POLYSTYRENE/OLIVE STONE FLOUR COMPOSITES: EFFECTS OF FILLER CONTENTS ON MORPHOLOGICAL, THERMAL, AND WATER ABSORPTION PROPERTIES

LES COMPOSITES A BASE DE POLYSTYRENE /FARINE DE GRIGNON D'OLIVE: EFFET DU TAUX DE CHARGE SUR LES PROPRIETES MORPHOLOGIQUES, THERMIQUES ET D'ABSORPTION D'EAU

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ABSTRACT

In this study, the influence of the filler content of olive stone flour (OSF) reinforced polystyrene composites (PS) on the morphological, thermal and water absorption properties were investigated. The composite was prepared by melt-mixing method, followed by compression molding process. Different filler loadings were prepared; namely, 0%, 10%, and 30% weight percent. It found that the incorporation of olive stone flour with polystyrene matrix result a poor interfacial adhesion between them. In other hand the increasing of the OSF content decreased clearly the degradation temperature of these composites. However, the water absorption in these species increased with the addition of OSF.

KEYWORDS: Polystyrene, olive stone flour, morphological, thermal properties, water absorption.

RESUME

Cette étude porte sur l'influence du taux de charges dans des composites à base de polystyrène (PS) renforcés par de la farine de grignon d'olive sur les propriétés morphologiques, thermiques et d'absorption d'eau. Les composites sont préparés par un procédé de mélangeage à l'état fondu, suivi par le moulage par compression à différent taux de charge à savoir 0%, 10% et 30% en poids. On a constaté que l'incorporation de la farine de grignon d'olive dans le polystyrène donne une mauvaise adhérence interfaciale entre la matrice polymérique et la farine. En revanche, l'augmentation de la teneur en OSF a diminué la température de dégradation des composites. Cependant, l'absorption d'eau a augmenté avec l'ajout de OSF.

MOTS CLE: Polystyrène, farine de grignon d'olive, morphologie, propriétés thermique, absorption d'eau.

الملخص

يتمحور هذا البحث حول دراسة تأثير نسبة طحين ثفل الزيتون في مركبات البوليسترين على الخصائص المورفولوجية، الحرارية و امتصاص الماء. تم تحضير المركبات بطريقة المزج في وسط ذائب متبوع بالقولبة تحت الضغط بنسب مختلفة للمدعم: 0٪، 10٪، و 30٪ من الوزن. وجدنا أن إدماج طحين ثفل الزيتون مع البوليسترين يؤدي إلى ضعف التصاق بين سطح البوليمر والطحين و من ناحية أخرى زيادة نسبة المدعم يؤدي إلى انخفاض درجة حرارة تدهور المركب، في حين انه تزداد نسبة امتصاص الماء مع إضافة طحين ثفل الزيتون.

الكلمات الدالة: البوليسترين، طحين ثفل الزيتون، الخصائص المورفولوجية، الحرارية، امتصاص الماء.

1 INTRODUCTION

Polymeric materials are one of the most general and practical resources in the 21st century owing to a reasonable price, processability, and good material properties [1]. Polystyrene (PS), which is one of the most important thermoplastics, has now been manufactured industrially for some 80 years. Generally, PS can be polymerized through most polymerization methods, including free-radical and ionic polymerization, etc. Also, PS, as one of the general polymers, is inexpensive and easy to use in a wide range of industrial processes. Despite these advantages, PS is difficult to use in some special areas, such as engineering applications [2].

There are many approaches to improve the properties of polymer film [3], the use of agro waste materials as a source of fillers or reinforcements provides a renewable source, and could generate a non-food source of economic development for farming and rural areas [4]. Among these materials, natural fibers were widely used as fillers, such as Pine Needles fiber [5] and Saccharin Ciliate fiber [6] Olive pomace is an industrial by product of the olive oil production process, obtained by squeezing the olive pulp without any chemical treatment [7]. In Algeria, huge amounts of olive pomace are generated; it represents 105 tons per year, this amount of agro waste is usually burned [8].

The present work aims to elaborate composites based on polystyrene PS containing Olive stone flour (OSF) obtained by conventional blending. The composite properties in function of OSF filler contents were studied. The chemical compositions, the morphological, thermal, water absorption properties were investigated.

2 MATERIALS AND METHODS

2.1 Materials

The polymer matrix used in this study was polystyrene (PS), having a molar mass of 104.15g/mol and solubility parameter 15.6-21.1MPa heat capacity (0.04737KJ/Kmol at 100K). The additives used in the preparation of the various formulations were Di-Iso-Décyl-Phtalate (DIDP) as a plasticizer produced by ENIP SKIKDA, Algeria, with a viscosity ranging from 120 to 130MPa.s, a density of 0.965-0.975 g/cm^3, a thermal stabilizer system based on Ca-Zn type BAROPAN MC 9917 KA.

Olive stone flour (OSF) used as filler for polystyrene composites was obtained from the residues of olive oil. The olives were collected from the region of Ain Zaatot, Biskra located in the south of Algeria. It was firstly air-dried for two weeks and ground into very fine particles of spherical shape.

2.2 Compounding and Composite Processing

The composite materials PS/OSF were prepared by mixing the polymer matrix and the flour in a single screw extruder Plasti-Corder kind PLE 330 at a temperature of 160-190°C and a mixing rate of 40 rpm/min. Different composites PS/OSF flour were prepared; the untreated and treated OSF flour amounts added was 0, 10 and 30 wt% (Table 01).

The strips obtained by extrusion are introduced into the mold between two sheets of aluminum and compressed with a hydraulic press type Schwabenthan polystat 300S, with a temperature of 170°C under a pressure of 300bar during 10min. Preheating is performed until an initial melting of the mixture to avoid the presence of air bubbles, a degassing is performed before the application of the final pressure. Sheets of 2mm thick are obtained; they are then cut for different characterization tests.

Table 01: Formulation Codes of PS/OSF Composites Used

Components	Formulation		
	F0	F10	F30
PS (wt %)	100	90	70
OSF (wt %)	0	10	30

3 CHARACTERIZATION TECHNIQUES

3.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed with a Quanta FEG250 SEM microscope operating at 2-12 kV. The specimens were carried out under liquid nitrogen not only to impede the plastic deformation of the matrix but also to get well-defined fiber-matrix interface prior to analysis. They were coated with a 50-100µm layer of gold to avoid sample charging under the electron beam.

3.2 Thermal analysis

Thermogravimetric analysis (TGA) was performed to determine weight loss as a function of temperature using SDT Q600 instrument. A sample of initial mass of 5–30 mg was introduced into a platinum crucible, the sample mass (TGA) variation was then measured as a function of temperature (or time) under an inert nitrogen atmosphere from 50°C to 700°C, at a heating rate of 10°C/min.

3.3 Water-absorption

The samples were immersed in distilled water at room temperature, that is, 25°C. After specific time intervals, the samples were removed from water. Next, their surface moisture was removed by tissue paper, weighed in a high precision balance to find the amount of water taken up and, then, submerged again in water. Moisture absorption was determined by the weight gain relative to the dry weight of the samples. The moisture content of a sample was computed as follows:

$$(W_A)\% = \left(\frac{W_t - W_0}{W_0}\right) \times 100 \qquad (1)$$

Where W_0 and W_t denote the dry weight of the sample and the weight at any specific time t, respectively.

4 RESULTS AND DISCUSSIONS

4.1 Morphological analysis

The matrix of the virgin polystyrene (Fig.01.a) shows a very smooth and very homogeneous surface, whereas for the composites PS/OSF (Fig.01.b and Fig.01.c) a rough surface is observed, Irregular and heterogeneous as well as the presence of microvoids and cavities on the surface due to the deposition of the load of the PS matrix during the fracture. These microvoids become more accentuated as the rate of the load increases due to deformation Of the flour in the matrix, demonstrating the incompatibility of the two phases due to the poor interfacial adhesion and the difference in the energies (or polarities) of the free surface of the hydrophilic filler and of the hydrophobic polymer [9, 10].

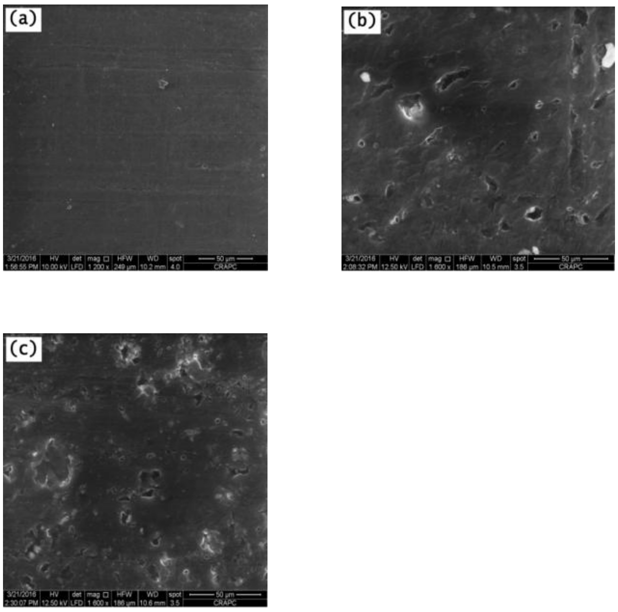

Figure 01: SEM micrographs of fracture surface of PS/OSF composites at various loading rates: (a): 0%, (b): 10 wt % and (c): 30% wt

4.2 Thermal analysis

From the thermograms (Fig.02), we observe that the thermal degradation of PS/OSF composites is similar. Indeed, we record only one stage of degradation for the polystyrene, unlike composites PS/OSF whose degradation is done in two decompositions due to the load of olive stone flour. Incorporation of the flour into the polymer matrix results in a decrease in the starting temperature of decomposition. It is 380°C for the virgin PS, 358.93°C, 329.16°C for composites at a loading rate of 10 and 30%, respectively. This decrease can be attributed to the presence of the three main constituents (cellulose, hemicellulose and lignin) of the flour, which is confirmed by Djefel et al. [11].

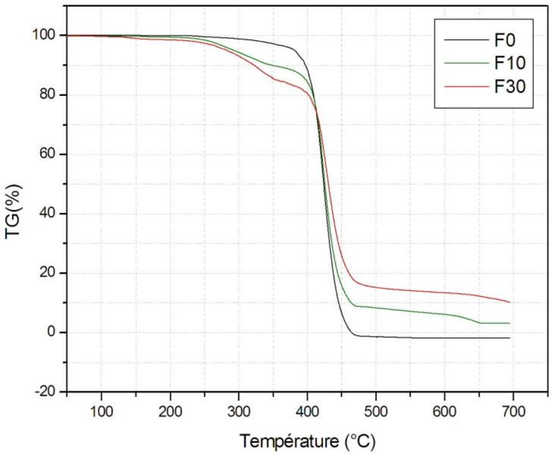

Figure 02: TGA thermograms of PS/OSF composites recorded at different loading rates, 0, 10, and 30wt %

Therefore, the thermal behavior of the composite is the sum of the individual behaviors of these two constituents (fiber and matrix). In the vicinity of 484°C, a stability step is recorded, attributed to the formation of a residue. These results are in agreement with the amounts of mineral substances incorporated in the lignocellulosic fibers. By way of example, there were recorded 3.052 and 10.16% residues for the F10 and F30 formulations respectively.

4.3 Water absorption

The water absorption evolution of the PS/OSF composites was monitored during immersion in distilled water for a period of 720 hours as shown in Fig.03. An increase in the rate of water absorption with the immersion time and the loading of olive stone flour in the polystyrene matrix can be clearly seen, which is quite expected, because the olive stone flour is rich in hydroxyl groups, forming hydrogen bonds with the water molecules, so the flour content is higher, the concentration of OH is the higher and the water absorption becomes more important. It is also noted that the rate of water absorption of PS/OSF samples is rapid and then decreases as time increases to saturation where the rate of water absorption becomes constant. For 10 and 30% formulations, the maximum swelling rates are estimated at 1.4227 and 8.2457%, respectively. For the virgin PS there is a very low water absorption due to the apolar nature of this polymer which gives it the hydrophobic character of about 0.0414% in 24 hours and does not exceed 0.1904% in 30 days, These values are confirmed by Boufi et al [12] and Pasquini et al [13].

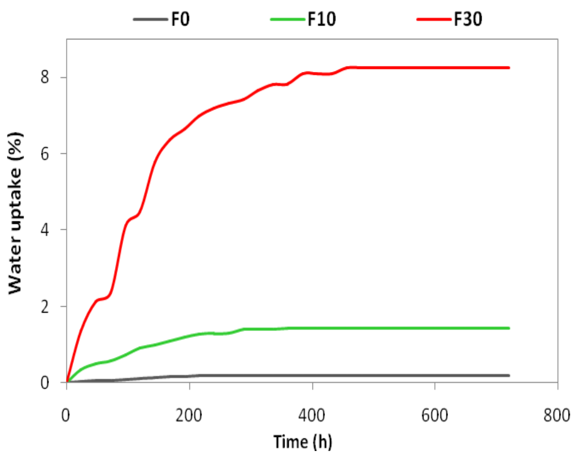

Figure 03: Water absorption of PS/OSF composites at different loading rates, 0, 10, and 30wt %

5 CONCLUSION

In the present work a composite material containing olive stone flour dispersed in PS matrix was manufactured and studied. The aim of this study was to investigate the effect of olive stone flour at different weight fractions on morphological, thermal, and water uptake properties of PS composite. The results indicate that the morphology of PS/OSF composites showed a rough morphology and many voids and cavities. This indicates poor interfacial adhesion that reveals the low affinity between the polymer matrix and the olive flour. Poor interfacial adhesion seems to facilitate debonding of the flour. TGA data showed that the incorporation of the olive stone flour into the PS matrix decreased the temperature of degradation. The percentage of moisture uptake increased as the weight percentage of flour increased due to the high cellulose content.

LIST OF ABBREVIATION

PS: Polystyrene.

OSF: Olive stone flour.

DIDP: Di-Iso-Décyl-Phtalate.

PS/OSF: Polystyrene / Olive stone flour composite.

TGA: Thermogravimetric analysis.

SEM: Scanning electron microscopy.

WA: The moisture content of a sample.

W0: Dry weight of the sample

Wt: Weight at any specific time t ,

REFERENCES

[1] J. T. Lee, M. W. Kim, Y. S. Song, T. J. Kang, J. R. Youn, Fibers and Polymers, 2010; 11: 60–66.

[2] S. Min Kwon, H. Sik Kim, D. Young Kim, Y. Soo Yun, H. Joon Jin, Journal of Applied Polymer Science, 2008, 110; 3737–3744.

[3] S. Hemsri, K. Grieco, A. D. Asandei, R. S. Parnas, Compos Part A Appl Sci Manuf, 2012; 43:1160–8.

[4] N. Kengkhetkit, T. Amornsakchai, Mater Des, 2014; 55:292–9.

[5] V. K. Thakur, A. Singha, Bull Mater Sci, 2010; 33:257–64.

[6] V. K. Thakur, M. K. Thakur, A. S. Singha, Int J Polym Anal Charact, 2013; 18:430-8.

[7] S. M. Cardoso, A. Silva, M. A. Coimbra, Carbohydr Res, 2002; 337; 917–24.

[8] M. Bengana, A. Bakhouche, J. Lozano-Sánchez, Y. Amir, A. Youyou, A. Segura-Carretero, Food Res Int, 2013; 54:1868–75.

[9] S. M. B. Nachtigall, G. S. Cerveira, S. M. L. Rosa, Polymer Testing, 2007; 26: 619–628.

[10] P. Antich, A. Vazquez, I. Mondragon, C. Bernal, Composites: Part A, 2006; 37: 139–150.

[11] D. Djefel, S. Makhlouf, S. Khedache, G. Lefebvre, L. Royon, International Journal of Scientific Research & Engineering Technology, 2015; 3: 1–4.

[12] S. Boufi, M. Abdelmouleh, M. N. Belgacem, A. Dufresne, Composites Science and Technology, 2007; 67: 1627–1639.

[13] D. Pasquini, E. M. Teixeira, A. A. Silva Curvelo, M. N. Belgacem, A. Dufresne, Composites Science and Technology, 2008; 68: 193–201.