Physical and Mechanical Properties of Polymer Composite Materials Based on Olive Husk Flour

Amar Boukerrou*, Dalila Hammiche, Djidjelli Hocine and Hassina Aouat

Laboratory of Advanced Polymer Materials, Department of Process Engineering, University Abderrahmane Mira, Route de Targa-Ouzemmour, Bejaia 06000, Algeria

Received July 16, 2014; Accepted November 2, 2014

ABSTRACT: The lack of compatibility between cellulose fibers and some polymers, such as thermoplastics, is due on one hand to the hydrophilic nature of the vegetable fibers and on the other hand to the hydrophobic character of the matrix. This incompatibility induces bad dispersion of the fibers and the formation of a heterogeneous material with mechanical properties which are not very satisfactory. The scope of this article is to describe the possibility of using Olive Husk Flour (OHF) as reinforcement in the elaboration of a composite material based on polyvinyl chloride (PVC). In this context, we used the PVC-g-MA as compatibilizer and investigated the effect of the loading and the effect of treatment on the mechanical properties and thermal behavior of these composites; the structures have also been characterized by scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD).

KEYWORDS: Composites, polyvinyl chloride, mechanical characterization, compatibilizer

1 INTRODUCTION

Advanced technology in petrochemical-based polymers has brought many benefits to mankind. However, it has become evident that the ecosystem is being disturbed because of non-biodegradable plastic materials [1]. Currently, there is considerable interest in natural fiber, which can be used as filler in traditional plastics, thus reducing the pollution caused by plastic wastes [2].

Polymer composites based on natural fibers (vegetal fibers, cellulosic and derivatives) are attracting great attention as alternative materials to glass or synthetic fiber-reinforced plastics. Fiber-reinforced polymers offer additional options over other conventional materials when specific properties are required and find applications in diverse fields [2]. The development of vegetal fiber-reinforced composites is a growing sector for many applications, mostly for automotive, appliance and packaging products [2–4].

Natural fiber exhibits a number of attractive advantages including low density, low cost, low requirements on processing equipment, less abrasion during processing, abundance, renewabality and certainly biodegradability [2,5,6].

The matrix filler interface plays a critical role in ensuring that the properties of each component contribute optimally to the bulk properties of the final product [7], so the first question is how to apply standard testing methods developed for homogeneous materials to composites, which are naturally heterogeneous [8]. However, certain drawbacks, such as poor compatibility with the hydrophobic polymer matrix, the tendency to form aggregates during processing and their low resistance to moisture, greatly reduce the potential of natural fibers to be used as reinforcement for polymers.

In order to improve the interfacial interactions between polymer and fibers, surface modification of the fibers and/or polymer functionalization, as well as addition of compatibilizers, are required [2,5,9]. Polymer modification with reactive molecules (such as anhydrides, epoxides, amines, etc.) is a largely explored way to enhance interfacial adhesion [10–12].

Many recent studies have investigated the incorporation of vegetal fiber into thermoplastic matrix. Hammiche *et al.* [13] investigated a composite based on hydrophobic polymeric matrix (PVC) and hydrophilic alfa fiber and have shown the interesting synthesis and the addition of a new compatibilizer PVC-g-MA on this composite; they confirmed that the choice of the compatibilizer must be made according to the matrix and to the application aim of the composite material.

Corresponding author: aboukerrou@yahoo.fr

DOI: 10.7569/JRM.2014.634119

Boukerrou *et al.* [14] studied the effect of PP-g-MA as coupling agent on the physico-mechanical and thermal properties of polypropylene (PP)/Olive husk flour (OHF) composites and they concluded that the treatment contributed to the improvement of the interfacial properties of PP/OHF.

In this work an attempt has been made to prepare an organic composite based on a thermoplastic matrix (PVC) and a load lignocellulosic (OHF). Our prepared material has been characterized through techniques, namely SEM, TGA and XRD, to ascertain the impact on structural, mechanical and thermal properties. As an extension of the same work, various other properties like tensile strength, elongation and morphology studies have been done.

2 EXPERIMENTAL

2.1 Materials

All the PVC/OHF formulations used in this work were based on PVC type SE-1200 provided by CABEL "Cablerie Electrique" located in Algiers (Algeria). The polymer has the following physical characteristics: Kwert (parameter that characterizes the viscosity of a material), 70.2–72.0; powder density, 0.521. The additives used in the preparation of the various formulations were dioctyl phthalate as a plasticizer, a thermal stabilizer system based on Ca/ Zn, and stearic acid as a lubricant. The olive husk (OHF) of a granular form was obtained from the olive treatment plant in the region of Bejaia (Algeria). The grafted PVC was synthesized in the laboratory and we have followed the procedure described earlier by Hammiche *et al*. [13].

2.2 Preparation of the Composites

The polyvinyl chloride resin, stearic acid and the stabilizer (Ca/Zn) were introduced into the chamber of a turbo mixer type TG6HK8. The temperature of the mixture was increased by friction and then we added the plasticizer (DOP). The mixture was allowed to cool. The compound obtained, called dry blending, was used for the preparation of the various formulations. PVC compounds/OHF was prepared in a SCUYER type A80 brand calender. The temperature of the two cylinders was maintained at 140°C. We incorporated load HFO at different concentrations with and without the compatibilizer. These formulations have been used in compression molding for the preparation of the plates. The formulations obtained by calendering were introduced between the plates of a FONTJINE model TP400 brand press, under a pressure of 300 KN and at a temperature of 170°C for 5 min. The plates obtained with dimensions of 300 × 300 × 2 mm^3 were cooled to room temperature. The proportions of each component in the formulations are presented in Table 1.

Table 1 The detailed composition of different samples

Formulations	PVC(g)	OHF (g)	PVC-g-MA
F_1	100	–	–
F_2	90	10	–
F_3	80	20	–
F_4	70	30	
F_5	85	10	5
F_6	75	20	5
F_7	65	30	5

2.3 Techniques

Mechanical tests were carried out according to NFC 32-200 specifications; five specimens from each composition were tested in an Instron (model ZWICK TYPE BTC-FR 2.5TN.D09), operating at a grip separation speed of 10 mm/min.

Observations in the cross-sections of the specimens took place with the use of a FEI CONTA 200 electron microscope. The compression molded sheet was cryogenically fractured in liquid nitrogen.

The thermograms of our various samples were recorded using a Setaram TGA 92 type of thermogravimetric device, controlled by a microcomputer. A mass of 10 to 20 mg was placed in a platinum crucible. The mass loss was measured using a thermobalance in an inert nitrogen atmosphere with a temperature range between 20 and 700°C and heating rate of 20°C/min.

Measurements of X-ray diffraction (XRD) were performed using Cu-K line wavelength $\lambda = 1.54059$ A°. The source of X-ray tube was a ceramic with a copper anode and was fed by a current of 45 kV and an intensity of 30 mA. Each scan was performed with a measurement time of 6.05 seconds per step. The range of angles swept was between 1° and 70°.

3 RESULTS AND DISCUSSION

3.1 Tensile Strength

The tensile test is an intrinsic property which reflects the resistance of a material. Unfortunately, this test for brittle materials like composites is extremely delicate, which leads to a large dispersion of results.

Figure 1 shows the variation of tensile strength as a function of load rate with and without PVC-g-MA. We recorded the highest value with virgin PVC (29.17

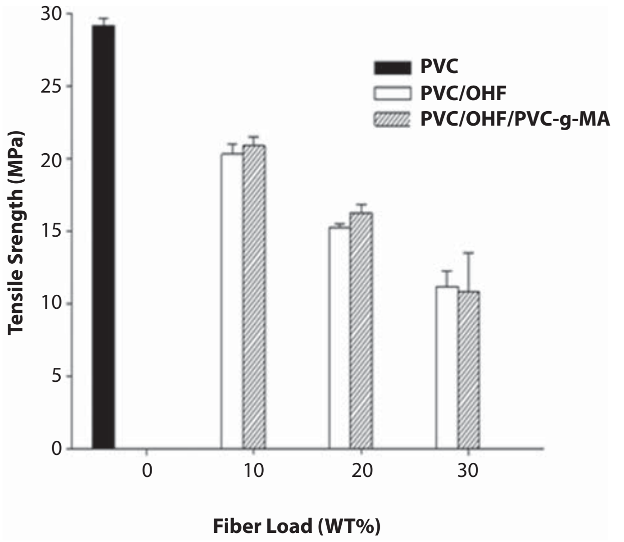

Figure 1 Effect of the load rate and PVC-g-MA on the Tensile strength.

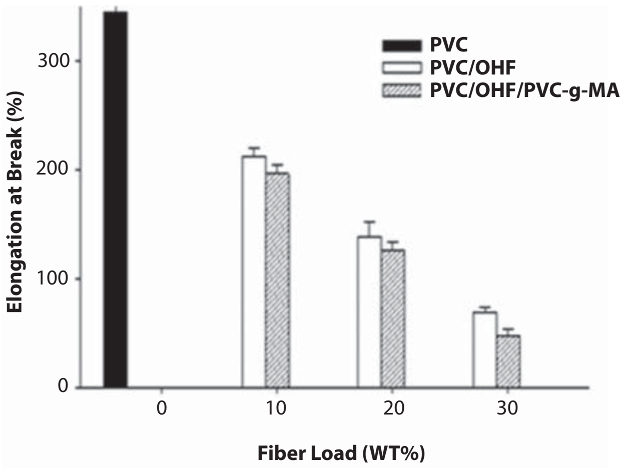

Figure 2 Effect of the load rate and PVC-g-MA on the elongation.

MPa) due to its high rigidity; this value decreases by incorporation of OHF in the matrix. The value of the tensile strength increases slightly with treated composites compared to untreated ones, which may be due to a high sensitivity to internal defects or small microfiber of composite. With the load rate of 30%, the values are close but with a slight increase in the untreated composite, which can be explained by the fact that the addition of low concentration of filler in the matrix causes good dispersion; but in high concentrations, the particles occupy volume, which is more important, easily weakening the composites [13].

According to Neher *et al.* [14], the tensile strength depends on a number of factors: fiber loading, matrix strength, fiber adhesion between fiber and matrix, orientation of fiber, etc. Seung-Hwan *et al.* [15] showed that the tensile strength gradually decreased with the increase of fiber content. This may be due to poor interfacial adhesion between polymer matrix and fiber. This is a general phenomenon in incompatible composites with different characteristics, such as hydrophobicity of the polymer matrix and hydrophilicity of the filler.

3.2 Elongation at Break

Elongation is a characteristic without dimension of composites. It corresponds to the deformation of the useful area reached during the break and characterizes the maximum elongation that can withstand a specimen before break.

The histograms in Figure 2 illustrate the evolution of elongation at break as a function of load rate and PVC-g-MA added as coupling agent. The PVC with plasticizer added becomes ductile, which increases the elongation before it is broken. This elongation decreases with increasing load rate because the OHF causes certain fragility in composite [16–18]. It has been reported that elongation at break decreases with increasing fiber content. This may be due to the increase in the discontinuity of the polymer matrix with the increase in the dispersed phase [19].

The elongation is more reduced with the addition of the compatibilizer; it causes a loss in deformation compared to untreated composites, and this decrease may be due to the addition of the coupling agent which confers rigidity to the composite material.

3.3 Young's Modulus

The modulus of elasticity, or Young's modulus, characterizes the rigidity of a material: the higher it is, the more rigid it is. The modulus of elasticity gives a good appreciation of the behavior of a material under stress. It measures at what force the material will be deformed [20]. The evolution of Young's modulus as a function of load rate of treated and untreated composites is shown in Figure 3. Differences in the values of modulus were observed between samples of untreated and treated composites of the same load rate, and the highest values were recorded with highly-loaded treated composites (368.69 MPa). Also, this figure clearly shows the increase of Young's modulus by incorporation into the OHF. This increase in the Young modulus indicates that the regidity of the composites increased.

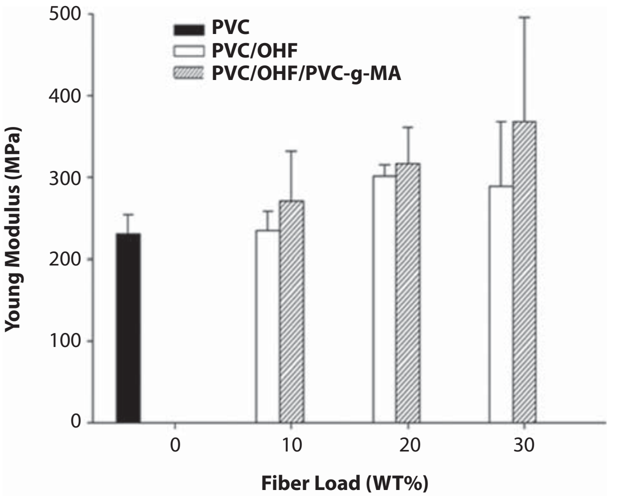

Figure 3 Effect of the load rate and PVC-g-MA on the Young's modulus.

3.4 Scanning Electron Microscopy (SEM)

Figures 4 and 5 show the images obtained by scanning electron microscopy of the composite having a load rate of 20% with and without coupling agent and untreated composites of 20% and 30% load rate.

For the same load rate, the images show the effect of the introduction of compatibilizer on the interfacial adhesion between the reinforcement and the polymer matrix.

Figure 4 clearly shows that the adhesion between the lignocellulosic fibers and the polymer matrix is low; this may be explained by the absence of physical contact between the two components. The appearance of cracks and agglomerates were also observed by us.

The low polarity thermoplastic matrix and high surface energy of cellulosic fibers are responsible for the lack of compatibility and lack of contact between the matrix and the reinforcement.

To the contrary, for treated composites in which the compatibilizer has been introduced, SEM analyses show that this agent improves the adhesion between the polymer matrix and OHF (Figure 4b).

Based on these observations by SEM, it is expected to obtain better mechanical properties for composites in which the coupling agent is introduced; moreover, the test results are confirmed by pulling these images

Figure 5 shows the effect of load rate of OHF on the interfacial adhesion fiber/matrix; we noted that the surface roughness increases as a function of load rate with a tendency to create more aggregates. These aggregates cannot be formed if there is a bad affinity between the polymer matrix and the OHF.

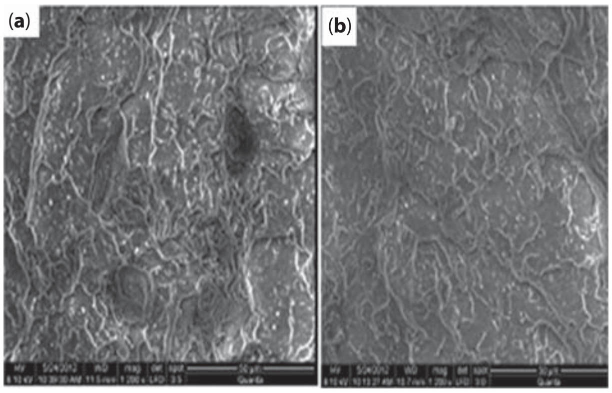

Figure 4 Images from scanning electron microscopy of composites to 20% of the load rate without (a) and with (b) compatibilizer.

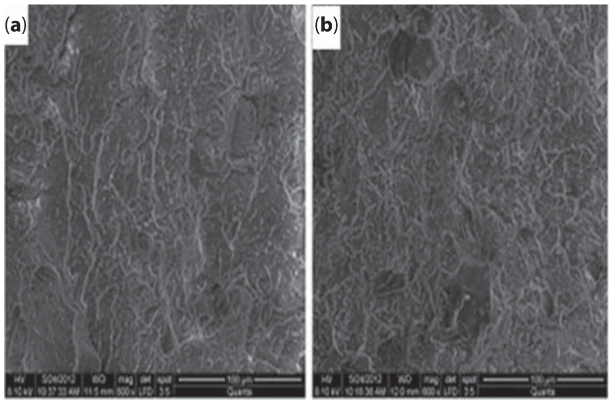

Figure 5 Images from scanning electron microscopy of composites untreated to 20% (a) and 30% (c) of load rate.

3.5 Thermogravimetric Analysis

Thermogravimetric analysis follows the evolution for the mass of a sample as a function of temperature and the parameters of the decomposition of a material.

The decomposition of the PVC was done in two steps (Figure 6); the first step begins at 206°C and ends at 310.9°C with a maximum temperature of degradation of about 270°C. During this step, we recorded a weight loss of 60.49%, which is attributed to the elimination of HCl and the formation of the double bonds along the macromolecular chains of PVC. This yields a new, thermally stable polymer (with polyene sequences) that forms in the temperature range from 310°C to 372°C. The second stage of degradation ranges from 372°C and 509.2°C, during which the polyene degrades to form a residue made up of a carbonaceous residue which is stable beyond 510°C and which presents 11.11% by weight [21].

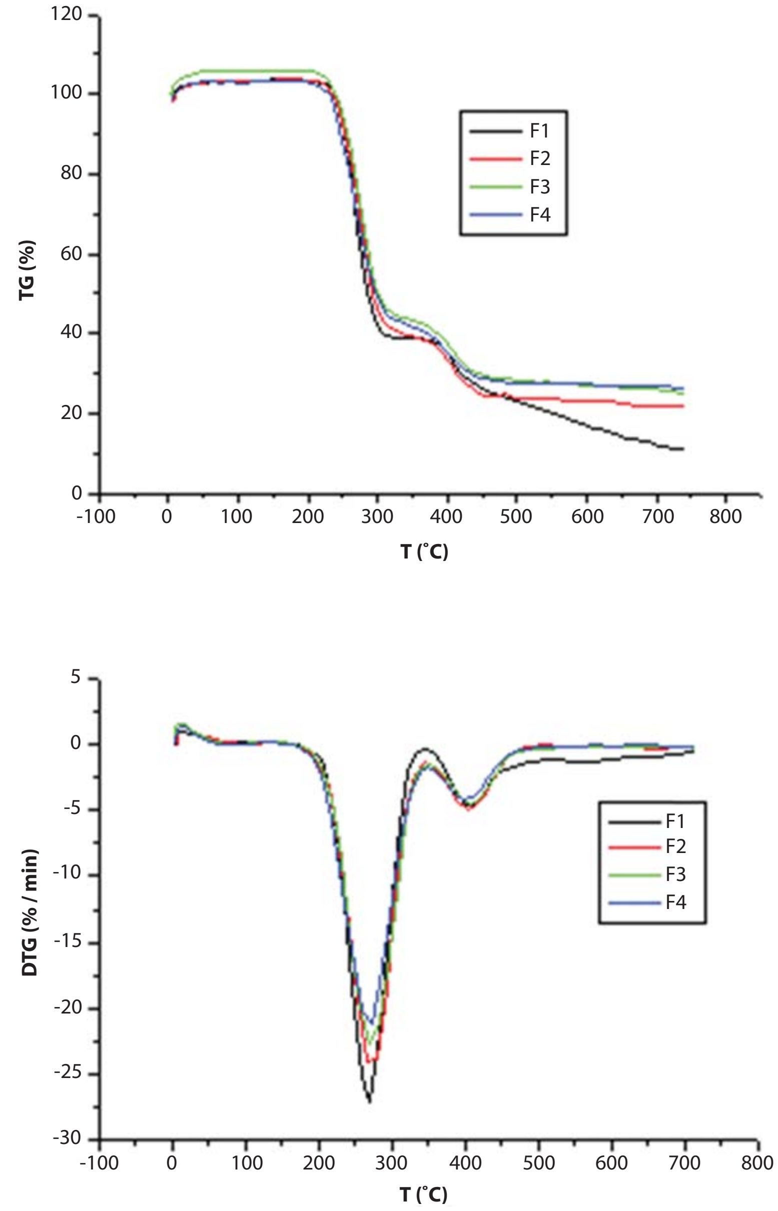

Figure 6 TGA/DTG thermograms of composites as a function of load rate without PVC-g-MA.

The TGA and DTG thermograms for PVC virgin and untreated composites with different load rates are shown in Figure 6. It is clear that the incorporation of fibers increased the overall thermal stability of PVC, which can be explained by the fact that the incorporation of fiber lignocellulosic retards the degradation of the polymer. In other words, it acts as an inhibitor of thermal degradation [16].

The composite has a thermal stability intermediate between that of the fiber and that of the matrix. This curve shows a decrease in the temperature at the beginning of decomposition and this decrease is continuous with an increasing load rate of OHF, which is 206°C for virgin PVC (F1), 186, 190 and 178°C for rates of F2, F3 and F4 respectively. This can be recorded by analyzing the peaks represented in Figure 7 in which there was a decrease in maximum degradation rates: 27, 24, 23, 21 (%/min) for formulations, F1, F2, F3 and F4 respectively.

For the formulation F3, we recorded a temperature of the beginning of decomposition higher than that of F2. This result can be explained [22] by the fact that, at the low load rate, the decomposition of the fiber appears only as a shoulder of low intensity and it must reach the levels of the order of 20% for a peak to be clearly observable. The examination of the major peak decomposition shows that the decomposition temperature is a maximum when the load rate is at

20% fiber. These differences are mainly due to reactions and complex interactions between the fiber and the matrix, which can cause polymer chain scission and thus affect the thermal stability.

The effect of treatment with the compatibilizer on the thermal behavior of composites is represented in Figure 7 (with a load rate of 20%).

It can be clearly observed that the incorporation of the compatibilizer has no apparent influence on the composite, also the the temperatures of beginning of decomposition and maximum degradation rates are very close before and after the addition of the compatibilizer.

3.6 X-ray Diffraction of Composites

In order to examine in more detail the influence of the load rate of fibers and the treatment with PVC-g-MA

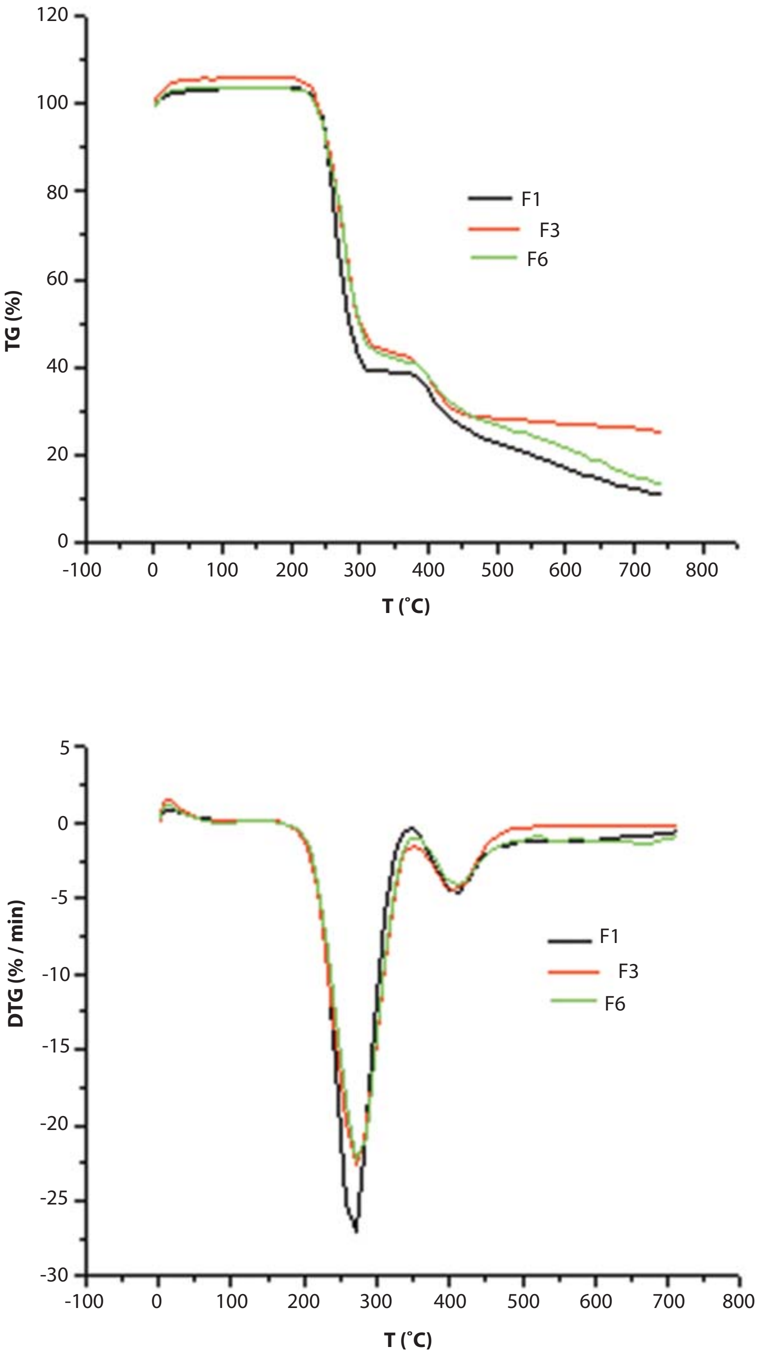

Figure 7 TGA/DTG thermograms of treated and untreated composites with load rate of 20%.

on the crystalline phases of the polymer, analyses by X-ray diffraction were performed.

Figure 8 presents the diffractogram of the virgin PVC and composite with different load rate (10, 20 and 30%):

- There is no sign of crystallinity in the virgin PVC because it is an amorphous view in the absence of peaks.
- The analysis by X-ray diffraction allows the observation of the crystalline structure of the composites. The diffractograms of the figure show two peaks [23]:
  - **(I)** Peaks of high intensity at 22° and 26° (θ 2) correspond to the plane (0 0 2), relating to the presence of the cellulose molecules; and
  - **(II)** Peaks of low intensity between 17° and 20° (θ 2) correspond to the plane (1 1 0), relating to the presence of lignin and hemicelluloses.
- The general appearance of the diffractograms is similar for all formulations. The same peaks appear but with much higher intensities, which can be attributed to reinforcements containing "the cellulose," which is crystalline.

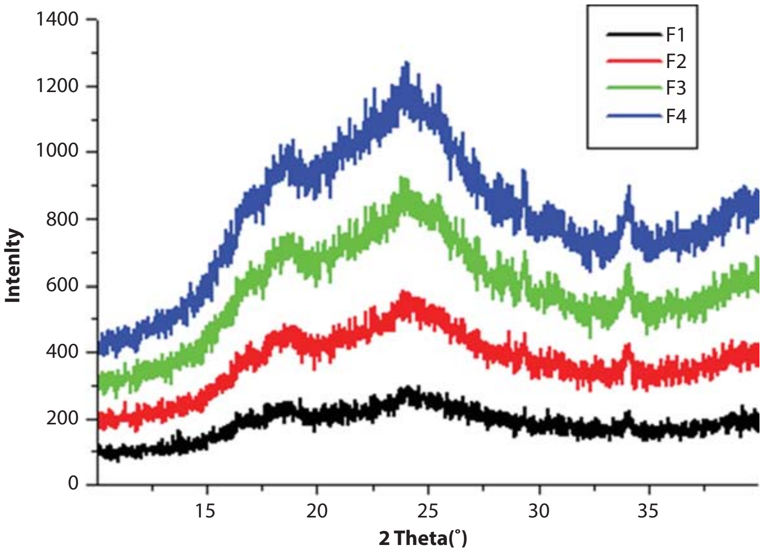

Figure 8 Diffractogramms of composites as a function of load rate.

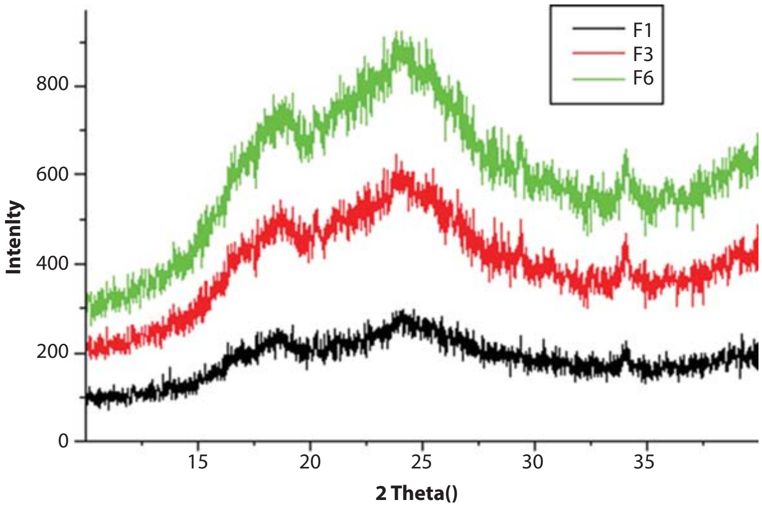

Figure 9 Diffractogrammes of treated and untreated composites with load rate of 20%.

Figure 9 illustrates the appearance of the diffraction peaks obtained by composites treated and untreated with load rate of 20%. When the composites are treated, the peaks are more intense, thus indicating that the compatibilizer caused a certain crystalline organization on the composite (nucleation agent).

4 CONCLUSION

This is an integrated work addressing the general problems associated with the development of innovative materials with limited environmental and health impacts. It is also a contribution to the search for solutions to remedy the lack of compatibility between the polymer matrixes, particularly PVC and reinforcement plants.

In this work, we have developed composites (PVC/OHF) with the incorporation of a compatibilizer (PVC-g-MA), and the materials were prepared by calendering.

After a review of the different experimental techniques for characterization, we have reached the following conclusions:

- Upon studying the mechanical behavior of PVC/OHF composites, an evaluation of their properties shows better behavior in the treated composite materials. This improvement is the result of higher interfacial adhesion fiber/matrix. The incorporation of fiber reinforcement allows the increase of rigidity in materials and the treatment allows for the obtainment of even higher mechanical properties (Young's modulus); on the other hand, the elongation at break decreases whatever load rate or treatment, which is due to the rigidity of the OHF in the PVC matrix.
- The thermal behavior of composite materials shows that the incorporation of fiber reinforcement has resulted in overall improvement. Treatment does not seem to be useful to the PVC/OHF interface. We have found that the thermal stability of polymer materials is very affected by the incorporation of fiber reinforcements, and that the compatibilizer PVC-g-MA does not affect the thermal stability of the composites.
- From a microstructural point of view, the overall degree of crystallinity was increased by the presence of fibers and the incorporation of the compatibilizer. It seems that the two factors, fiber rate and treatment, increase the degree of crystallinity of composites.

All this work shows that the fibers of Olive Husk Flour can be used successfully as "vegetable fiber" in a thermoplastic matrix PVC, and that the introduction of a compatibilizer (PVC-g-MA) results in an amelioration of the mechanical, physical, thermal and morphological properties.

ACKNOWLEDGMENTS

First and foremost we express our sincere thanks to CABEL Company "Cablerie Electrique" located in Algiers (Algeria) for supplying the PVC and additives used in this study. We extend our heartfelt thanks to all of our staff members who contributed to this work. We also thank all those who were directly involved or indirectly helped in the successful completion of this research work.

REFERENCES

1. S.S. Ray, K. Yamada, M. Okamoto, and K. Ueda, Control of biodegradability of polylactide via nanocomposite technology. *Macromol. Mater. Eng.* **288**, 203 (2003).
2. S.D. Nabi and J.P. Jog, Natural fiber polymer composites: A review. *Adv. Polym. Technol.* **18**, 351 (1999).
3. L. Yu, K. Dean, and L. Li, Polymer blends and composites from renewable resources. *Prog. Polym. Sci.* **31**, 576–602 (2006).
4. M. Pervaiz and M.M. Sain, Carbon storage potential in natural fibre composites. *Resour. Conserv. Recy.* **39**, 325 (2003).
5. A.K. Bledzki and J. Gassan, Composites reinforced with cellulose based fibres. *Prog. Polym. Sci.* **24**, 221 (1999).
6. S. Th. Georgopoulos, P.A. Tarantili, E. Avgerinos, A.G. Andreopoulos, and E.G. Koukios, Thermoplastic polymers reinforced with fibrous agricultural residues. *Polym. Degrad. Stab.* **90**, 303 (2005).
7. D. Maldas and B.V. Kokta, Current trends in the utilization of cellulosic materials in the polymer industry. *Trends. Polym. Sci.* **1**, 174 (1993).
8. D. Zhao and J. Botsis, Experimental and numerical studies in model composites, part I: Experimental results. Int. *J. Fract.* **82**, 153 (1996).
9. I.S. Wichman, A.B. Oladipo, and I. Hermann, The influence of moisture on fibre/matrix adhesion for wood/HDPE-composites, in *Proceedings of 9th Annual ASM/ESD Advanced Composites Conference, ESD*. The Engineering Society, pp. 265–276 (1993).
10. J. George, M.S. Sreekala, and S. Thomas, A review on interfacial modification and characterization of natural fiber reinforced plastic composites. *Polym. Engi. Sci.* **41**, 1471 (2001).
11. L.Y. Mwaicambo, E. Martuscelli, and M. Avella, Kapok/cotton fabric–polipropilene composites. *Polym. Test.* **19**, 905 (2000).
12. M.A. Lopez Machado, M. Arroyo, J. Biagiotti, and J.M. Kenny, Enhancement of mechanical properties and

interfacial adhesion of PP/EPDM/flax fiber composite using maleic anhydride as a compatibilizer. *J. Appl. Polym. Sci*. **90**, 2170 (2003).
13. D. Hammiche, A. Boukerrou, H. Djidjelli, M. Beztout, and S. Krim, Synthesis of a New Compatibilisant Agent PVC-g-MA and Its Use in the PVC/Alfa Composites. *J. Appl. Polym. Sci*. **124**, 4352 (2012).
14. B. Neher, M. Bhuiyan, H. Kabir, R. Qadir, A. Gafur, and F. Ahmed, Study of mechanical and physical properties of palm fiber reinforced acrylonitrile butadiene styrene composite. *Mater. Sci. Appl*. **5**, 39 (2014).
15. S.-H. Lee and S.Q. Wang, Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. *Composites: Part A* **37**, 80 (2006).
16. A. Boukerrou, S. Krim, H. Djidjelli, C. Ihamouchen, and J.J. Martinez, Study and characterization of composite materials based on polypropylene loaded with olive husk flour. *J. Appl. Polym. Sci*. **122**, 1382 (2011).
17. A. Karmarkar's, S.S. Chauhan, J.M.R. Modak, and M. Chanda, Mechanical properties of wood-fiber reinforced polypropylene composites: Effect of a novel compatibilizer with isocyanate functional group. *Compos. Part A-APPL.S*. **38**, 227 (2007).
18. H. Demir, U. Atikler, D. Balkose, and F. Tıhmınlıoglu, The effect of fiber surface treatments on the high tensile strength and water sorption properties of polypropylene-luffa fiber composites. *Part A-APPL.S*. **37**, 447 (2006).
19. I. Ahmad, D.R. Abu Bakar, and S.N. Mokhilas, Recyled PET for rice husk/polyester composites AJSTD, **22**, 345 (2005). http://eprints.utp.edu.my/3294/
20. J. Vreven, A. Raskin, J. Sabbagh, G. Vermeersch, and G. Leloup, Composite resins. Encycl Med Chir (Elsevier SAS, Paris), Dentistry, 23-065-E-10:1-21 (2005).
21. A. Boukerrou, M. Beztout, H. Djidjelli, S. Krim, and D. Hammiche, The effect of chemical treatment of cellulose with epoxidized soybean oil (ESO) on the properties PVC/cellulose composites. *Mol. Cryst. Liq. Cryst*. **556**, 223 (2012).
22. A. Nada and M. Hassan, Thermal behavior of cellulose and some cellulose derivatives. *Poly. Degrad. Stab*. **67**, 111 (2000).
23. V. Tserki, N.E. Zafeiropoulos, and F. Simon, A study of the effect of acetylation and propionylation surface treatments on natural fibers, *Composite Share A: Appl. Sci. Manuf*. **36**, 1110 (2005).