Effect of Olive Residue Benzylation on the Thermal and Mechanical Properties of Poly(vinyl chloride)/Olive Residue Composites

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ABSTRACT: The changes in mechanical properties, the thermal stability, and the water absorption capacity of poly (vinyl chloride)/olive residue flour composites were studied as a function of various residue olive flour ratios, i.e., 0, 5, 15, and 25% by weight taking into account the effect of benzylation chemical treatment of the filler. The study showed that composite samples prepared with the untreated filler exhibited higher tensile modulus and hardness compared with the neat resin, whereas elongation and tensile strength were observed to decline. On the other hand, the PVC hardness was found to increase with addition of the untreated olive residue flour (ORF), however the composite samples prepared with the benzylated flour exhibited lower hardness than those prepared with untreated olive residue. Moreover, the amount of absorbed water depends on the amount of filler in the composite. The comparison of the results obtained from the samples of F5, F20, and F30 formulations between the untreated and treated ORF indicated a reduction in absorbed water for the composite samples containing treated ORF with benzyl chloride. As a result, the mechanical properties of the treated composites were improved. Furthermore, the thermal characterization of the different samples carried out by color change test and thermogravimetric analysis revealed an increase in the onset temperatures of decomposition for the treated composites. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1459–1465, 2008

Key words: PVC; wood flour; olive residue, mechanical properties; thermal stability; water absorption

INTRODUCTION

In the last decade, polymer composites filled with natural lignocellulosic fibers have attracted the attention of many researchers and technologists.[1–5] Both polymer matrices and natural filler systems have been widely investigated.[6–10] As a matter of fact, Oksman and Lindberg[11] as well as the team of Liao et al.[12] studied the mechanical behavior of composites based on polyethylene and wood flour samples.[11,12] On the other hand, Zaini et al.,[13] Nitz et al.,[14] and Kaci et al.[15,16] investigated the mechanical behavior of polypropylene/wood flour composites. Some authors examined also the mechanical behavior of PS/PEHD/wood flour.[17] On the contrary, the research work dealing with PVC/wood flour composites is rather scarce. Although, some papers have been reported in literature including those of F. Mengeloglu, L.M. Matuana,[18] B.M.A. Pedro, E.E.C. Monteiro devoted to a comparative study of the mechanical behavior of PVC/CaCO$_3$ with PVC/Agalmatolithe, while M.M. Sain et al. investigated the filled PE/WF, PVC/WF, and PP/WF formulations.[19,20]

On the other hand, there is a few works, which has been reported in literature on olive residue rejects and their uses in many applications involving mainly the production of thermal energy as well as food for animals.[21–24]

In the present work, Algerian olive residue was used as filler to reinforce poly(vinylchloride) composites. Every year, during the season of transformation of olive to oil, thousands 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.

Chemically, the olive residue contains cellulose, hemicellulose, and lignin, and cannot be processed as plastics due to both the high degree of crystallinity in the cellulose and the three-dimensional network.

To solve this problem, this study examined the plasticization of the olive residue by chemical treatment with benzyl chloride, therefore expecting better processability of the composite materials and higher interfacial adhesion between the polymer and the filler.

EXPERIMENTAL

Materials

All the PVC-Olive residue composite formulations used in this work were prepared based on PVC type 4000 M produced by the Algerian Company named ''Entreprise Nationale des Industries Pétrochimiques (ENIP)'' in Skikda on the Eastern Coast of Algeria. The polymer has the following physical characteristics: K_{wert}, 67; powder density, 0.56 g mL^{-1}; thermal stability, 60 min at 180°C. The additives used in the preparation of the various formulations were dioctyl phthalate (DOP) as a plasticizer with a viscosity ranging from 80 to 85 MPa s, a molecular weight of 390 g mol^{-1}, a boiling temperature of 233°C, a thermal stabilizer system based on Ba-Cd-Zn and soya bean oil as a lubricant.

The blend obtained with PVC resin and the different additives (dry blend) were used to prepare the composites formulations. Olive residue flour was used as a filler having a length of around 100 μm and the composition of the olive residue was determined and the results are illustrated on Table I.

Chemical treatment of olive residue flour by benzylation

The Algerian olive residue was subjected to several pretreatments, i.e., washing with hot water to eliminate pulp, drying with the free air during 24 h then in a drying oven with 80°C during 24 h, crushing, and finally sifting to obtain a flour of size lower than 100 μm, which was dried under vacuum at 80°C during 12 h.

After being preswelled by 18% NaOH for 1 h, the powder was transferred into a flask containing phase transfer catalyst and benzyl chloride.

The reaction was carried out under vigorous stirring at 120°C for 4 h at reflux. The products were purified through washing several times with distilled water to remove inorganic salts, and with ethanol to remove residues of benzyl chloride. Finally, the treated flour was dried again under vacuum at 60°C during 72 h for being used as filler in composite matrix.

Five formulation of PVC with the olive residue were prepared, the reference F0 only made of PVC without olive residue, the two formulations with PVC and the untreated olive residue at 5 and 25% in weight noted by F5 and F25 and finally two formulations PVC with the treated olive residue with chloride benzyl at 5 and 25% in weight noted by F5B and F25B.

Sample preparation

Blends based on PVC powder, various additives, and olive residue flour before and after treatment were mixed in a random way in a high-speed twin steel-wall mixer and processed at a speed of 3000 rpm at 50°C, below the glass transition temperature of PVC. The different PVC formulations obtained were used to prepare preblended films by calendaring process at 180°C with a residence time of 8 min. The films obtained were placed in an aluminum mold, which was placed between two steel platens. A *Fontume Holand* hydraulic oil heated press with a nominal maximum pressure level up to 250 kN was used for compression molding. The press platens were maintained at 170°C for 3 min. The plates obtained are 2-mm thick and they will be used for testing. The sample preparation was carried out in the laboratory of CABEL ''*Cablerie Electrique*'' located in Algiers (Algeria).

Spectroscopic analysis

FTIR measurements were carried out on a SPECTRUM 100 Fourier–transform infrared spectrometer. The FTIR spectra were measured in KBr pellets containing 1% finely ground samples.

Electric conductivity

Conductivity measurements were carried out on a conductivity meter HANNA Instruments EC215, the calibration of the apparatus is carried out with a solution of KCL 0.1M at 20°C.

Mechanical properties

Five samples of each test were used to determine tensile (elongation and strength at break) and impact properties. The tensile test was performed on a ZWICK/ROEL Z 2.5 tensile testing apparatus at a cross-head speed of 10 mm min^{-1}, according to ISO 527-1 procedure. The size of the specimen was 75 × 13 × 4 mm^3.

Charpy impact tests, were performed on CEAST TORIWO (6546/000) Impact tester according to ISO178. The size of the specimens used for the impact test was 8 × 1 × 0.2 cm^3.

The hardness test was carried out on a Durometer Shore D according to standard NF ISO T 51–123 with specimen dimensions of 10 × 10 × 0.2 cm^3. Hardness is the average of five measurements taken on each sample.

TABLE I
Chemical Composition of Olive Residue

Composition	Rate (% w/w)
Cellulose	40.2
Hemicellulose	26.5
Lignin	27.2
Extractable substances	5.32
Ash	0.78

Water absorption

Water absorption measurements were performed according to ASTM standard method D 570 99 (ASTM 1999). For each composite, five samples of the following dimensions: $3 \times 12 \times 50$ mm^3 were cut from the plates of the compression molded sheets.

The samples were subjected to heat treatment in an oven at 50°C for about 24 h, then immediately weighed (W_0). To measure water absorption in the composite, all the samples were then immersed in distilled water at ambient temperature for 24 h, then taken out and weighed again (W_f). The percent weight gain (PWG) was calculated.

Thermal stability

For thermal stability analysis, the decomposition rates were measured by a SETARAM TGT DTA 92 thermogravimetric apparatus. A sample of initial mass of 15–20 mg was introduced into a platinum crucible; the sample mass (TG) variation was then measured as a function of temperature (or time), and the rates of mass loss (DTG) were determined by using a thermobalance under an inert argon atmosphere up to 600°C, at a heating rate of 10°C min^{-1}.

RESULT AND DISCUSSION

Benzylated treatment of olive residue

Infrared spectra

FTIR spectra of olive residue flour before and after benzylation are illustrated in Figure 1. It can be observed clearly that the chemical structure of benzylated of olive residue flour is quite different from that of the untreated flour. The intensity of the absorption band of hydroxyl groups which appear at about 3500 cm^{-1} decreases after benzylation process as a result of etherification. The results obtained from infrared spectra prove that the hydroxyl concentration decreases with the chemical treatment because the hydroxyl groups are substituted by the benzyl groups. In addition, a reduction in the absorption band, which appears at 1730 cm^{-1} corresponding to the carbonyl groups is well detected for benzylated of olive residue flour sample compared with the untreated sample. This reduction can be attributed to the partial extraction of the lignin and the hemicellulose, which contain these groups by the chemical treatment.[20] The appearance of a new absorption band characteristic of the phenyl groups located approximately at 736–695 cm^{-1} indicates that the reaction of the monosubstitution of the sodium ions by the benzyl groups was occurred.

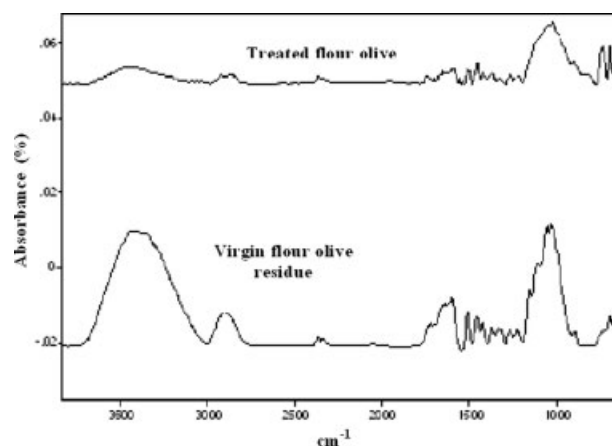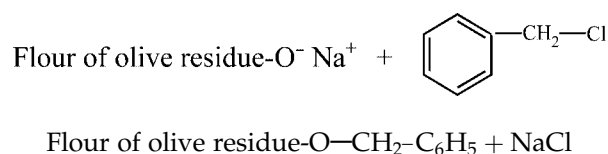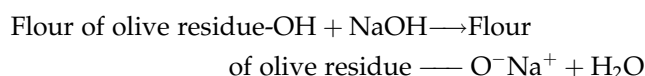The heterogeneous structure of the olive residue renders more complicated quantitative study of

Figure 1 FTIR spectra of untreated flour of the olive residue and benzylated olive residue.

the reaction of benzylation. Instead, the degree of advance of this reaction can be evaluated by measuring the weight gain of the sample at the end of the reaction. This weight gain is attributed to the fact that the benzyl groups are heavier than the hydrogen groups. Indeed, as shown in Table II, it is obtained 30% weight gain of the sample and a drastic increase in the electric conductivity which passes from 49.4 to 1.94×10^3 µs after 4 h of reaction.

All these results confirm the reaction of etherification according to the following mechanism

Flour of olive residue-OH + NaOH$\longrightarrow$Flour of olive residue —— O$^-$Na$^+$ + H$_2$O

Flour of olive residue-O$^-$ Na$^+$ + [benzyl chloride structure]—CH$_2$—Cl

Flour of olive residue-O—CH$_2$–C$_6$H$_5$ + NaCl

Characterization of composites PVC/olive residue

Mechanical properties

Tensile properties. The effect of the olive residue incorporation on the mechanical properties of PVC/

TABLE II
Gravimetric and Conductimetric Results

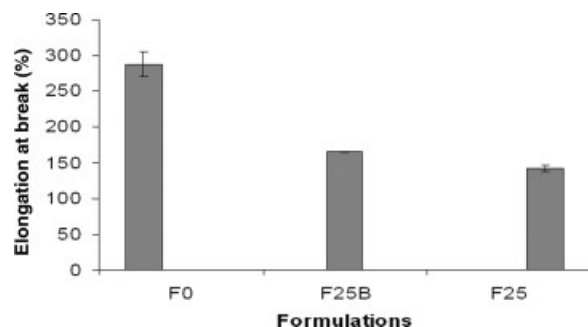| Solution	Weight gain	Conductivity (µS)
Distilled water	–	48.4
Distilled water + benzyl chloride	–	49.4
Filtrate of the benzylation reaction + distilled water	–	1.94×10^3
Sample of benzylated olive residue	30%	–

Figure 2 Effect of the benzylation of the olive residue on elongation at break of composites.

untreated olive residue composites was examined. Figures 2 and 3 show the histograms of elongation and strength at break of virgin PVC and PVC/olive residue flour composites before and after treatment, respectively. Generally, the incorporation of untreated olive residue results in a very similar trend of decrease in both elongation and strength at break. In terms of tensile properties, the decrease of elongation and strength at break was probably caused by a number of factors, including moisture pick-up, poor dispersion of olive residue in the matrix and increase of interfacial defects in debonding between polymer and olive residue. The results obtained were in a good correlation with those found by Sombatsompop et al. with the samples of PVC/sawdust composites.[25] The tensile properties of highly viscous thermoplastics, rubber materials, or plasticized PVC depend on several factors, such as dispersion of fiber, increase in stress concentration at fiber ends and amount of air retained in the composite during mixing.[18] However, it can be noticed an increase in both elongation and strength at break for the composite samples prepared with the modified fillers with benzyl chloride. It was found a value of elongation at break of almost 141% for the F25 and 166% for the F25B. The improvement of both elongation and strength at beak of benzylated composites is due to the thermoplastic character of the benzylated of olive residue flour and consequently the
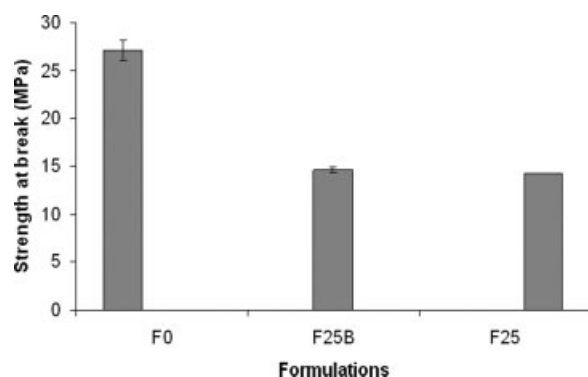

Figure 3 Effect of the benzylation of the olive residue on strength at break of composites.
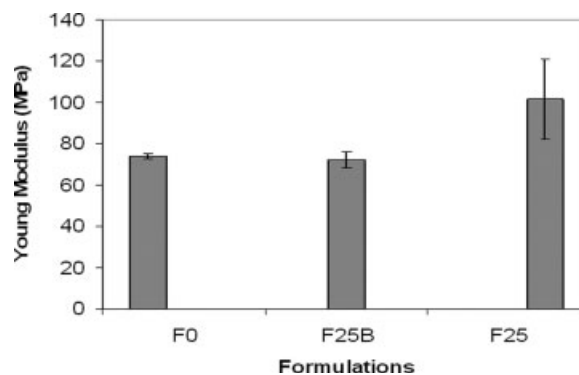
Figure 4 Effect of the benzylation of the olive residue on Young's Modulus of composites.

good interfacial adhesion matrix/filler. Figure 4 illustrates the effect of the benzylation of the olive residue on the Young's modulus of various composites.

It can be noticed that the Young modulus is influenced by the addition of olive residue and benzylation. The incorporation of 25% wt of untreated olive residue in the PVC matrix increase the Young modulus by 40%, it provides to the composite higher rigidity because of the rigid filler character. On the other hand, the addition of 25% wt of olive residue treated by benzyl chloride, no change in the modulus was observed when compared with that of unloaded PVC matrix. Generally, the tensile test shows clearly that the olive residue flour has undergone a plasticization after treatment with benzyl chloride as reported by many authors. The olive residue flour has been converted into a thermoplastic material after benzylation and acquired thermoforming ability leading to improvement in the mechanical properties of the composites compared with the untreated ones.

Hardness property. Figure 5 shows the effect of olive residue flour on the hardness of the different com-
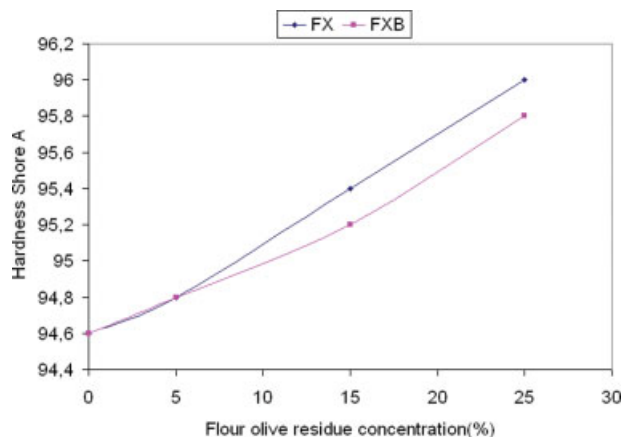

Figure 5 Effect of the benzylation of the olive residue on hardness shore A of composites. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
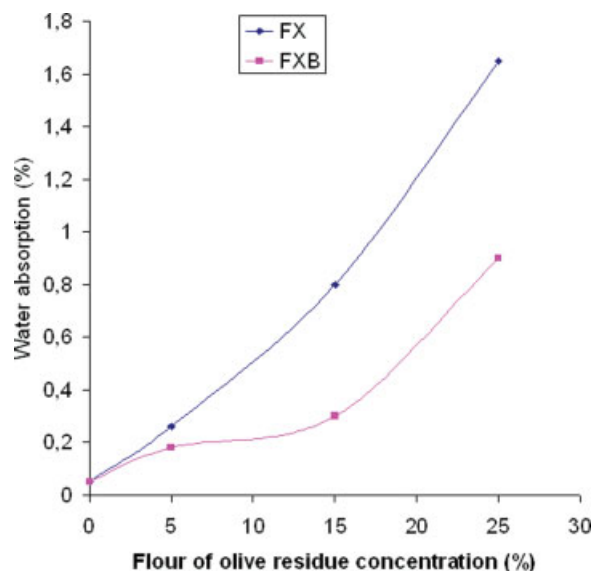
Figure 6 Water absorption of different composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

posite samples. It is noticed a light increase in hardness with incorporation of the flour, and the variation becomes increasingly important when the load factor increases. Hardness passes from 94 for F0 to 96 for the F25. For the composites manufactured with the benzylated olive residue flour, the hardness was slightly lower than those manufactured with the untreated olive residue flour. The benzylation causes the plasticization, which decreases the rigidity of material.

Water absorption. In this section, results of water absorption testing for virgin PVC and different PVC/olive residue flour composite samples are described.

To minimize the errors of experiments on such uneven surfaces, the presence of microvoids on the surface, nondistribution of olive residue flour in the
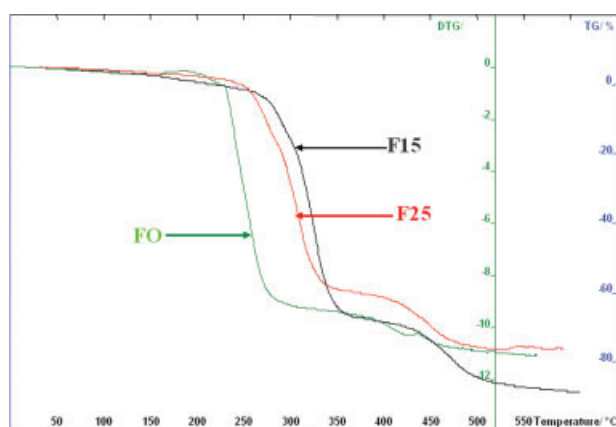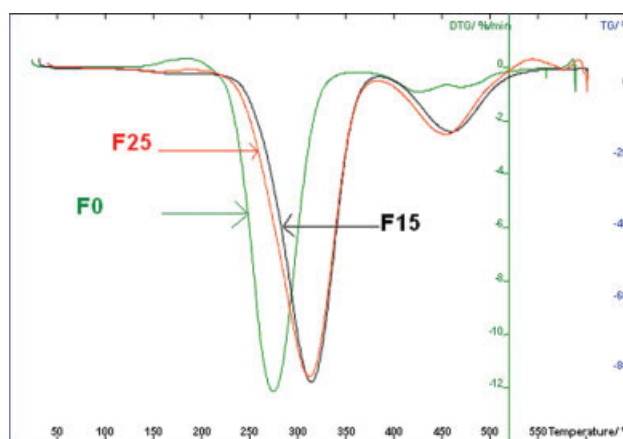

Figure 8 Thermograms DTG of the untreated composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composite samples and balance error, we have used five specimens for each formulation.

The graph in Figure 6 illustrates the amount of water absorption in different samples of the PVC/olive residue flour composites. We can clearly see an increase in the water absorption rate with the increase in olive residue flour quantity. However, water absorption was greatly reduced to about 50% for composites made of benzylated olive residue flour. The benzylation generates a new protection for the particle surface. With this treatment the filler with hydrophilic character changes and becomes hydrophobic.

Thermal properties

The different composites were subjected to thermogravimetric analysis in argon atmosphere to understand their thermal behavior. TG and DTG thermograms are shown in Figures 7–10 and the values of onset degradation temperature, mass loss in the first
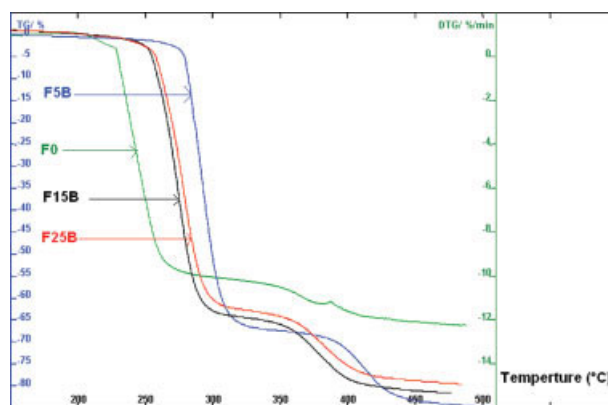

Figure 7 Thermograms TG of the untreated composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 9 Thermograms TG of the benzylated composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
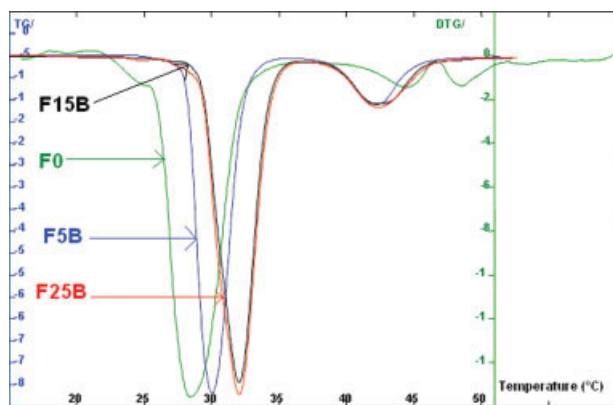
Figure 10 Thermograms DTG of the benzylated composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

stage of decomposition . . ., are deduced from the various thermograms and summarized in Table III. In the decomposition temperature range, the DTG thermogram exhibits two decomposition peaks. The first DTG peak, which appears at approximately 279–315°C function of the rate and the nature of the filler (untreated or benzylated) is attributed to the release of HCl for the F0 sample due to the thermal degradation of PVC, and both the release of HCl and the hemicellulose degradation for the composites samples. The second peak with approximately 429°C for F0 and 455°C for the composites. This second peak is due to the thermal decomposition of the poly(acetylene) for F0 and cellulose plus poly(acetylene) for the composites. The results show clearly that the incorporation of the treated OFR or the untreated one in the matrix PVC permits a gain in the onset temperature of the decomposition. In other words, the sample of the loaded PVC present a onset temperature of decomposition higher than that of F0, this is verified for the samples loaded with the virgin or the treated olive residue flour. For example, a gain of 47°C is recorded by the F5B and 14°C by F25B. Moreover, the effect of the chemical treatment on the onset temperature of the decomposition, a gain of 12°C is recorded by F25B in comparison to

F25 sample. Concerning the temperature at which the sample decomposes to 50%, it can be noticed that it changes slightly with the rate of olive residue flour (300–310°C), and it is higher than that of the sample F0 (290°C) and the treatment has almost no effect on this temperature. Concerning the weight loss recorded in the first stage of the decomposition, we can clearly see that the treated sample has almost the same rate of weight loss and lower than the sample of reference F0. This result is expected considering the treated samples, which have undergone an extraction of hemicellulose that is degraded thermally at this temperature range. On the other hand, the samples loaded with the virgin olive residue flour present a loss of weigh clearly superior to that of F0, which can be explained by the degradation of hemicellulose and PVC at this temperature range. The rate of residue has undergone a drastic decrease for the untreated samples (6–7% of residue), on the other hand, it varies less for the treated samples in comparison with F0 (20–27%). This result is in a good correlation with those obtained during the analysis of chemical composition of the different samples showing an increase in the rate of the mineral substances with the chemical treatment.

Study of thermal degradation by color change test

The color change during heat exposition of PVC composite is a sign of thermal degradation, it occurs at the time of the hydrochloric acid release giving rise to double bonds groups along the macromolecular chain resulting in color change. The samples are transparent for virgin PVC and become yellow and red for the degraded samples. At the last stage of thermal degradation the samples become dark. The test was carried out in an oven regulated at 175°C. The samples were periodically taken each 40–80 min. The maximum exposition time was 260 min.

The photographs on Figure 11 confirm the results already obtained in the thermal test of stability (TG-DTG), which shows that the F5B is the best formulation. Indeed, the color of this sample is almost the

TABLE III
TG-DTG Results of Different Formulations

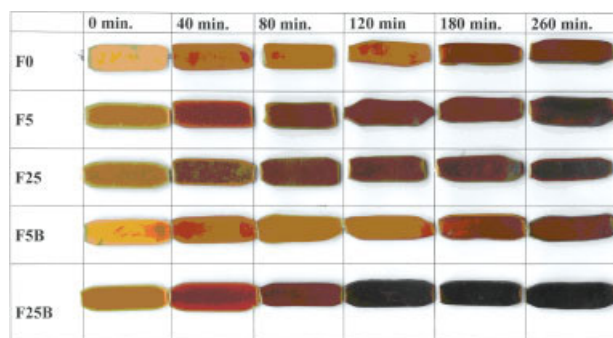| Sample	On set degradation temperature (°C)	Temperature at 50% of mass loss (°C)	Maximal rate of the first stage of decomposition (%/min)	Maximal rate of the second stage of decomposition (%/min)	Mass loss in the first stage of decomposition (%)	Mass loss in the second stage of decomposition (%)	Residue (%)
F0	239.18	290	279.44	429.27	63.90	8.36	27.74
F5B	286.90	300	286.90	460.34	65.12	14.64	20.24
F15	255.00	305	309.68	455.58	75.64	17.53	6.83
F15B	255.20	300.55	315	454.03	63.57	14.29	22.14
F25	241.01	310	307.64	450.34	73.59	19.33	7.08
F25B	253.85	310	299.95	450.99	63.70	13.96	22.34

Figure 11 Photography of the composites samples and the color change during the thermal degradation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

same one as that of F0 during all the period of the exposure. By comparing the colors of PVC/virgin olive residue flour samples and PVC/benzylated olive residue, in both cases we can note that the colors become increasingly dark with the increasing of the concentration of the olive residue in the composite. For a fixed rate of the olive residue, we can notice that the treated samples are more thermally stable than the untreated samples for the exposure times not exceeding 80 min beyond, the phenomenon is reversed.

CONCLUSION

The present work has allowed us to elaborate by calendaring and compression molding, the composite materials, by associating thermoplastic resin ''PVC'' and natural olive residue. On the other hand, we can make the evidence of the importance of the previous treatment of the olive residue with benzyl chloride and its role in improving some physicochemical and thermal properties of composite material.

The effects of addition of benzylated and virgin olive residue on the properties of the composite have been studied. The results obtained have permitted us to conclude that the treatment of olive residue with benzyl chloride is realized by etherification reaction demonstrated by several methods: conductimetric, gravimetric, physicochemical characterization of the treated and untreated flour and FTIR spectroscopy.

The PVC absorbs less water when compared with the composites of PVC/olive residue. The hardness of PVC is increased with the addition of untreated olive residue. The hardness of composite PVC/ untreated olive residue is higher than that of PVC/ benzylated olive residue. The thermal characterization carried out by the measurement of the time of thermal stability, test of color changing and the thermogravimetric show an improvement in temperature of the onset of decomposition and the degradation for the composites.

The mechanic characterization by tensile test shows that the Young's modulus has increased with the incorporation of untreated olive residue in PVC matrix. The strength and elongation at break have undergone a decrease for the PVC/untreated olive residue and PVC/benzylated olive residue composite comparing to virgin PVC, but it is more pronounced for the untreated olive residue.

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