ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

The Effect of Alkali Treatment on the Mechanical and Water Absorption Characteristics of Olive Stone Flour Reinforced Polystyrene Composites.

Hamida BOUSSEHEL[1], Ahmed MEGHEZZI[1], Nadia NEBBACHE[1], Samira MAOU[2*], Mohamed SLIMANI[1] , Amina LOUCIF**

[1] Laboratoire de Chimie Appliquée, Faculté des sciences exactes et des sciences de la nature et de la vie, Université de Biskra, B.P. 145, RP 07000 Biskra, Algérie.
[2]* Centre de recherche scientifique d'analyses physico-chimiques Bou-Ismail Tipaza, Algérie.
** Laboratoire de physico-chimie et des plastiques, Entreprise de l'industrie de la câblerie de Biskra, Algérie.

ABSTRACT

Natural fibers offer many advantages over synthetic fibers but the notable disadvantage of natural fibers is its hydrophilic nature. Due to this nature an incompatibility between the fiber and matrix exist which decreases the properties of the composite. This defect can be overcome by chemical modification of fiber surface so as to make it less hydrophilic. The objective of this study was to investigate the effects of olive stone flour content, alkali treatment with different concentration of NaOH (0%, 2%, and 4%) solution for 1 hour. The mechanical properties of olive stone fibre reinforced polystyrene composites were studied and compared. FTIR results showed that there is a partial removal of lignin and hemicelluloses after treatment which improved the interfacial adhesion matrix/fiber. Also, the alkaline treatment improved notably the tensile strength and increased the elongation at break of polystyrene / olive stone flour composites compared to those with untreated flour.
Keywords: Polystyrene, olive stone fiber, alkaline treatment, mechanical properties, water absorption.

Corresponding author

INTRODUCTION

The use of natural fibers as reinforced material in composite manufacturing was incredibly increased due to environmental awareness, depletion of non-renewable petroleum resource and growing demand on sustainable product development [1-3]. A tremendous number of publications over the past two decades have agreed that natural fibers give competent potential to be used as an alternate for glass or other's man made synthetic fiber reinforcement materials in composites [4-9].

However, one drawback that limits the potential use of bio-fillers as reinforcing agent is their hydrophilic nature which causes poor interfacial adhesion with the hydrophobic matrix, leading to poor mechanical properties of the composites [10-12]. Therefore, in order to process natural fiber reinforced composites with properties comparable to that of synthetic fiber reinforced composites, surface modifications of the fiber, matrix or both are required to improve the adhesion between the fiber and matrix [13].

Chemical pretreatment of the natural fibre can help to overcome such drawbacks to enhance the compatibility between fibre and the matrices, resulting in improved performance of fibre-reinforced composites [14]. Natural fibres have a good potential for chemical treatment due to presence of hydroxyl groups in lignin and cellulose. Reaction of hydroxyl groups can change the surface energy and the polarity of the natural fibres [15]. In pretreatment of natural fibre, either the hydroxyl groups get activated or new moieties are added that can effectively interlock with the matrix [16]. Different surface treatment methods such as mercerization (alkali treatment), isocyanate treatment, acrylation, benzoylation, latex coating, permanganate treatment, acetylation, silane treatment and peroxide treatment have been applied on the fibre to improve its strength, size and its shape and the fibre-matrix adhesion [17].

Alkali treatment of natural fibres is known to improve the stiffness, strength, and dynamic flexural modulus of the composites, indicating an increased interfacial bond strength and adhesion between the matrix and the fibres [18]. Alkaline processing directly influences the cellulosic fibril, the degree of polymerization and the extraction of lignin and hemicellulosic compounds [19]. Polystyrene is an aromatic polymer made from styrene, an aromatic monomer which is commercially manufactured from petroleum. Polystyrene is commonly injection moulded or extruded while expanded polystyrene is either extruded or moulded in a special process. Solid polystyrene is used in disposable cutlery, plastic models, CD, DVD cases, etc. Foamed polystyrene is mainly used for packaging materials, insulation, foam drink cups, etc. Polystyrene foams are good thermal insulators and therefore used as building insulation materials such as in structural insulated panel building systems. They are also used for non-weight-bearing architectural structures [20].

In this study, Alkali treated olive stone fibers were used at various weight ratios to evaluate the impact of added OSF on the mechanical proprieties and the moisture absorption of polystyrene composites.

MATERIALS AND METHODS

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 130 mPa.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 from the region of Biskra located in the south of Algeria. It was firstly air-dried for two weeks and ground into very fine particles of spherical shape. Chemicals used for olive stone fiber treatment include sodium hydroxide (NaOH, 98%) are from BIOCHEM-chemopharma (United Kingdom)

Treatment of Olive stone flour

The flour was treated with sodium hydroxide (NaOH) aqueous solution (2%, 4% w/v) for 1 hour at room temperature. The ratio of the fibers and the solution was 1:20 (w/v). Then, it was washed with distilled water until all the sodium hydroxide was eliminated, and the washing water pH was neutral. Subsequently, flour was dried at 80°C until constant weigh was found.

Compounding and 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 30 wt%.

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 in the form of dumb-bell and squares to serve in different characterization tests.

CHARACTERIZATION TECHNIQUES

Infrared spectroscopy

The spectrometer, FTIR-8400S Shimadzu, was used in the transmission mode with a resolution of $2cm^{-1}$ in the range of $4000–400cm^{-1}$. The samples were tested after being pressed with 2wt% of KBr to form a disc.

Tensile Test

The mechanical properties (tensile strength, elongation at break) of the composites obtained are measured using traction machine type Zwick / Roell, according to the standard ISO 527-1. For each type of composite, six samples are tested and used in calculating the average value.

Hardness

Shore D hardness of the samples was evaluated by using a hardness tester type Zwick/Roell. Samples were placed on a horizontal surface. Tester was kept in vertical position and pressed on the specimen so that the presser foot was parallel to specimen. Five readings at different points were noted, and average value is reported according to ISO 51-123T.

Moisture content

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:

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

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

RESULTS AND DISCUSSIONS

FTIR spectroscopy

Figure 1 shows the FTIR spectra of untreated and alkaline treated olive stone flour for different concentration of treatment at 25°C.

The intensity of 3430 and 1034 cm^{-1} peaks assigned to the stretching vibrations of hydroxyl groups of cellulose and C–O groups of hemicelluloses [21], respectively, decreased with the chemical treatment of the filler. In the untreated olive stone flour spectra, the absorption peak was observed at approximately 1746 cm^{-1}, corresponding to the C=O stretching of hemicellulose, but this peak was almost missing in the spectrum of the 2% and 4% NaOH treated fibers, indicating the elimination of hemicelluloses and lignin as a result of alkali treatment. The elimination of this peak was observed in a previous study [22- 24]. The peak at 1644 cm^{-1} in the untreated OSF flour is associated with the adsorbed water.

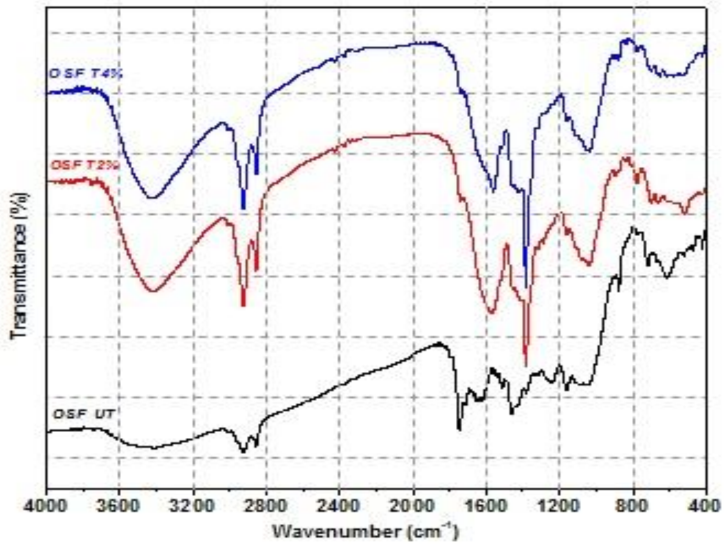

Figure 1: FTIR spectra of untreated (OSF UT), Alkali treated for different concentration of treatment (OSF T2%, OSF T4%).

The possible chemical reaction between the alkaline solution and the hydroxyl groups of the OSF flour is as follows:

$$\text{Fiber} - \text{OH} + \text{NaOH} \rightarrow \text{Fiber - O - Na} + H_2O \quad (2)$$

Weight Loss

Natural fiber contains mainly cellulose, hemicellulose, and lignin. Hemicellulose is a compound containing several molecules of sugar and substances which are soluble in water or in alkaline solution. Lignin is also soluble in alkaline solution. It is possible that some of the hemicellulose and lignin will dissolve during the treatment which will cause a decrease in the mass of OSF flour [25].

Figure 2 shows the effect of the treatment concentration on the percentage of weight loss of OSF flour.

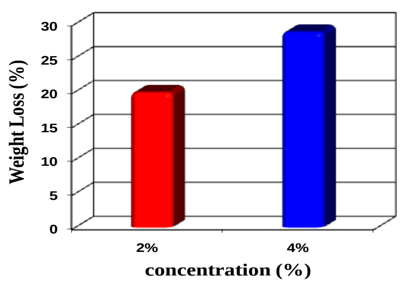

Figure 2: Effect of treatment concentration on percentage of weight loss flour.

The effect of alkali treatment on tensile test

Composites were prepared with olive stone fibers that were treated with varying concentrations of NaOH solution for 1 h. The variation of tensile strength with chemical treatment is given in Figure 3. It is seen that alkali treated composites show an increase in tensile strength as compared to untreated composites. Maximum tensile strength was shown by composite containing fibers treated with 4% NaOH. It has been reported that alkali treatment increases the roughness of fiber surface, hence increasing the surface area available for contact with the matrix [26, 27]. Because at high concentration there is delignification of natural fiber taking place and as a result damage of fiber surface [28, 29].

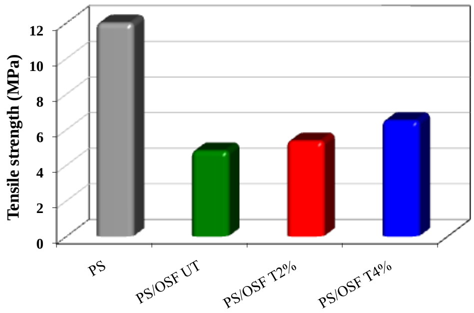

Figure 3: Effect of treatment concentration on the tensile strength of composites PS/OSF

Figure 4 show the elongation at break according to the content unmodified olive stone fibers (OSF UT) and modified olive stone fibers (OSF T). The elongations at break of treated fiber composites are higher than those containing untreated olive stone fibers. This is due to probably for mechanical interlocking between olive stone fiber treated by alkali treatment and PS [30].

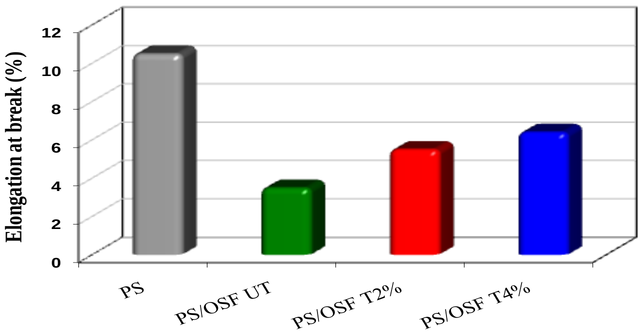

Figure 4: Effect of treatment concentration on the elongation at break of composites PS/OSF

The effect of alkali treatment on hardness properties

Figure 5 shows the hardness results of OSF/ PS composite. With alkali treatment of 2% and 4% NaOH the hardness value of composites decreased. The highest result of the hardness test, 99.0, derived from the untreated olive stone fibers composite, meanwhile for the modified olive stone fibers treated with 2% and 4% NaOH; the obtained results for the hardness test had lower values, 96.7 and 96.43. Contrary results were found by Siregar et al [31].

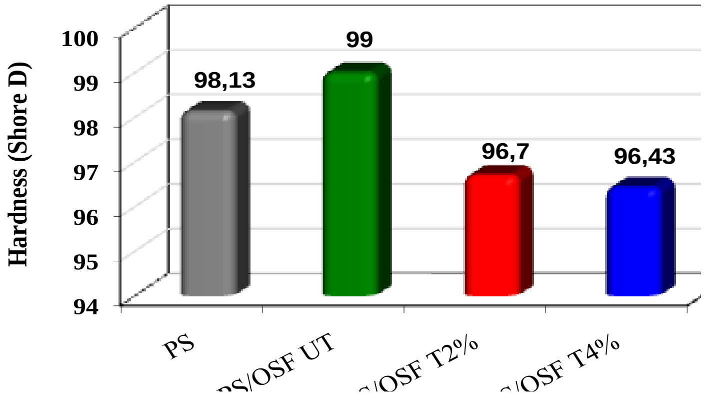

Figure 5: Effect of treatment concentration on the hardness of composites PS/OSF

Effect of the Treatment on Water Absorption Behavior of Composites

Figure 6 depicts the moisture content of the PS/OSF that had been subjected to several treatments after 5 days immersion. It can be seen that water absorption behaviour of the untreated and alkali-treated fiber, increased initially with time before reaching a maximum. It also shows that the percentage of water uptake stabilized with an immersion time. Where the water diffuses into the fibers until reaching a maximum absorption. When the immersion time becomes significant, a stabilize in the water absorption is due to the hydrophilic property of cellulosic fibers as more water molecules penetrate into the micro cracks present in these fibers, making the fibers swell [32,33].

The effect of alkali treatment on water absorption of olive stone fibers had improved the ability of olive stone fibers to absorb water. This improvement is likely due to the removal of the gummy and waxy substances from the raw fibers. As stated in the literature an alkali treatment results in the partial dissolution of hemicellulose [34]. Hemicellulose, however, is responsible for the water absorption of the fiber [32]. The alkali treatment leads to a partial removal of waxes and therefore an increased accessibility of the protanable surface functions. An increased number of 'polar' surface functionalities will increased the amount of water absorbed on the fibers [35, 36]. As observed for an alkalization 2%, 4% NaOH solutions leading the removal of all other hydrophobic compounds from the fibers, the fiber treated with 4% NaOH shown maximum water uptake. This means that swelling process was much faster leading to higher water uptake and also the alkali treatment had removed the protecting cell-fibers, thus increasing the water absorption [37].

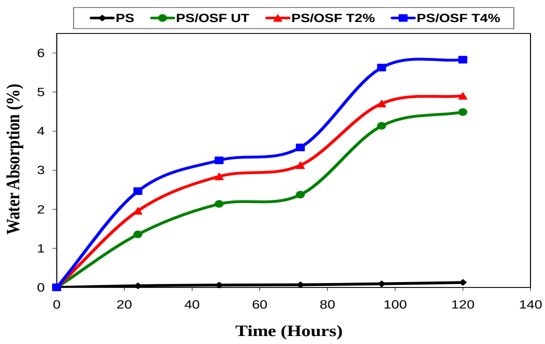

Figure 6: Effect of treatment concentration on water absorption of composites PS/OSF

CONCLUSION

This study explained mechanical properties of the OSF fiber- PS composites, before and after alkalization. Such fibers were immersed in various alkali concentrations for 1 h, then, they (constant weight ratio $(W = 30\%)$) were mixed with polystyrene. From the results explained above, some conclusions can be drawn as follows:

- The chemical treatment removes waxes and other non-cellulosic components to increase their compatibility with the PS matrix.
- The NaOH concentrations of 2% and 4% used to treat the fibre increased the value of all mechanical properties of composites such as tensile strength, elongation at break. The maximum improvement of the mechanical properties of olive stone fibre (OSF) reinforced polystyrene (PS) was obtained from the experiment of treated OSF with 4% NaOH.
- The adhesion of fibre/matrix can be improved by treating the OSF fibres with alkali solution before production of a composite.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the technical personnel of the Cable Industry Company of Biskra (ENICAB - Biskra. Algeria) where the samples were prepared and characterized.

REFERENCES

[1] Bledzki K, Gassan J. Progress in Polymer Science 1999; 24: 221-274.
[2] Dweib MA, Hu B, O'Donnell A, Shenton HW, Wool RP. Composite Structures 2004; 63: 147-157.
[3] Graupner N, Herrmann AS, Jörg M. Composites Part A: Applied Science and Manufacturing 2009; 40: 810-821.
[4] S.J. Eichhorn, C.A. Baillie, N. Zafeiropoulos, L.Y. Mwaikambo, M.P. Ansell, A. Dufresne, K.M. Entwistle, P.J. Herrera-Franco, G.C. Escamilla, Groom L, M. Hughes, C. Hill, Rials TG, Wild PM. J Materials Science 2001; 36: 2107-2131.
[5] Eichhorn SJ, Dufresne A, Aranguren M, Marcovich NE, Capadona JR, Rowan SJ, Weder C, Thielemans W, Roman M, Renneckar S, Gindl W, Veigel S, Keckes J, Yano H, Abe K, Nogi M, Nakagaito AN, Mangalam A, Simonsen J, Benight AS, Bismarck A, Berglund LA, Peijs T. J Materials Science 2010; 45: 1-33.
[6] Summerscales J, Dissanayake NPJ, Virk AS, Hall W. Composites Part A: Applied Science and Manufacturing 2010; 41: 1329-1335.
[7] Kalia S, Dufresne A, Cherian BM, Kaith BS, Avérous L, Njuguna J, Nassiopoulos E. International Journal of Polymer Science, 2011, 1–35.
[8] Ku H, Wang H, Pattarachaiyakoop N, M. Trada. Composites Part B: Engineering 2011; 42: 856-873.
[9] La Mantia FP, Morreale M. Composites Part A: Applied Science and Manufacturing 2011; 42: 579-588.
[10] Essabir H, El Achaby M, Hilali EM, Bouhfid R, Qaiss A. J Bionic Engineering 2015; 12: 129–141.
[11] Boujmal R, Essabir H, Nekhlaoui S, Bensalah MO, Bouhfid R, Qaiss A. J Biobased Materials and Bioenergy 2014; 8: 246–252.
[12] Fauzani MdS, Hassan A, Rosiyah Y, Azzahari AD. Composites: Part B 2014; 58: 259–266.
[13] Lu N, Oza S. Composites Part B: Engineering 2013; 44: 484-490.
[14] Beg M DH, Pickering KL. Proceedings of SPPM 2004; 240-247.
[15] Hetal S, Srinivasulu B, Subhas S. International Journal of Scientific Engineering and Technology 2012; 1: 86-90.
[16] Ganan P, Mondragon I. J Materials Science 2004; 39: 3121-3128.
[17] Luo S, Netravali AN. Polymer Composites 1999; 20: 367-378.
[18] Sharifah HA, Ansell MP. Composites: science and technology 2004; 64(9): 1219-1230.
[19] Jähn A, Schröder MW, Füting M, Schenzel K, Diepenbrock W. Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy 2002; 58: 2271-2279.
[20] Shinoj S, Visvanathan R, Panigrahi S, Kochubabu M. Industrial Crops and Products 2010; 33: 7–22.
[21] Barreto ACH, Rosa DS, Fechine PBA, Mazzetto SE. Composites Part A: Applied Science and Manufacturing 2011; 42: 492–500.
[22] Fávaro SL, Ganzerli TA, de Carvalho Neto AGV, da Silva ORRF, Radovanovic E. Express Polymer Letters 2010; 4: 465–473.
[23] Arrakhiz FZ, El Achaby M, Malha M, Bensalah MO, Fassi-Fehri O, Bouhfid R, Benmoussa K, Qaiss A. Materials & Design 2013; 43: 200–205.

[24] El-Shekeil YA, Sapuan SM, Khalina A, Zainudin ES, Al-Shuja'a OM. Express Polymer Letters 2012; 6: 1032–1040.
[25] Madhuban G, Bhaduri SK, Banerjee SK, Sao KP. Indian Journal of Textile Research 1985; 10: 68–70.
[26] Yan L, Yiu WM, Lin Y. Composites Science and Technology 2000; 60: 2037–2055.
[27] Jacob M, Thomas S, Varughese KT. Composites Science and Technology 2004; 64: 955–965.
[28] Mishra S, Mohanty AK, Drzal LT, Misra M, Parija S, Nayak SK, Tripathy SS. Composites Science and Technology 2003; 63: 1377–1385.
[29] Rakesh k, Sangeeta O, Aparna S. Pelagia Research Library 2011; 2: 219–228.
[30] Boukerrou A, Rahmoune A, Kaci M. Academic Journal of Manufacturing Engineering 2010; 8: 24-29.
[31] Siregar JP, Sapuan SM, Rahman MZ, Zaman HMDK. J of Food, Agriculture and Environment 2010; 8: 1103-1108.
[32] Saheb D N, Jog JP. Advances in Polymer Technology 1999; 18: 351-363.
[33] Saikia D. International Journal of Thermophysics 2010; 31: 1020-1026.
[34] Min Zhi Rong MZ, Zhang MQ, Liu Y, Yang GC, Zeng HM. Composite Science and Technology 2001; 61: 1437-1447.
[35] Sampathkumar D, Punyamurth R, Venkateshappa SC, Bennehalli B. J Applied Sciences Research 2012; 8: 5298–5305.
[36] Alexander Bismarck A, Mohanty AK, Aranberri-Askargorta I, Czapla S, Misra M, Hinrichsen G, Jürgen S. Green Chemistry 2001; 3: 100-107.
[37] Bal KE, Bal Y, Lallam A. Textile Research Journal 2004; 74: 241-247.