International Journal of Composite Materials 2015, 5(5): 133-141
DOI: 10.5923/j.cmaterials.20150505.05

Olive Oil Waste Filled High Density Polyethylene Bio-Composite: Mechanical, Morphological and Water Absorption Properties

Raid Banat[1,*], **Mohammad M. Fares**[2]

[1]Department of Chemistry, Al al-Bayt University, Mafraq, Jordan
[2]Department of Applied Chemical Sciences, JUST, Irbid, Jordan

Abstract The effect of olive shell flour, Exocarp & Mesocarp, on the mechanical, morphological, and water uptake properties of high density polyethylene (HDPE), with and without using coupling agent, were investigated. In this research, HDPE filled with olive shell flour at 0, 5, 25, and 50 wt. % loading level in the absence and presence of 1% and 5% coupling agent. Environment-friendly composites were fabricated by extrusion and compression molding processing technologies. Tensile strength of the composite decreases with the increase of the filler loading; and increases in the presence of coupling agent. The modulus of elasticity at 5 and 25 wt. % filler showed higher values on the order of 5% compared to that of neat HDPE. The impact strength was increased for low filler loading level (5 wt. %) on the order of 16% and decreased for medium and high filler loading level (25 and 50 wt. %) on the order of 61% and 91% respectively. The interfacial properties of the polymer composites were improved at low filler loading level 5 wt. % and enhanced by the addition of 5 wt. % coupling agent (5F+5C). Morphological illustrations reflect the mechanical behavior findings and the effect of coupling agent on the enhancement of the composite interfacial adhesion. Water uptake of the composite; increased with filler content and decreased in the presence of coupling agent. The results of the study demonstrate that olive shell flour can be used as reinforcement for HDPE bio-composite material

Keywords Olive oil waste, HDPE composite, Coupling agent, Mechanical & physical properties

1. Introduction

Agro crop residues can serve as a source material for bio-energy and developing bio-based polymer composites [1-3]. Wastes of biomass based fillers are increasingly used as reinforcement material for thermoplastic composite materials [4-6]. In order to minimize the negative effects on the environment of certain plastic structures, promoting clean technologies and recycled products, the use of olive stone as plastic filler was studied [7-9]. The preparation of composite samples by mixing olive stone and polypropylene to produce a new thermoplastic polymer was performed [10, 11]. There are industrial films that have developed a homogeneous polymer compound incorporating olive stone as a natural and biodegradable raw material [12-14]. Products such as panels, pipes, tubes or profiles amongst others, have been elaborated by extrusion and injection technologies [15].

The olive oil extraction processes generates huge amounts of solid lignocellulosic waste, representing 30-35% by weight of the olive fruit. The chemical composition of which; mainly composed of lignin, hemicellulose and cellulose. Olive waste has a growing potential as a reinforcement filler materials among many other uses [16-18].

Modern olive oil mills use centrifugal separation methods where the olive cake (waste) residues represent 35% of the whole olive fruit, and composed of oil 9%, shell 22%, water 24% and stone45%. The mentioned values varied depending on the process used for olive oil production [19-21].

In literature, most studies were performed on the olive stone part (Endocarp) and no specific research mention the use of the olive shell part, skin and pulp or (Exocarp & Mesocarp) as a reinforcement filler material. In this study a novel biodegradable composite material containing olive shell flour dispersed into HDPE was manufactured and studied. In general natural fiber composites can be classified into green or partially green composite based on the polymer matrix in use [22]. In the last two decades the developments of such kinds of polymer composite reduce the consumption of non-biodegradable polymer matrix which partially fulfills the global environmental needs toward less hazardous materials. The aim of this study was to formulate less hazardous composite form HDPE and OSF and to investigate

* Corresponding author:
raidbanat@aabu.edu.jo (Raid Banat)
Published online at http://journal.sapub.org/cmaterials

the effect of olive shell flour at different weight fractions on the physical and mechanical properties of HDPE composites. Moreover, commercially available coupling agent was used to evaluate its effect on olive shell flour/HDPE polymer composite.

2. Materials and Methods

2.1. Materials

The composites were prepared using homopolymer HDPE (ExxonMobil HDPE HMA 018) as the polymer matrix. This HDPE is an easy flow grade with a melt flow index of 30 g/10 min (according to ASTM D1238 standard) to facilitate the dispersion and processability of the composite material. Fusabond M603 resin, a random ethylene copolymer incorporating a monomer, which is classified as being a maleic anhydride equivalent, was kindly provided by Dupont Company and used as coupling agent to improve the interface adhesion and to promote the compatibility of powder/matrix composite. Olive waste was kindly provided by local olive oil processing plant in Jerash region/Jordan and used after certain conditioning as a filler material.

2.2. Methods

2.2.1. Olive Pulp and Skin Flour Preparation

Olive waste was obtained from the residues of the olive oil production. After the separation of the olive oil, the residue is composed of skin, pulp, and stone. The solid residue was used without any chemical or solvent treatment. Then the residue was dried and separated into shell (pulp and skin) and stone by means of screening ventilation. The resulting shell residues were ground into fine flour that represents about 10-15% of the whole olive fruit. Olive shells (pulp and skin) were grinded using Pulverisette 9 vibrating cub mill (Fristch, Germany). The obtained particles mesh size was measured with a set of sieves from 140 to 325. Olive shell flour was oven dried at 103℃ ± 2℃ for 24 h to adjust moisture content to approximately 1.5%.

2.2.2. Compounding and Composite Processing

Before processing (Figure 1) HDPE and flour are dried at 103℃ ± 2℃ for 24 h. Compounding is achieved by a parallel co-rotating twin screw extruder (TSE 20, L/D: 40:1, diameter 22 mm, 8 × 78 mm^2 flat die) with 7 heating zones (temperature profile: 160℃ / 180℃ / 180℃ / 175℃ /175℃ / 170℃ /180℃). Screw speed rate is 60 rpm and feed rate is 3 kg/h.

After extrusion, compression molding is then carried out on digital thermal (XH-406B) press machine. Plate temperature is set at 160℃ and the mold temperature is maintained at 150℃. The compression cycle time is fixed at 90 s. Olive shell flour and coupling agent contents vary in the 0–50 wt. % and 0-5 wt.% range in HDPE matrix respectively. The formulation of composites was summarized in Table 1.Sheet samples were prepared by using aluminum mold in a compression-molding machine (XH-406B). Several sheets (L: 30 x W: 20x T: 2 mm) from each obtained polymer composite recipe were compression molded. Tensile test samples of standard dumbbell shaped specimens were cut out from the composite sheet according to ASTM D-638 type IV specimen die. The impact toughness test samples were prepared by using aluminum mold with 20 cells of (L: 63.5 ± 2, W: 6.4±0.2 T: 12.7 ± 0.2 mm).

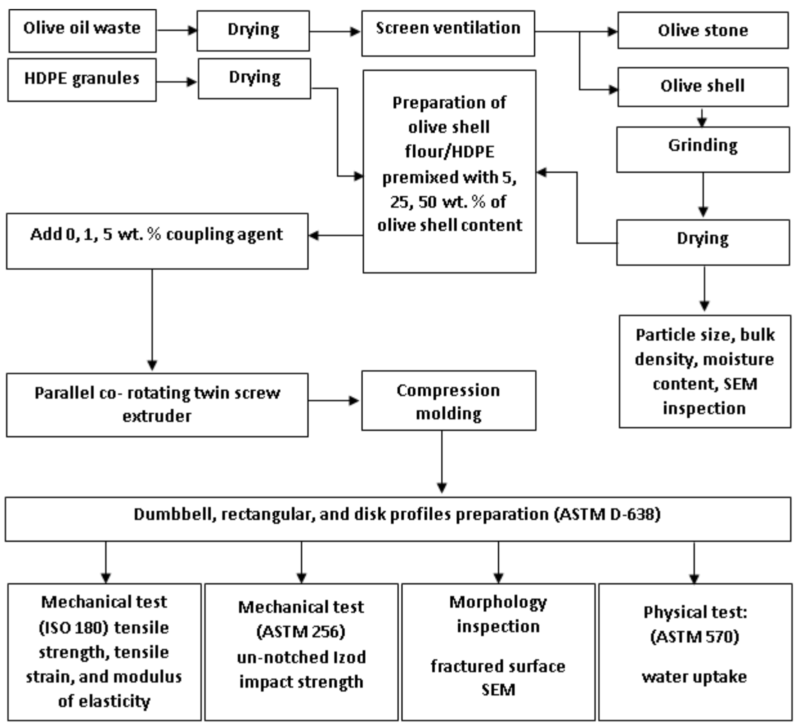


Figure 1. Process for olive shell flour filled high density polyethylene composite production

Table 1. Formulation of the composites

Sample	Weight Percent (%)		
	HDPE	Olive Shell Flour	Coupling Agent
0F+0C	100	0	0
5F+0C	95	5	0
25F+0C	75	25	0
50F+0C	50	50	0
0F+1C	99	0	1
5F+1C	94	5	1
25F+1C	74	25	1
50F+1C	49	50	1
0F+5C	95	0	5
5F+5C	90	5	5
25F+5C	70	25	5
50F+5C	45	50	5

2.3. Bulk Density Measurement of Olive Shell Flour

Bulk density of olive shell flour filler was measured by using conventional standard method, where the volume of 50 g olive shell flour was determined by using high precision graduated cylinder, after 24 h drying at 80℃.

2.4. Moisture Content

Aluminum dish was weighted using digital balance. Samples (10 g) with mesh size 140-325 were placed in the dish and the dish and sample were weighted. The sample and the dish were then placed in drying oven and kept at 103 ± 2℃ for 48 h until constant weight was reached. The moisture content was calculated according to equation (1)

$$\text{Moisture content (\%)} = [(Mw\text{-}Mo)/Mo] \times 100 \quad (1)$$

Where; Mw and Mo stand for the weight of the wet and oven dry specimen respectively.

2.5. Mechanical Characterization

The specimens were stored at 23℃ and 30% relative humidity for 48 h. Afterwards, composites were assayed in a computer control electrical universal testing machine (WDW-5), fitted with a 5 kN load cell and operating at a rate of 1 mm/min. Tensile strength and Young's modulus were analyzed using dog-bone specimens according to ISO 180. The un-notched Izod impact strength was measured according to ASTM: D256 using digital display Izod impact testing machine (FI-68) provided with impact speed of 3.5 m/s, a hammer of 2.270 kg weight and 335 mm arm length. Results were obtained from the average of at least 5 samples.

2.6. SEM

For morphological characterization, Scanning Electron Microscopy (SEM) photomicrographs were taken on the fractured surface of the specimens from tensile measurement. Fractured surface was made conductive through sputter-coating for 40 s at a beam current of 38–42 $mM \cdot L^{-1}$ with a 100 Å layer of gold/palladium alloy in vacuum chamber. Investigation was done using Quanta 600 SEM. Representative micrographs were taken in the magnification of the order 800-1000 for all samples.

2.7. Water Absorption Test

The water absorption of the composite was conducted according to ASTM D570 standards. Samples (50 mm diameter disks, 6.23 mm thick) were oven dried at 50℃. Composite samples were then immersed in distilled water (23℃ for 24h) and taken out after a constant interval of time, wiped with tissue paper, and weighted in high precision digital scale balance with a resolution of 0.001g. The water absorption uptake was recorded on daily basis for 30 days after which the water absorption % was calculated accordingly to equation (2).

$$\text{Water absorption (\%)} = [(Mt\text{-}M)/M] \times 100 \quad (2)$$

Where; M and Mt stand for dry weight of the sample and the weight of the immersed sample at any specific time t, respectively.

3. Results and Discussion

3.1. Size of the Olive Shell Flour

Olives shell flour fractions with mean sizes of approximately 140-325 mesh, was obtained using vibrating cup mill Pulverisette 9. 70% of the flour was in the range of less than 50μm particle size. Flour fractions were subsequently retained for further investigation.

3.2. Density and Moisture Content Measurements of Olive Shell Flour

The bulk density of olive shell flour was found to be 0.71 g/cm^3 and the moisture content was determined to be 1.5% for all flour samples used in processing of the composites material.

3.3. Mechanical Characterization of Composites

3.3.1. Tensile Stress and Strain

Experimental results represent the mean value of at least five specimens tested. Figure 2 shows the olive shell flour/HDPE composite tensile stress variation in the absence and in the presence of coupling agent as a function of filler content.

A systematic decrease in tensile stress was observed as filler contents increase. At high weight fractions of olive shell flour, tensile stress decreases due to the filler high volume incorporated into the HDPE matrix. The agglomeration and the poor dispersion of the fillers into the HDPE matrix had a significant impact on the mechanical properties of the composite in comparison to the neat matrix strength. This behavior might be attributed to the grinding method applied which affects the olive granule size as well as their physical and morphological characteristics. On the other hand, the tensile stress increases as the % coupling agent increases in the polymer composite. The effect of coupling agent was clear in increasing the tensile stress on the order of 20% to 40% in case of high level filler loading (50F) for 1% and 5% coupling agent respectively (i.e. for samples with 50F+0C, 50F+1C, and 50F+5C compositions). On the other hand, the effect of coupling agent comparatively was less profound on the samples with 5% and 25% filler content (5F and 25F), and the increase was on the order of 10% and 20% for samples with %1 and %5 coupling agent (1C and 5C) respectively. When the smaller particle size is used (olive shell flour), a reduction in both tensile and strain at break (Figure 3) is obtained for various weight fractions used which might be connected with agglomeration phenomena existed in the compounded materials [14]. Nevertheless, the olive shell flour which was dried and used without further solvent extraction or processing as a filler was able to interact with the coupling agent which in turn enhanced the compatibilization of the polymer composite.

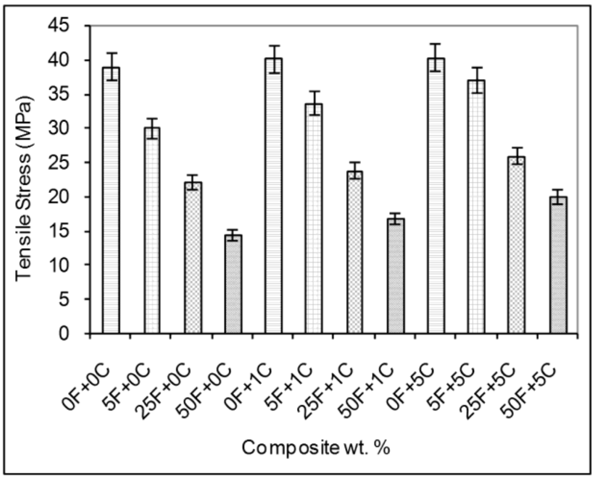


Figure 2. Comparison of tensile stress of olive shell flour/HDPE composites as a function of the filler and coupling agent loading. F: filler % (olive shell flour) and C: coupling agent %

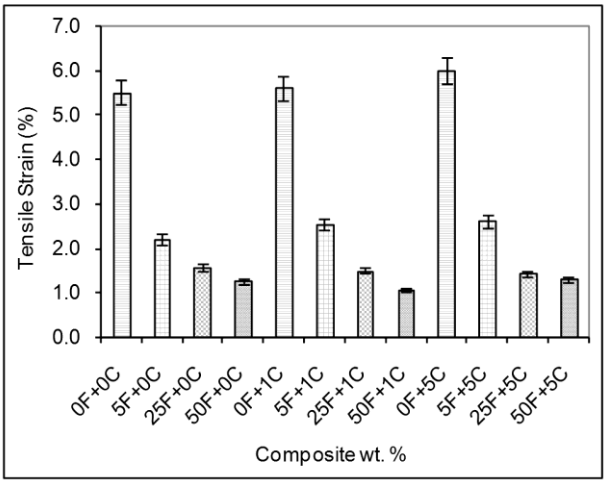


Figure 3. Comparison of tensile strain of olive shell flour/HDPE compoites as a function of the filler and coupling agent loading. F: filler % (olive shell flour) and C: coupling agent %

Figure 3 shows the tensile strain. A decrease in strain as the filler content increases is observed indicating the presence of a poor interfacial adhesion between the hydrophilic lignocelluloses flour and the hydrophobic HDPE which does not allow efficient stress transfer between the two phases of the biocomposite. For olive shell flour, agglomerates induce a decrease in strength. Such a decrease was also described in the literature [14]. The used coupling agent (Fusabond M603) is commercially recommended to wood filled HDPE, the coupling agent with 1% and 5% loading level do improve the compatibility between filler and matrix, hence add value to the composite properties.

3.3.2. Modulus of Elasticity

Modulus of elasticity of olive shell flour/HDPE specimens measured in tensile test. Figure 4 shows the variation of the tensile modulus as a function of the olive shell flour content of the composites. Tensile modulus gradually increases at low level filler loading (5F) followed with a decrease attributed to the filler agglomeration phenomena at medium (25F) and high (50F) level filler loading. For the composite with 5 wt. % olive shell content, the highest modulus was observed in specimen with 5% filler and 0% coupling agent (5F+0C), on the order of 4% compared with the modulus value of neat HDPE. This was probably due to the improved dispersion quality of olive shell flour particles in the polymeric matrix at low filler loading level. In case of medium and high filler loading level (25F and 50F) the modulus of elasticity showed a decreasing trend on the order of 4% and 13% respectively. The use of %1 and %5 coupling agent enhanced the modulus of elasticity on the order of % 8 and %17 for low level loaded filler content (5F+1C and 5F+5C) respectively. Addition of %1 and %5 coupling agent to composites of medium and high filler loading level enhanced the modulus values on the order of %4 for each addition and for both composites.

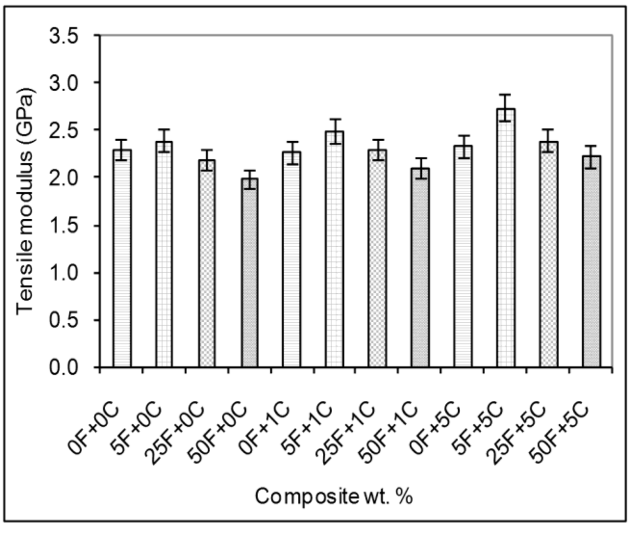


Figure 4. Comparison of tensile modulus of olive shell flour/HDPE composites as a function of the filler and coupling agent loading. F: filler % (olive shell flour) and C: coupling agent %

3.3.3. Un-notched Izod Impact Strength

The impact strength is the ability of a material to withstand fracture or the amount of energy required to propagate a crack. It depends on certain factors such as fiber and matrix strength, load transfer efficiency, resistance to crack propagation, bonding strength, volume fraction, fiber distribution, and geometry [23]. The measured values of the impact strengths are presented in Figure 5.

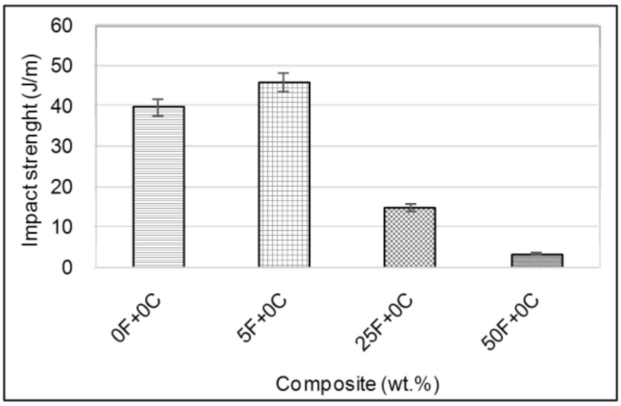


Figure 5. Effect of olive shell flour loading on the impact strength of the olive shell flour/HDPE composite. F: filler % (olive shell flour) and C: coupling agent %

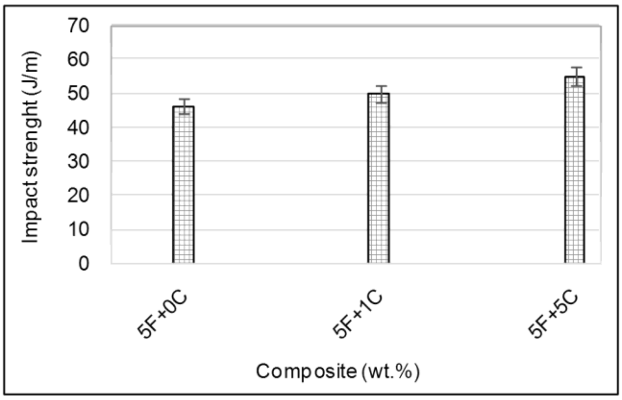


Figure 6. Effect of coupling agent loading on the impact strength of 5% olive shell flour/HDPE composite, F: filler % (olive shell flour) and C: coupling agent %

The un-notched impact resistance tests concluded that as the filler loading increases below 5 wt. % (5F), the impact resistance also increases. This means that the energy absorbed by the specimen increases and with it its toughness also increases. It is observed that at medium and high level of filler loading; the increase in olive shell content (25-50%) has a negative effect on the impact strength of composite which agrees well with the study carried out by Rahman et al [24]. For the composite with 5 wt. %olive shell content, the highest impact strength belongs to 5F+5C composite. Figure 5 shows that inclusion of olive shell flour content up to 50wt. % decreased the impact strength of the composites by almost 91%. The impact strength values of the composites at low filler content 5 wt. % are superior to those of neat HDPE and (25-50 wt. %) loaded olive shell/HDPE composites. Figure 6 shows the positive effect of coupling agent % addition on the impact strength of low filler loading of 5 wt. % olive shell content which increase the impact values on the order of 8% to 19% for 5F+1C and 5F+5C sample composites respectively.

Figure 7 shows the same trend of increase in impact strength upon increasing the coupling agent % of various olive shell filled polymer composites. The inferior impact strength exhibited by, (25-50 wt.%), the medium and high olive shell loading level composites compared with others may be attributed to the formation of agglomerates, which made good dispersion difficult, by the very fine olive shell flour particles.

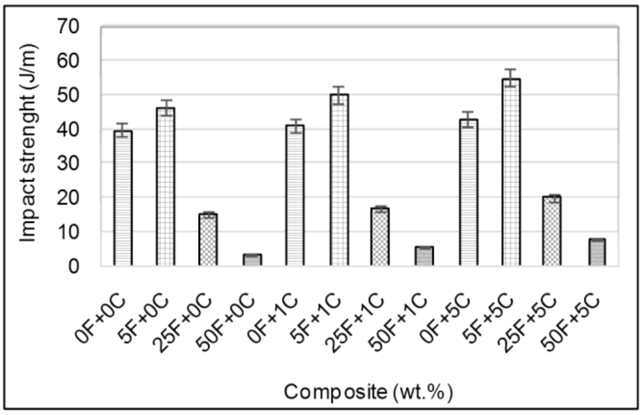


Figure 7. Comparison of impact strength of olive shell flour/HDPE composites as a function of the filler and coupling agent loading. F: filler % (olive shell flour) and C: coupling agent %

3.4. Fractured Surface Morphology

The obtained olive shell flour particles mesh size was measured with a set of sieves from 140 to 325 meshes. Figure 8 represents the morphology of the olive shell flour which apparently showed irregular particle shapes with particle size distribution range from 40 to 100 µm. The assumption of obtaining spherical particle shape is not a realistic one, since a complex shape of particles usually exists.

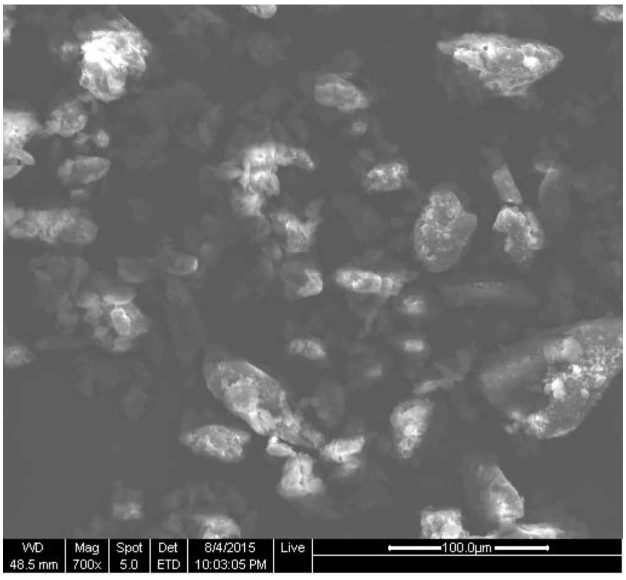


Figure 8. SEM micrograph of the olive shell flour

The fractured surfaces of polymer composites were examined with SEM are presented in Figure 9. Interfacial tension between polymer and filler is very important for phase morphology. It is clear that the filler at low loading level (5%) (Figure 9B) morphology slightly differs from that of neat HDPE polymer (Figure 9A). Low level pullout was observed which reflects a relative good tensile stress performance of the polymer composite compared to that of neat HDPE. At medium and high olive shell flour loading, (%25 and 50%) as shown in Fig 9 C and D respectively, more filler pullout and deponding were observed. This was probably due to poor adhesion between olive shell flour and polymer matrix. The presence of voids due to filler debonding is more pronounced in the (50F0C) polymer composite, where the olive shell flour is (50%) and the coupling agent is (0%). The polymer composite with more voids due to high filler content and high pullout exhibited inferior tensile properties compared to other polymer composites.

Coupling agent plays an important role in lowering the interfacial tension and thereby enhancing the formation of finer morphology which in turn affects the physical, mechanical and other properties of the polymer composite. Olive shell flour filled HDPE polymer composite was compatibilized by using (%1 and %5) coupling agent. Filler pullout and voids formation were reduced upon compatibilization with %1 coupling agent (Figure 10 C and D) when compared to uncompatibilized polymer composite (Figure 9 C and D) which comparatively resulted in superior tensile properties.

To enhance the compatibilization between olive shell flour and HDPE polymer matrix, %5 coupling agent was used for successive polymer composites. Figure 11 represents the effect of coupling agent on the high level loading polymer composites (C and D). The filler confined by, surrounded and adhered well with the polymer matrix resulted in an improvement in the tensile properties of the polymer composite compared with those of the same polymer composite composition for %0 and %1 coupling agent.

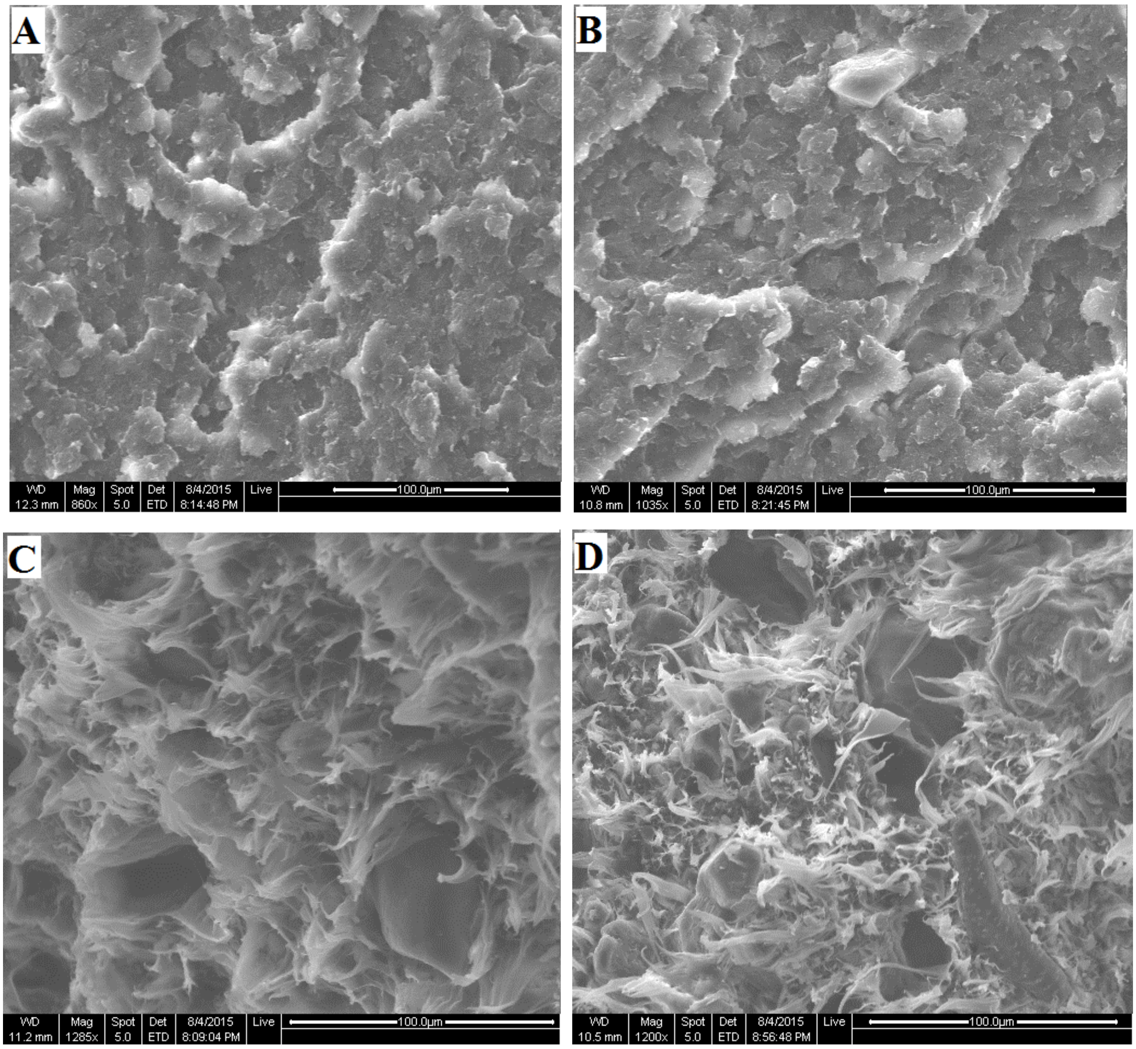


Figure 9. SEM micrographs of the tensile fractured specimens of olive shell flour/HDPE composite at different filler content (A) 0, (B) 5, (C) 25, and (D) 50 wt.%

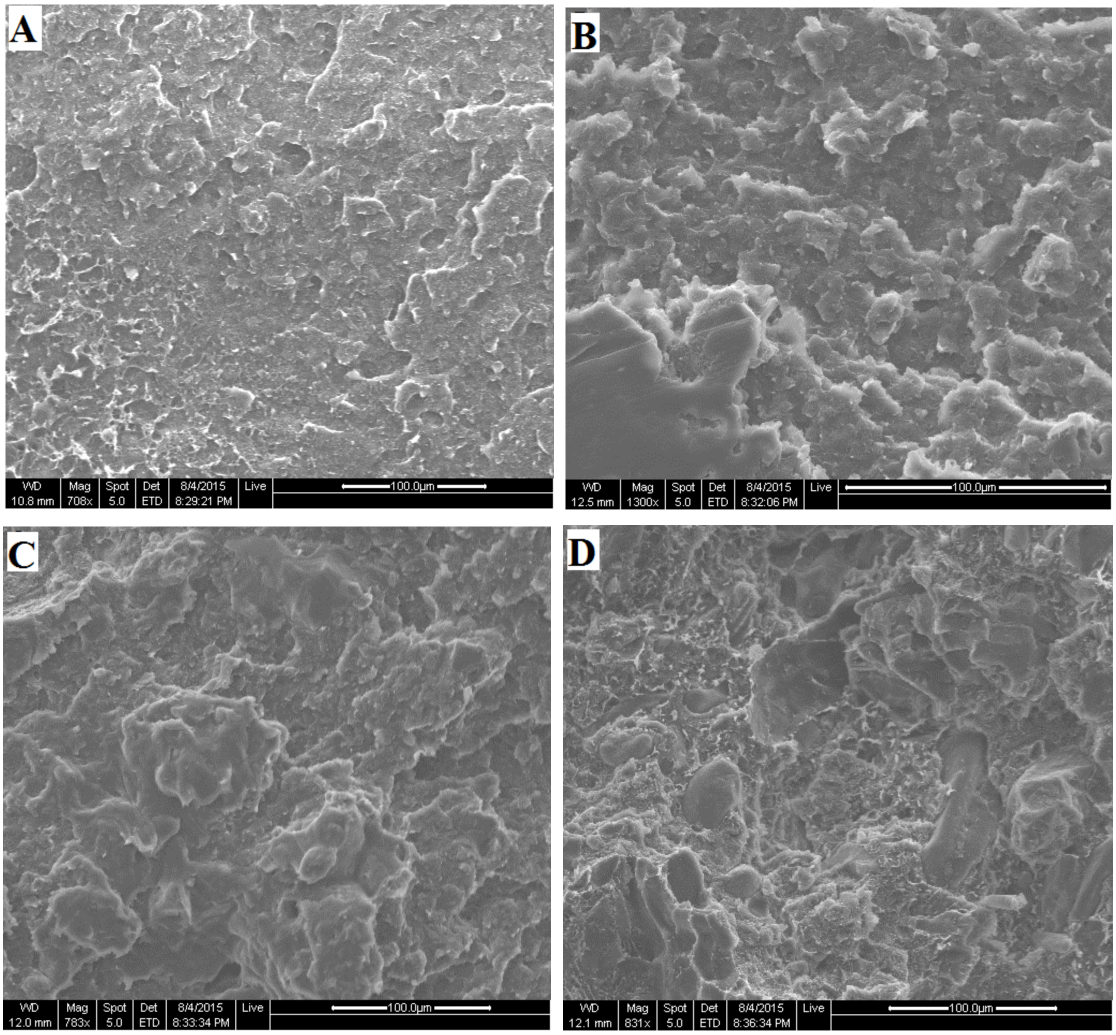
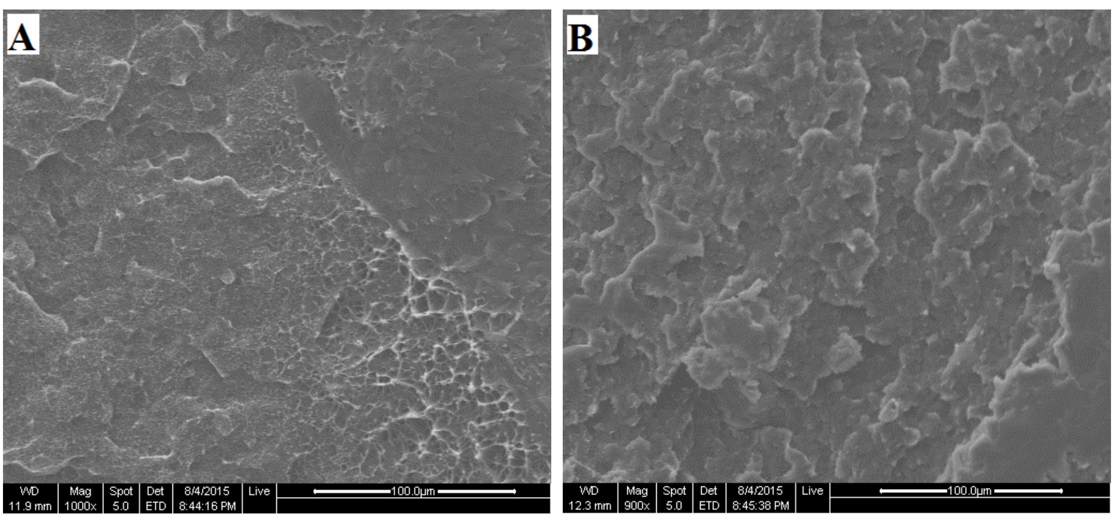


Figure 10. SEM micrographs of the tensile fractured specimens of olive shell flour/HDPE composite with %1 coupling agent at different filler contents (A) 0, (B) 5, (C) 25, and (D) 50 wt.%



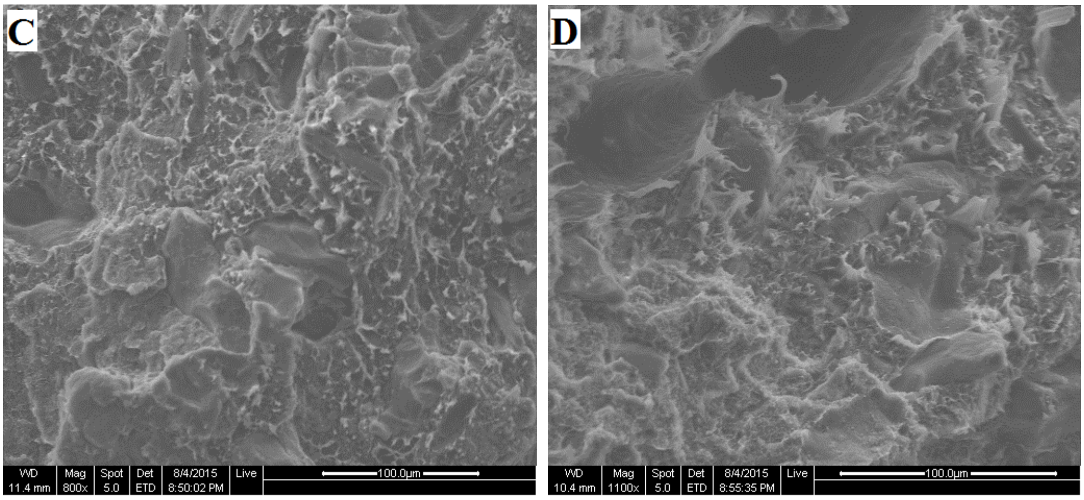


Figure 11. SEM micrographs of the tensile fractured specimens of olive shell flour/HDPE composite with %5 coupling agent at different filler contents (A) 0, (B) 5, (C) 25, and (D) 50 wt.%

3.5. Water Absorption Properties

Composites based on lignocellulosic fillers are sensitive to water environment. The mechanical properties of such polymer composites are in general adversely affect by water contact. The filler hydrophilic characters and the poor interfacial adhesion of the filler polymer matrix are believed to induce such adverse performance for the polymer composite. Water absorption % vs. time at different filler and coupling agent loading level is shown in Figure 12. The water absorption % increased rapidly at the first stage of absorption and then gradually slowed down until saturation region was reached after about 20 day's immersion in water.

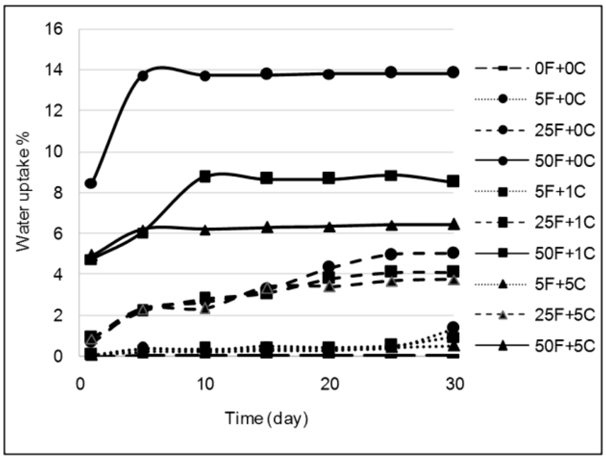


Figure 12. Water absorption of olive shell flour filled high density polyethylene composite as a function of time

The water absorption increased with the filler content, which is in accordance with the results noted for other lignocellulosic fillers [25]. One of the major obstacles to wider use of these materials is their sensitivity to environmental effects, especially heat and moisture, which can cause components to deteriorate prematurely [26]. The coupling agent inclusion within the polymer composite significantly reduced the water uptake. Composite with filler loading of 50% and coupling agent of 5%, showed a decrease in water absorption uptake from about 13.8% to about 6.5% for the uncoupled and coupled composites, respectively. The better interfacial adhesion between polymer and filler in presence of coupling agent is believed to be responsible for the reduction of water uptake hence composite water sensitivity decreased.

4. Conclusions

In the present work a novel composite material containing olive shell flour (pulp and skin) dispersed in HDPE matrix was manufactured and studied. The aim of this study was to investigate the effect of olive shell flour at different weight fractions without and with coupling agent on mechanical, morphological, and water uptake properties of HDPE matrix composite. Olive shell flour/HDPE composite with 5, 25, and 50 wt. % olive shell flour contents are under taken in an extrusion and compression molding processes. In the production of the polymer composites with the desired olive shell flour content, one can use a single stage process, in which olive shell flour, coupling agent, and polymer are directly fed into the hopper. The results indicate the variation of the composite properties with varying the filler and coupling agent content. Composites, with low filler loading, showed good performance when compared to composite with high filler content. The tensile stress and modulus of elasticity reduction at medium and high filler loading may be due to the poor interfacial bonding between olive shell flour and HDPE. The decline in mechanical properties could be reversed and even improved on the use of definite proportion of coupling agent in the polymer composite. From a general point of view interfacial adhesion is the main disadvantage encountered during the incorporation of natural lignocellulose materials into polymers. Therefore suggestions to achieve a better interfacial bonding are accomplished by using coupling agent. Olive shell flour can be used as reinforcements in HDPE by the help of certain coupling agent, so that a bio-based composite is produced.

Morphological illustrations and water uptake results were in good agreement with the mechanical properties variation with filler and coupling agent contents. The developed partially green OSF/HDPE polymer composite would be considered as an alternative to conventional polymers in packaging application.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Scientific Research Support Fund (Jordan) and Al al-Bayt University for their financial support of this research through SRF grant (Bas/2/03/2013).

REFERENCES

[1] Lou, R., Wu, S-B., Lv, G.-J., and Guo, D.-L., 2010, Pyrolytic products from rice straw and enzymatic/mild acidolysis lignin (EMAL). Bioresources; 5: 2184-2194.

[2] Nagarajan V, Mohanty AK and Misra M., 2013, Sustainable green composites: value addition to agricultural residues and perennial grasses. ACS Sustain Chem Eng; 3: 225-233.

[3] Kengkhetkit, N., Amornsakchai, T., 2014, A new approach to ‘‘Greening’’ plastic composites using pineapple leaf waste for performance and cost effectiveness. Mater Des; 55:292–9.

[4] Ogah, A., and Afiukwa, J., 2014, Characterization and comparison of mechanical behavior of agro fiber-filled high-density polyethene bio-composites. Journal of reinforced plastics & composites, 33(I): 37-46.

[5] Koutsomitopoulou, A.F., Bénézet J.C., Bergeret, A., Papanicolaou, G.C., 2014, Preparation and characterization of olive pit powder as filler to PLA-matrix bio-composites. Powder Technology, 255, 10–16.

[6] Pattara, C., Cappelletti, GM., Cichelli, A., 2010, Recovery and use of olive stones: commodity, environmental and economic assessment. Renew Sustain Energy Rev, 14: 1484–9.

[7] Ihemouchen, C., Djidjelli, H., Boukerrou, A., Fenouillot, F., Barres, C., 2013, Effect of compatibilizing agents on the mechanical properties of high-density polyethylene/olive husk flour composites. J Appl Polym Sci., 128: 2224–9.

[8] Papanicolaou, G.C., Koutsomitopoulou, A.F., Sfakianakis, A., 2012, Effect of thermal fatigue on the mechanical properties of epoxy matrix composites reinforced with olive pits powder. J Appl Polym Sci., 124:67–76.

[9] Naghmouchi, I., Mutjé P., Boufi, S., 2014, Polyvinyl chloride composites filled with olive stone flour: mechanical, thermal, and water absorption properties. J Appl Polym Sci., 131: 41083–93.

[10] Amar, B., Salem, K., Hocine, D., Chadia, I., Juan, MJ., 2011, Study and characterization of composites materials based on polypropylene loaded with olive husk flour. J Appl Polym Sci., 122: 1382–94.

[11] Naghmouchi, I., Francesc, X., Espinach, Mutjé, P., Boufi, S., 2015, Polypropylene composites based on lignocellulosic fillers: How the filler morphology affects the composite properties. Materials and Design, 65, 454–461.

[12] Ghazy, S.E., Samra, S.E., May, A.E.M., El-Morsy, S.M., 2006, Removal of aluminum from some water samples by sorptive-flotation using powdered modified activated carbon as a sorbent and oleic acid as a surfactant. Anal. Sci., 22, 377–382.

[13] Rodríguez, A. Lama, A., Rodríguez, R., Jiménez, A., Guillén, R., Fernández-Bolaños, J., 2008, Olive stone an attractive source of bioactive and valuable compounds. Bioresour. Technol. 99, 13, 5261–5269.

[14] Tserki, V., Matzinos, P., Kokkou, S., Panayiotou, C., 2005, Novel biodegradable composites based on treated lignocellulose waste flour as filler. Part I. Surface chemical modification and characterization of waste flour. Compos. A: Appl. Sci. Manuf. 36, 7, 965–974.

[15] Cristofaro, D., ‘‘A process for the realization of plates and panels consisting of exhausted olive husks of crushed olive stones and polypropylene, and derived product. ’’ Patent, International Publication Number: WO 9738834, 1997.

[16] Azwa, ZN., Yousif, BF., Manalo, AC., Karunasena, W., 2013, A review on the degradability of polymeric composites based on natural fibers. Mater Des., 47: 424–42.

[17] Ashori A., 2008, Wood-plastic composites as promising green-composites for automotive industries. Bioresour. Technol., 99: 4661–7.

[18] John, M.J., Thomas S., 2008, Biofibres and biocomposites. Carbohydr Polym., 71:343–64.

[19] Brlek, T., Pezo, L., Voca, N., Kircaka, T., Vukmirovic, D., Colovic, R., Bodroza-Solarov, M., 2013, Chemometric approach for assessing the quality of olive cake pellets. Fuel Processing Technology, 116, 250-256.

[20] Benatenta, V., Fullana, A., 2015, Torrefaction of olive mill waste. Biomass and Bioenergy, 37, 186-194.

[21] Dermeche, S., Nadour, M., Larroche, C., Moulti-Mati, F., Michaud, P., 2013, Olive mill wastes: biochemical characterizations and valorization strategies. Process Biochemistry, 48, 10, 1532-1552.

[22] V. K. Thakur and M. R. Kessler, Green biorenewable biocomposites: from knowledge to industrial applications. Toronto: Apple Academic Press, 2015.

[23] Bax, B., and Mussig, J., 2008, Impact and tensile properties of PLA/cordenka and PLA/flax Composites. Compos Sci. Technol., 68: 1601–1607.

[24] Rahman, W.A.W.A., Isa, N.M., Rahmat, A.R., Adenan, N., Ali, R.R., 2010, Rice husk/high density polyethylene biocomposite: effect of rice husk filler size and composition on injection molding processability with respect to impact properties. J Adv Mat Res, 38-86: 367-374.

[25] Gasparovic, L., Korenova, Z., Jelemensky, L., 2010, Kinetic study of wood chips decomposition by TGA. Chem. Pap., 64, 174.

[26] Toubal, L., Cuilliere, J. C., Bensalem, K., Francois, V., and Gning, P. B., Hygrothermal effect on moisture kinetics and mechanical properties of hemp / polypropylene composite: experimental and numerical studies, Polym. Compos., 2015. doi:10.1002/pc.23414.