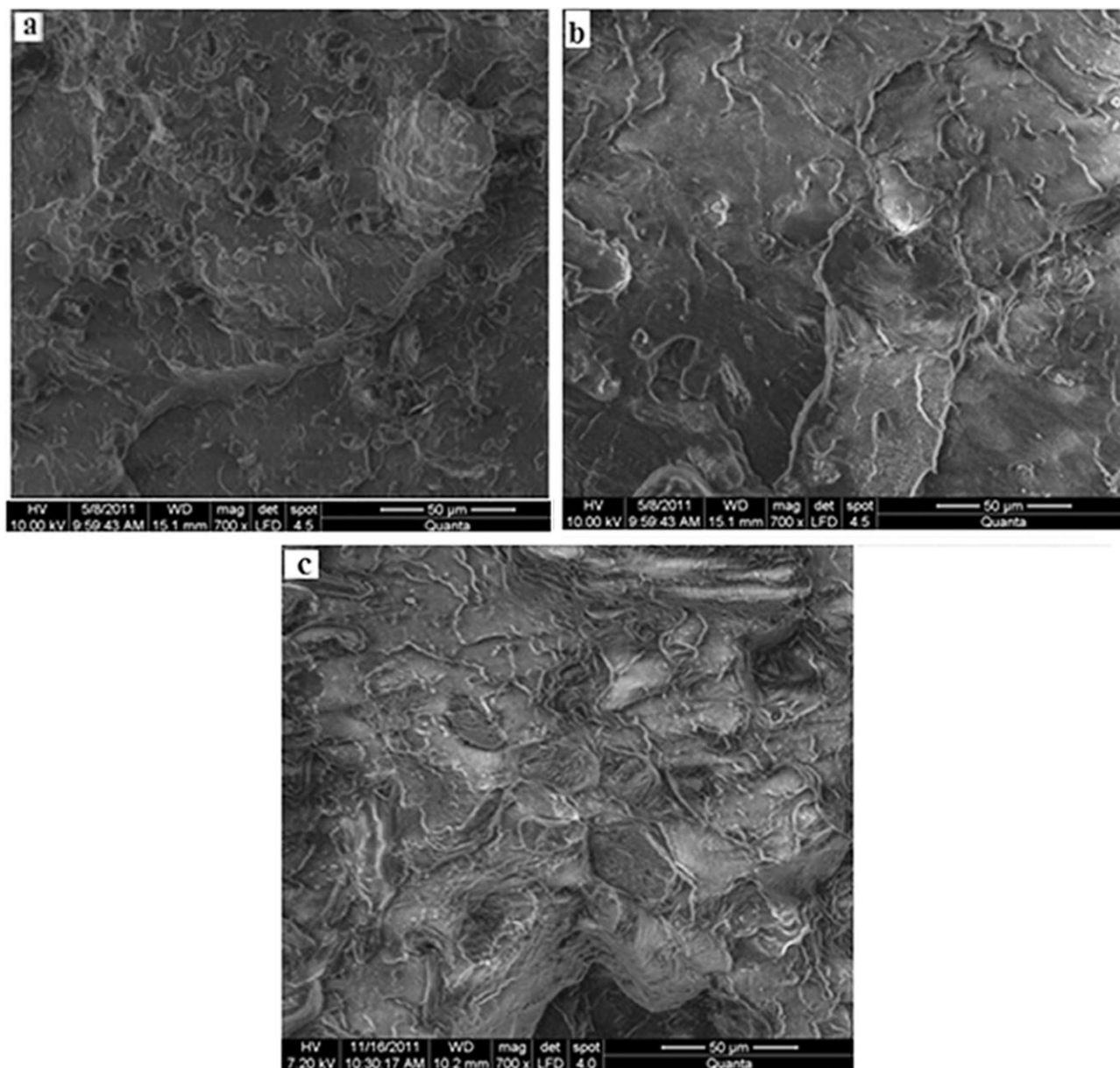


Figure 6. Scanning electron micrographs ($\times 700$) of fractured surface of HDPE/OHF composite (a) composite untreated, (b) composite treated with 5% MAPE, and (c) composite treated with 5% XA255.

sufficiently cooled down.¹⁹ T_m of composites was not significantly changed by the addition of MAPE and XA255 (Table I).

The evolution X_c of the composites with increasing MAPE content can also be observed in Table I. The increasing in the X_c value of the composites is due to the coupling effect of MAPE, which extend the predominance of the crystallization process. This is also due to the cellulose flour acting as an efficient nucleating agent for the crystallization of HDPE/OHF composites treated with MAPE, consequently increasing the crystallization rate and making the crystallization faster. The nucleating effect increased with the presence of MAPP. This is likely due to the stronger interaction between cellulose flour and the PE matrix compatibilized by MAPP, which improved the nucleating activity of cellulose fibers for PE.²⁰

But for the XA255-treated composites, the X_c of the composites with increasing XA255 content decreases, and this decrease of crystallinity is explained by Shiraishi et al.²¹ by the fact that the chemical reagent reacts first in amorphous regions, where there is better accessibility. Conversely, this chemical reaction is more difficult in the crystalline regions of compact and ordered structures. Then it reacts at the end of chains or the surface of crystallites. This causes the opening of some cellulose chains linked by hydrogen bonds, leading to the formation of amorphous cellulose. Marcovich et al.²² demonstrated that treatment of wood flour with MA led to the reduction of crystallinity. Similar behavior was found by Liao et al.²³ and Moharana and Tripathy²⁴ for jute fiber and wood modified with different reagents.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) micrographs of the fractured surface of HDPE/OHF composite reinforced with 30 wt % are shown in Figure 6. For the untreated composites, Figure 6(a) reveals that no cracks are visible on the surface. In the case of untreated composite samples, the micrograph shows that the addition of OHF to HDPE matrix results in a phase-segregation morphology. OHF aggregates are formed on the surface, and well-defined holes around the OHF particles can be seen. This is mainly due to weak interfacial interactions between the cellulosic filler and the HDPE matrix. These defects are responsible for failure and could affect the functional properties of HDPE/OHF composites. The presence of olive husk aggregates provides an evidence of the poor dispersion of the filler within the polymeric matrix.^{3,25}

On the contrary, with the chemical treatment of OHF with MAPE, the SEM micrograph in Figure 6(b) exhibits clearly a finer OHF dispersion. This is probably a result of chemical interactions between hydroxyl groups of OHF and MA reducing the strong filler interactions resulting from hydrogen bonding. The addition of XA255 in composites also improves the dispersion of the wood filler particles in the HDPE as illustrated in Figure 6(c).

CONCLUSION

MA was effectively grafted to HDPE in a solution state in the presence of the peroxide. The studies of well-defined amounts of anhydride compounds by titration and the FTIR analyses of their reaction products confirm that MAH reacts with HDPE. Calorimetric investigations showed that the percentage of crystallinity of MAPE is higher than that of HDPE; these effects can be attributed to the MAPE acting as nucleating sites for the crystallization.

The mechanical behavior of composites PE/OHF shows that when the untreated olive husk flour is introduced, the tensile strength and elongation at break decrease. This phenomenon can be explained by the tendency of OHF particles to form agglomerates that induce heterogeneities and no-uniform stress within the matrix. But the modulus increases, which is due to the rigid nature of the olive husk flour. After adding the MAPE and XA25, the mechanical properties of the composite were positively affected. The maximum tensile strength of the composite prepared with MAPE was obtained at 7% wt, and for the composite prepared with XA255, it was obtained at 5% wt. The T_m of the composites was not significantly changed by the addition of MAPP or XA255. However, the X_c of the composites treated with compatibilizing agent was slightly increased due to the coupling effect of MAPE, but it decreased with XA255. However, the use of MAPE and XA255 in HDPE/OHF composites produces finer morphology, better enhancement of mechanical properties when compared with the untreated composites. On the basis of our experimental results, we suggest that the proper method of enhanced interfacial adhesion of composites with HDPE matrix polymer is treatment with XA255 as a compatibilizing agent and that the optimal XA255 content is 5%.

ACKNOWLEDGMENTS

The authors thank all members of the laboratory of Polymer Materials Engineering (IMP), INSA Lyon, Villeurbanne, France.

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