Chemical Modification of Olive Pomace by Various Esters and Silane

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ABSTRACT: The olive pomace was modified chemically to improve the interface between the polymer matrix and the cellulosic fillers. The modification was done using various ester types having the same nature, however, with different chain lengths and one silane. Before the surface treatment, the olive pomace was extracted with acetone to remove contaminants on the surface, using Soxhlet apparatus. The transesterification of olive pomace with the different ester components, i.e., vinyl acetate, vinyl propanoate, and vinyl butanoate, and the condensation reaction with dichlorodimethylsilane was confirmed by Fourier transform infrared (FTIR) analysis. Moreover, the treatment of olive pomace with vinyl acetate improves the thermal stability and the sample records higher onset temperature of degradation as measured by thermogravimetric analysis (TGA). The results obtained indicated also that the reaction between the hydroxyl groups of waste flour and the acetyl, propionyl, pivalyl, and silane groups have occurred. The modified wood flours exhibited a decrease in the hydrophilicity as supported by the lower moisture content. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 535–540, 2010

Key words: olive pomace; chemical modification; thermal stability; FTIR; thermogravimetric analysis

INTRODUCTION

Polymer composites are a special group of composite materials produced by combining organic polymer resins with different kinds of filler materials. Natural composites have gained significant popularity in the last decade.

The use of waste materials as a lightweight and economical source of reinforcement in thermoplastic composites has received substantial interest in scientific literature.[1–3] The advantages of natural fillers over traditional reinforcing materials, such as, glass fibers, talc, and mica are acceptable specific strength properties, low cost, low density, high toughness, good thermal properties, reduced tool wear, reduced dermal, respiratory irritation, and biodegradability.[4–6] However, the primary disadvantages are (a) poor interfacial adhesion and dispersion in olefin thermoplastic matrix materials due to hydrophilic character of cellulose, (b) high moisture absorption leading to dimensional instability, and (c) low permissible temperatures of processing and use due to their limited thermal stability.[5] The hydrophilic groups present in unmodified cellulose are detrimental to the performance of the cellulose based composites if the fibers are exposed to the outside atmosphere. Water, in liquid or vapor form, can diffuse into the composite, and the properties undergo deterioration. Also, the processing temperature for cellulose based reinforced composites is limited to 200°C, though higher temperatures can be used for short periods of time.[2] Wood-plastics composites are a novel class of materials with a myriad of applications owing to their versatility. Properties of fillers reinforced composites are largely determined by three factors: fiber content, fiber aspect ratio, and fiber orientation.

Modifying agent is the subject of this study. During the past two decades, several methods have been reported in the literature for improvement of the adhesion between the filler and the thermoplastic matrices. Many papers have been published about the effect of chemical treatments on composite properties.[1,2] Many studies concerned the thermoplastic matrices, such as, polypropylene, the coupling agents, such as, maleic anhydride, maleated polyethylene, or polypropylene, and the fillers used like the wood flour.

This study is aimed to improve the interface between the matrix and the lignocellulosic material. Some chemical filler treatments have been carried out in order to ameliorate the interfacial adhesion between the filler and the matrix. Chemical modification of olive pomace with vinyl acetate, vinyl propionate, and vinyl butanoate substitutes the cell wall hydroxyl groups with acetyl, propionyl, pivalyl, and

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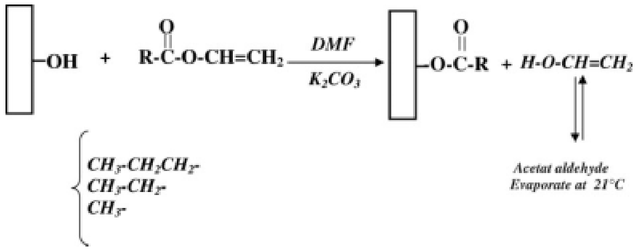


Scheme 1 Proposed reactions of esterification of olive pomace flour with C2, C3, and C4.

silane groups. Every year, during the season of transformation of olive to oil, 1000 tons of olive residue are rejected to nature or incinerated causing environmental pollution. The recovery of this renewable waste may have a double positives impact, economic, and ecological.

The great part of the publications deal with the use of cellulosic fibers treatment with chemical agents and the characterization of the properties performances of such composites, however, very few publications are devoted to olive residue, the chemical aspect (natures, dimensions of the molecules) of the modifying agents. Therefore, the aim of this study is to investigate both the chain length and the nature of the modified compounds in composites.

Another very important aspect of this study is to replace the silanes which are very expensive by the vinyl esters. The performance of these modified composites will be studied.

EXPERIMENTAL

Materials

Filler

In this study, olive pomace was friendly supplied by a local factory producing olive oil in Bejaia Province of Algeria. It was dried in the oven at 105°C for 24 h and then kept in a desiccator at room temperature before use. The particle size is almost 40 μm.

Coupling agents

To study the influence of the chain length and the nature of the modifier agent, four types of components were used for the surface treatments of olive pomace: Acetate of vinyl (C2): $CH_3-COO-CH=CH_2$, propionate of vinyl (C3): $CH_3-CH_2-COO-CH=CH_2$, butanoate of vinyl (C4): $CH_3-CH_2-CH_2-COO-CH=CH_2$, and dichlorodimethylsilane $(Cl_2)\ Si\ (CH_3)_2$.

Before the surface treatment, the olive pomace was extracted with acetone for 48 h using the Soxhlet extractor, to remove contaminants or impurities on the filler surface. After extraction, the filler was stored at room temperature during 2 h. The sample was air dried for 24 h and then oven dried at 105°C until a constant weight was achieved. A total of 5.32 wt % of impurities were obtained.

Treatments with vinyl esters groups

Chemical modifications were carried out by immersion of the olive pomace sample at 90°C for 3 h after extraction, in solution of DMF (*N*,*N*-dimethylform amide), containing the agent of chemical modification: acetate of vinyl (C2), propionate of vinyl (C3), or butanoate of vinyl (C4).

K_2CO_3 was used as a catalyst. The treatment of olive pomace with C2, C3, and C4 were also performed in a solvent system. These treatments were followed by two extractions, with the Soxhlet system. The first for 2 h with water to eliminate catalyst and the second for 6 h, with mixture of (toluene/acetone/ethanol) (4/1/1), to eliminate untreated coupling agents. After extraction, the olive pomace was air dried for 24 h at 105°C.

Probable chemical reactions of the various esters with olive pomace can be illustrated in the following Scheme 1:

Treatments with silane

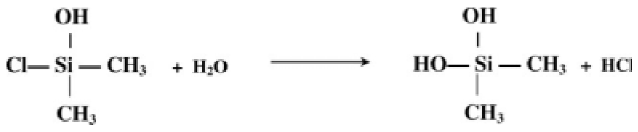
The silane was diluted to 6% in acetone before use for economical reasons. The olive pomace was immersed for 24 h in solution of silane in acetone at 23°C. Then, the cleaning with acetone and drying in a vacuum oven at 60°C for 4 h are necessary to remove any excessive solvent. In the presence of moisture, the dichlorodimethylsilane can react with water to form a silanol. This reaction can be illustrated in the following Scheme 2.

Silanol react with the hydroxyl groups attached to the molecules in the cell wall of olive pomace, thereby bonding itself to the cell wall with further rejection of water. The probable chemical reaction can be illustrated in the Scheme 3.

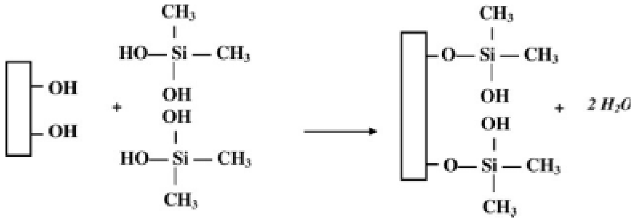
Chemical composition of the olive pomace

Mineral contents

The sample is charred in the furnace for 4 h at very high temperature (800°C), the sample is then removed and cooled in a desiccator. This experiment was repeated thrice. The mass of mineral residue is calculated as follows:



Scheme 2 The hydrolysis step during silane crosslinking.



Scheme 3 The condensation step during silane crosslinking.

$$\% \, C = \frac{M_1}{M_2} \times 100,$$

where M_1 and M_2 are the weights of the sample before and after the charring, respectively.

Rate of extractible

Before the chemical treatment of surface, the olive pomace samples have undergone extraction with a mixture of toluene/ethanol (2/1) for 16 h, to remove contaminants or impurities on the filler surface. After extraction, the filler was stored at room temperature during 2 h. The sample was air dried for 24 h and then oven dried at 105°C, until a constant weight was achieved.

Content of cellulosic materials

Content of lignin. Five grams (M_1) of olive pomace was immersed at 80°C for 8 h, in a tampon acetic solution. Every 2 h, 2 g of sodium chlorite are added to the mixture. At the end of experiment, a vacuum filtration was performed by washing with distilled water, then acetone, and finally, dried for 24 h at 105°C in an oven. The obtained mass was weighted and noted as M_2.

$$\% \text{ lignin} = (M_1 - M_2) \times 100$$

Content of cellulose and hemicelluloses. The mass produced in the elimination phase of lignin (bleaching) (M_2) was treated by immersion in sodium hydroxide (NaOH) 2*M* for 30 min and then washed with acetic acid and distilled water until reaching the pH = 7. The flour olive pomace was dried at 105°C for 24 h and weighted (M_3).

$$\% \text{ cellulose} = (M_3/M_2) \times 100$$
$$\% \text{ hemicellulose} = 100 - (\% \text{ cell} + \% \text{ lignin})$$

Characterization

The rate of humidity

The rate of humidity was determined by gravimetry. The sample was dried in an oven at 105°C for 24 h an the sample was cooled in a desiccator, and weighed immediately. The rate of humidity was calculated according to the following formula:

$$\text{Increase in weight} = \frac{\text{Initial weight} - \text{Conditioned weight}}{\text{Conditioned weight}} \times 100.$$

Fourier transform infrared spectroscopy

The spectrometer SHIMADZU FTIR-8300 was used to obtain the FTIR spectra of the various samples. For each spectrum, 64 scans were carried out with resolution of 4 cm^{-1}. All the IR spectra were recorded in the range 4000 cm^{-1} to 1000 cm^{-1}. The potassium bromide (KBr) was used as a reference substance.

TGA analysis

Thermogravimetric analysis (TGA) was conducted to study thermal stability of several samples of olive pomace. The experiments were performed with an apparatus type SETARM TGA 92 in a temperature range of 20–700°C at a scanning rate of 10°C/min in nitrogen atmosphere with a flow rate of 30 mL/min.

Thermogravimetric curves are reported as percent weight loss as a function of temperature. The sample size was about 5–10 mg.

RESULTS AND DISCUSSION

Chemical composition of the untreated olive pomace

Several tests were carried out in order to evaluate the olive pomace composition. Three main components are lignin, hemicellulose, and cellulose. According to others studies,[7] the results indicated that the olive pomace is composed mainly of cellulose (40.2%) with a crystalline structure and 27% of lignin, an amorphous phenolic polymer with a three-dimensional structure that could explain the rigid character of olive pomace.

Physico-chemical properties of the untreated olive pomace

The moisture present in olive pomace at normal atmospheric condition: 17°C and 50% relative humidity are listed in Table I. The moisture present in the waste is likely to change depending on the atmospheric conditions, type of filler, age of plant, soil condition in which the plant has grown, and the method and the duration of preservation.[7]

TABLE I
Physical and Chemical Properties of Olive Pomace

Parameters	Type of filler				
	Untreated	AC treated	PR treated	PI treated	Silane treated
Humidity (wt %)	7.11	3.25	5.01	5.22	4.22
Residual at 850°C (%)	0.78	0.78	0.78	0.78	1.03
Density	1.0688	–	–	–	–
Rate of grafting	–	15.25	8.69	8.129	22.66

It can be noticed that the amount of humidity is important, and it reaches a value of 7.11%. This result can be explained by the cellulose and hemicellulose contents, which are rich on hydroxyl groups. They form hydrogen bonds with the moisture present in air.

For the rate of minerals, it does not exceed a value of 0.78%. This is explained by the organic nature of olive pomace.

Characterization of flour olive pomace modified chemically

Rate of grafting

For the rate of grafting obtained with the different modifying agents, as shown in Table I, they are depending on the nature and length of the chain or the number of carbons. A better rate of grafting is obtained for silane and grafting is increasingly difficult to achieve as the number of carbons increases.

FTIR spectroscopic characterization

FTIR spectra of untreated and treated filler are shown in Figure 1. Obviously, there are many similarities and difference between the fillers.

The grafting content of agents depends on many factors, such as, initiator concentration, temperature, rotor speed, and residence time. The FTIR spectra of untreated olive pomace and treated with AC, PI, and PR show severals absorption bands in the range 400–4000 cm^{-1}.

The major difference between the FTIR spectra of filler materials are observed at 3400 cm^{-1} and 1739 cm^{-1} associated with hydroxyl group (OH) and carbonyl stretching vibration, respectively. The FTIR spectrum of untreated olive pomace has absorption band at 1739 cm^{-1} that are due to carbonyl C=O stretching present in the hemicelluloses lignin and extractives.[8,9] As seen in Figure 1 and Table II, the treatment of olive pomace with acetate, propionate, and pivalate of vinyles increased the absorbance in the region 1739 cm^{-1}. The appearance of the peak at around 1739 cm^{-1} for the treated flour proves that acetyl, propionyl, and pivalyl groups are involved in an ester bond with the hydroxyl groups of the flours. The esterification reaction is also confirmed by the absorbance observed at 1191–1295 cm^{-1} (C—O stretching). However, it is clear from the spectra of olive pomace that there is a reduction of this band as a result of esterification.

The results of the FTIR spectroscopy corroborate with the rate of grafting. The area of the absorption band of hydroxyl groups is decreasing, whereas the carbonyl absorption band increases with the chemical modification. This variation is more pronounced with modifying agents whose string contains less carbon.

The reaction of dichlorodimethylsilane with the olive pomace flour was also studied. Figure 2 shows the FTIR spectrum of untreated filler and filler treated with silane. Obviously, there are many similarities and differences between the FTIR analysis was used studying the formation of olive pomace-O—Si bonds and Si—O—Si bonds. Two small peaks at 1250 cm^{-1} and 1300 cm^{-1} were attibuted to unhydrolyzed Si—O—CH$_3$ groups and Si—O—Si bonding, respectivly.[10]

Determination of moisture content

The several chemical modifications of the olive pomace reduce its hygroscopicity (around 50% for AC treated filler) because a considerable amount of

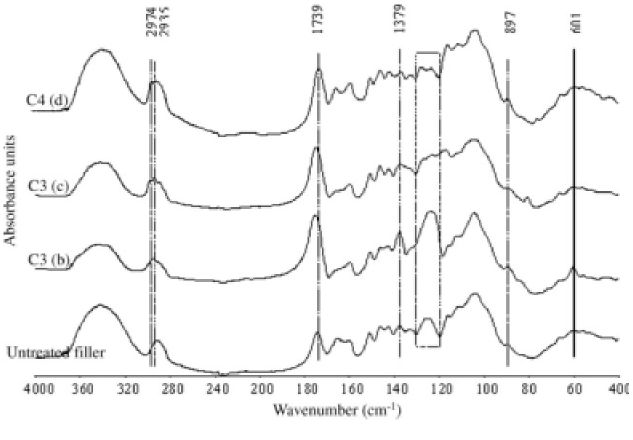


Figure 1 FTIR spectra of (a) untreated filler, treated filler with (b) acetate of vinyl (AC), (c) propionate of vinyl (PR), and (d) butanoate (pivalate) of vinyl (PI), in the region 4000 cm^{-1} to 400 cm^{-1}.

TABLE II
FTIR Absorption Bands in the Range 400–4000 cm^{-1}

Absorption bands	Untreated	AC treated	PR treated	PI treated	Silane treated
3400 cm^{-1}	Hydroxyl group (OH)				
1739 cm^{-1}	Carbonyl C=O stretching				
1191–1295 cm^{-1}	C—O stretching				
1250 cm^{-1}	–				Hydrolysed Si—O—CH$_3$
1300 cm^{-1}	–				Si—O—Si bonding

accessible —OH groups disappear to become firmly bonded to the polar ester or silane groups.

In Table I, the moisture values of untreated and treated flour are presented. The results are consistent with the results of both FTIR spectroscopy and the rate of grafting. Samples which absorb less moisture have affinity with those who have the least carbon atom, and hence, give the best rate of grafting.

The reduction of the moisture content of the sample modified with silane is linked also with the highest rate of grafting obtained by this change.[11] It is clear that the acetylation, propionylation, butanylation, and silane reaction treatements reduced the OH concentration, and thus the water adsorption.

Thermal characterization by TG-DTG

Figure 3 presents TG thermograms of various samples of olive pomace flour for both untreated and treated with various chemical agents AC : C2, PR : C3, BU : C4, and silane.

The TG curves have the same shape, and indicate a small loss of mass not exceeding 5% in the temperature range of 70–150°C. This is attributed to moisture evaporation in the sample. This value is very close with that measured by gravimetric method after drying in the oven. It can be seen clearly that the untreated olive pomace flour contains a more significant quantity of water compared with that treated with C2, C3, and C4, and this quantity is increasingly reduced as the carbonaceous chains of the modifying agent is small. Indeed, the C2 sample is better than the others from hydrophobic character point of view.

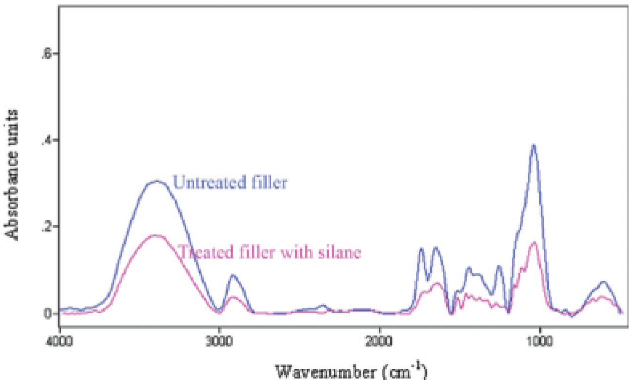


Figure 2 FTIR spectra of (a) untreated filler and (b) filler treated with silane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In the case of thermal stability, it can be observed in the TG thermograms and in Table III that the initial decomposition temperature (IDT) of C2 is better than those of C3, C4, and that of the untreated flour. A gain of 20°C on the initial temperature of decomposition is recorded for C2 compared with the untreated flour of olive residue. Such result is significant because the thermal stability is considered the major problem of use of lignocellulosic fibers when blended with polymeric matrices. Their low temperatures of decomposition cause problems during processing.

The reduction in the absorbent character of C2 and the increase in its thermal stability are due to its good reactivity related to the size of this C2 molecule which presents a weak steric embarrassment. Subsequently, it fits more easily than the largest molecules (C3 and C4) in the various components of the flour and mainly the hemicellulose, thus modifying its structure by giving a better grafting rate,

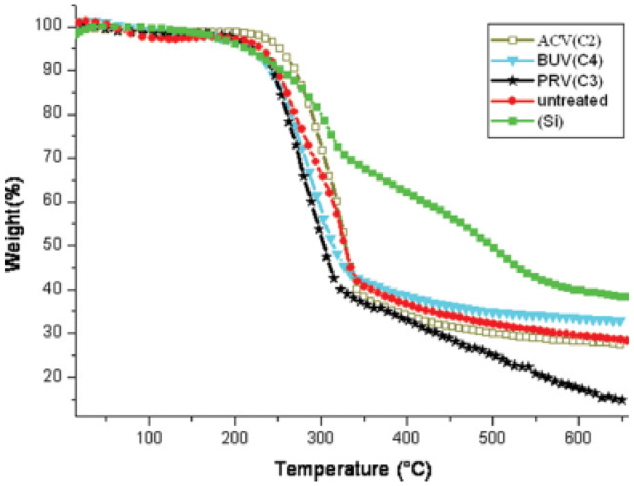


Figure 3 TGA curves of treated and untreated olive pomace. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decreasing the concentration of hydroxyl groups responsible for the hydrogen bonds with moisture.

It can be noticed the treated olive pomace with silane groups is more thermally stable than the other samples. However, the onset decomposition temperature is lower. This behavior is related to the residual silanes that start decomposition at 200–300°C.

TABLE III
Thermal Properties of Untreated and Treated Olive Pomace Flour by TGA

Filler	IDT (°C)	Maximum rate of degradation (%/min)	T_{max} (°C)
Untreated	227	4.82	269.2
AC treated	251	8.65	262.4
PR treated	203	7.45	279.9
PI treated	200	5.86	303.1
Silane treated	206	3.65	304.1

CONCLUSIONS

This study investigated the chemical reaction between olive pomace and several chemical modifying agents. The chemical changes resulting from these treatments were examined by FTIR and TGA analyses:

Both FTIR spectroscopy and TGA results provided clear evidence that the surface of olive pomace materials have changed after treatments with coupling agents. They indicated also that reaction on the filler with coupling agents have occurred.

The length of the chain of the chemical agent affects the rate of grafting on the olive pomace. The chemical treatment of olive pomace with the short chains like vinyl acetate (C2) or silane give the best grafting, and hence, a low affinity with water and better thermal stability. Such treatments can be recommended in the preparation of polymer composites/olive pomace.

Moreover, the chemical modification techniques used in this study could find potential applications in industry, because it uses dilute solutions and the process is a simple immersion at moderate temperatures.

References

1. Matuana, L. M.; Balatinecz, J. J.; Park, C. B.; Sodhi, R. N. S. Wood Sci Technol 1999, 33, 259.
2. Felix, J. M.; Gatenholm, P. J Appl Polym Sci 1993, 50, 699.
3. Pagnanelli, F.; Mainelli, S.; Veglio, F.; Toro, L. Chem Eng Sci 2003, 58, 4709.
4. Ceti, N. S.; Ozmen, N.; Tingaut, P.; Sèbe, G. Eur Polym J 2005, 41, 2704.
5. Tserki, V.; Matzinos, P.; Panayiotou, C. J Appl Polym Sci 2003, 88, 1825.
6. Tserki, V.; Matzinos, P.; Panayiotou, C. Compos A 2006, 37, 1231.
7. Tserki, V.; Matzinos, P.; Kokkou, S.; Panayiotou, C. Compos A 2005, 36, 965.
8. Djidjelli, H.; Boukerrou, A.; Founas, R.; Rabouhi, A.; Kaci, M.; Farenc, J.; Martinez-Vega, J. J.; Benachour, D. J Appl Polym Sci 2007, 103, 3630.
9. Kazayawoko, M.; Balatinecz, J. J.; Matuana, L. M. J Mater Sci 1999, 34, 6189.
10. Bengtsson, M.; Oksman, K. Compos A 2006, 37, 752.
11. Wang, B.; Panigrahi, S.; Tabil, L. W.; Crerar, T.; Powell, M. Kolybaba; Sokhansanj, S. In CSAE/ASAE Annual Intersectional Meeting; North Dakota, USA, 2003.