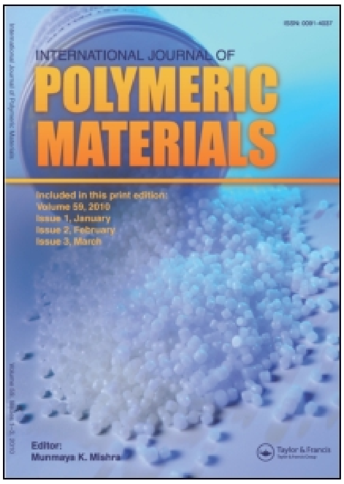

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Thermoplastic Composites Based on Renewable Natural Resources: Unplasticized PVC/Olive Husk

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The current study explores the potential of eco-friendly biomaterials, namely olive husk (OH) as a reinforcing filler for PVC composite. Thus, composite-based unplasticized poly(vinyl chloride) (u PVC) and olive husk were mixed by a Brabender two-roll mill at 180°C and 25 rpm. The olive husk concentration was progressively varied from 0–20 phr. The fabricated samples were inspected with respect to their tensile properties, impact strength, thermal stability, and density and water uptake. It has been found that stress at peak increased with filler loading up to certain loading. This scenario was related to hydrogen bond formation due to polar-polar interactions. Evidence of the hydrogen bond formation between the polymer matrix and the olive husk was examined with the aid of attenuated reflectance infrared spectra (ATR-IR). Such interactions were cited to justify the improved performance of the composites. Fracture mode and filler dispersion of the composites were compared to the unfilled counterpart by scanning electron microscopy (SEM). The influence of olive husk on the thermal stability of the PVC composites was studied by differential scanning calorimeter (DSC). It has been found that the enthalpy of fusion was improved with OH loading. The observed trend was correlated with the phenolic hydroxyl group of the lignin component used as an antioxidant.

Keywords blends and composites, calorimeter, ohp

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INTRODUCTION

Environmental concerns undoubtedly drive the greening of the thermoplastic composites industry. Thermoplastics, eventually reinforced with natural fillers or fibers, are developing significantly and the demand is increasing steadily. Plant fibers are mainly composed of cellulose and are the most abundant renewable biomaterial on the earth. The utilization of natural fibers residues are readily available, rich resources of lignocellulosic materials. Composites consisting of lignocellulosic fibers and synthetic thermoplastic polymers are gaining popularity in both scientific and industrial focus due to ecological and economical reasons (1,2). The potential of such materials as reinforcing fillers is of interest because of their low density, non-abrasiveness, availability with low cost, and ease of surface modification (3). Furthermore, increasing ecological concern together with the difficulty of synthetic polymer biodegradability at the end of their aging time brings about a major environmental pollution. This again has triggered the use of natural fiber-reinforced polymer composites based on renewable and biodegradable materials in the thermoplastic industry. Nevertheless, natural fibers such as jute, sisal, wood flour, and pineapple leaf have gained popularity as fillers in polymer composites for the same reasons mentioned earlier. Polymer composites filled with various natural lignocellulosic fibers are extensively evaluated in the open literature. For example PE and PP/wood flour and PS/SBR/wood-toughened PVC/wood flour was investigated with respect to their mechanical, chemical and electrical properties (3–6). According to the author, knowledge of organic fillers derived from biomaterial-based olive husk, a material that has great relevance to Mediterranean countries, is very limited. Considering the commercial value of PVC and its applications as well as the abundance of OH with its functional groups, it is worthwhile to investigate the contribution of OH to composites-based PVC. It is expected that certain types of polar-polar interactions between both polymers could occur. Therefore, the purpose of this work is to prepare and evaluate composites obtained from uPVC and OH. The work has two aims: to prepare dark-colored articles-based PVC for external applications in construction sectors, and to aid the eco-friendly disposal of olive husk. This is an attempt to replace wood and aluminum in the building sector via the proper combination of petrochemical- and bio-based materials (agricultural, “green” etc.).

EXPERIMENTAL

Materials

A suspension of PVC grade in powder form with a k-value of 67 was supplied by SABIC of Saudi Arabia. The olive husk was delivered in powdery form from a local refinery of Jordan. The olive husk was subjected to heat treatment in an oven at 105°C for about 24 h until constant weight was achieved followed by size reduction using a ball mill. The powder was sifted using a Retsch AS 200 shaker for 10 min. The average particle size was $\leq 100\,\mu m$. Details on the surface analysis of the olive husk can be found in our recent investigation (6). The formulations were based upon typical commercial rigid PVC window frame formulations. The recipe used to fabricate PVC composites is PVC: 100 phr, organic filler: various from 0–20 phr.

Sample Fabrication

Brabender two-roll mills were used to mix the U-PVC with olive husk at 180°C and 25 rpm for 6 min. Mixing was carried out until even distribution of the whole ingredients was achieved.

Compression Molding

2 mm thick sheets were compression-molded at 10 MPa and 180°C for 6 min using a Carver Auto series hot press.

Attenuated Total Reflectance Infrared Spectra (ATR-IR)

ATR-IR experiments were carried out on a Bruker ATR-IR spectrometer at room temperature on pure samples and composites, with 4 cm^{-1} resolution from 400–4000 cm^{-1} in the transmission mode.

Tensile Properties

Tensile properties were measured on an Ekktron tensile testing machine according to ASTM D638 at room temperature and crosshead speed of 5 cm/min. Five specimens were tested and the median value was reported.

Water Absorption

2 mm thick rectangular samples were weighed in air. The samples were immersed in distilled water for seven days at room temperature. The samples were removed from water and wiped with tissue paper and reweighed. The %water uptake was calculated according to the following equation:

$$\%Water\ Uptake = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

where, W_1 is the sample weight in air and W_2 is the weight after immersion. The average of three samples was calculated.

Density

The densities of the composites were measured using the water displacement method according to the following equation:

$$\rho = \left(\frac{W_1}{W_2 - W_1}\right) \times \rho_w \tag{2}$$

where, W_1 and W_2 are the weights of the samples in air and water, respectively, and ρ_w is the density of water.

Izod Impact Test

The Izod impact test was conducted using a CEAST impact testing machine according to ASTM D256–88. The notch depth was fixed at 2.5 ± 0.02 mm using the notching tool. The test conditions used were as follows: velocity = 3.0 m/s, the angle = 145° and the hammer energy = 7.5 J. Five readings were measured and the average value was reported.

Fractography

The tensile fractured surfaces of the prepared materials were inspected using a scanning electron microscope (SEM) type (Geol Toleyo, Japan). The specimens were sputtered with Au-Pd alloy prior to scanning.

Differential Scanning Calorimeter

Differential scanning calorimeter (DSC) model Perkin-Elmer DSC-6 was used to study the impact of the olive husk on the PVC fusion and melting characteristics. A sample of 15–20 mg was scanned in a broad temperature range under nitrogen atmosphere, the heating and cooling rate was 10°C/min. In the first heating scan, the samples were heated from 25 to 250°C, held at that temperature for 1 min to eliminate thermal history, and then a second run was performed to have a DSC thermogram. The endothermic peak was integrated and the value of the heat of fusion was calculated with the aid of machine software.

RESULTS AND DISCUSSION

Mechanical Properties

Table 1 shows the influence of OH dosage on the tensile properties at yield of PVC composites. It can be seen that the tensile strength at yield increased with OH loading up to 20 phr, while further addition leads to a decrease in the tensile properties, therefore the results for such doses were not reported here. The increased tensile strength at yield should be attributed to polar-polar interactions (namely hydrogen bonding) between the polar filler (i.e., olive husk in this case) and the moderately polar PVC matrix. This indicates that good embedding and improved wetability of the organic filler into the matrix have been achieved, and consequently, improved yield tensile strength. One should not forget the reinforcing role of the filler due to its high modulus. The results recorded here agree quite well with earlier works on PS/SBR alloys filled rice husk powder (7), where the tensile properties of SBR/PS were improved with rice husk powder up to certain loading. Table 1 shows the influence of OH loading on the % strain at yield for PVC/OH composite. It is obvious that the strain has been enhanced with OH loadings. Such a trend could be attributed to the lubrication role practiced by the fatty acid left in the olive husk after the extraction process. Similar results were reported earlier on the effect of oil palm empty fruit bunch on the mechanical properties of PVC and PP composites, respectively (8,9). The Young's modulus as a function of filler loading is demonstrated in Table 1 as well. It is clear that Young's modulus of the composites has increased with OH loading. As expected the addition of rigid and stiff filler particles would increase the modulus due to restricted chain mobility. The polar-polar interactions between the PVC and the OH will decrease the free volume. This is expected to participate in increasing the modulus as well, as evidence of hydrogen bond formation, which was cited to explain the improved tensile properties. The ATR-IR spectra for the OH, PVC and their combination were carried out and presented in Figure 1. The virgin olive husk spectrum demonstrates an intensive peak at 3293 cm^{-1}. This peak was assigned to the hydroxyl group of the OH involved in hydrogen bond.

Table 1: The influence of olive husk on the mechanical properties of PVC composites

OH content (phr)	Stress at peak (MPa)	Strain at peak (%)	Tensile modulus ($\times 10^2$) E(MPa)	Density (g/ml)
0	26	2.3	6.20	1.50
5	29	2.8	7.77	1.48
10	30	3.2	8.18	1.45
15	31	3.6	8.50	1.42
20	32	3.7	8.76	1.40

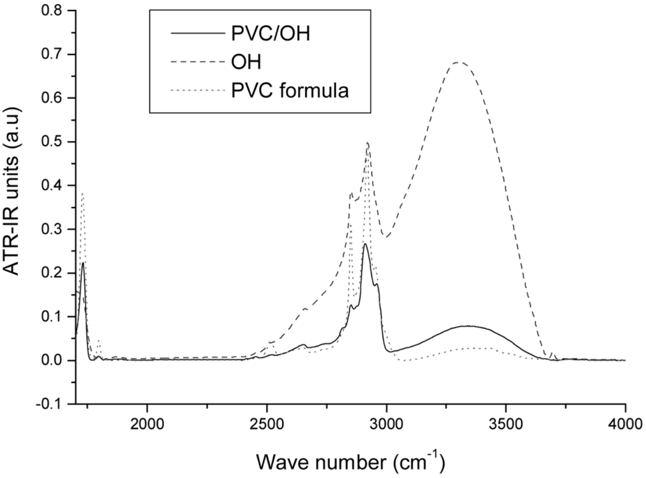

Figure 1: ATR-IR spectra of a) plain PVC, b) olive husk, and c) PVC/olive husk composites.

The small finger at 3696.4 cm^{-1} belongs to free hydroxyl groups of the OH. The peaks located at 1507.5 and 1595 cm^{-1} were assigned to the lignin component of the OH. The PVC spectra shows a peak at 1730 cm^{-1} which is the carbonyl of the stearic acid and some calcium carbonates as appeared in at 1415.6, 1795.5 and 2513.4 cm^{-1}, respectively. Based on the spectrum of both OH and PVC it can be concluded that both OH and PVC, are individually capable of forming hydrogen bonding. Figure 1 also depicts the IR spectra of PVC/olive husk composites at 15 phr filler loading. Two facts could be extracted out of the PVC/olive husk spectrum; the former is that the addition of olive husk to the PVC has reduced the peak intensity of the olive husk hydroxyl group. This is a hint that the hydroxyl groups have been involved in physical interaction with the α hydrogen of PVC. The latter is that the broad peak at 3306.2 cm^{-1} could be ascribed to the hydrogen bond between OH and PVC as compared to the pristine polymers. The observed trend concerts an earlier work on PVC/XNBR blends and toughened PVC-based natural fiber composites, where the hydrogen bond was detected in these reports (6,10). The influence of fiber on the density of the PVC composites is shown in Table 1. Note that the olive husk resulted in a decrease of the density of PVC composites. This is due to the light weight of the natural fiber-based agro-waste material.

Impact Strength

Figure 2 reflects the influence of the OH loading on the impact strength of the PVC composites. It can be noted that the impact strength decreased with filler loading. This trend could be attributed to the fact that the polar-polar

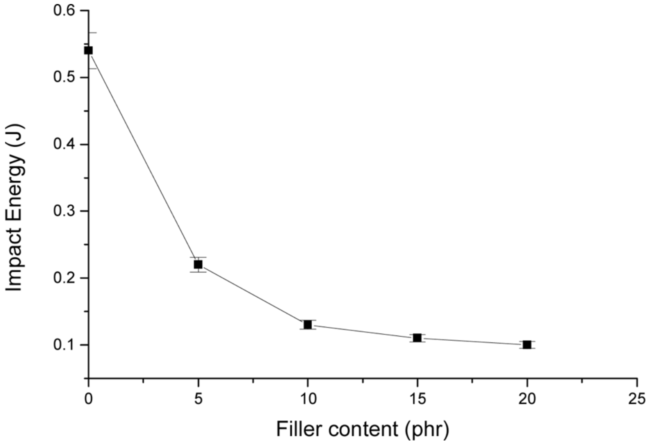

Figure 2: The influence of olive husk loading on Izod impact energy.

interactions between the filler and matrix will reduce the free volume. As a result the chain flexibility will be reduced. Furthermore the fillers are unlike the matrix, and are incapable of dissipating stress through the mechanism known as shear yielding prior to fracture. Therefore, the total ability of the material to absorb energy is decreased. Hence, the impact strength tends to decrease with increasing OH content.

Water Absorption

Figure 3 shows the influence of OH loading on the water uptake pattern for PVC composites after seven days of immersion. Water absorption is mainly due to the hydrogen bonding of water molecules with the hydroxyl groups on

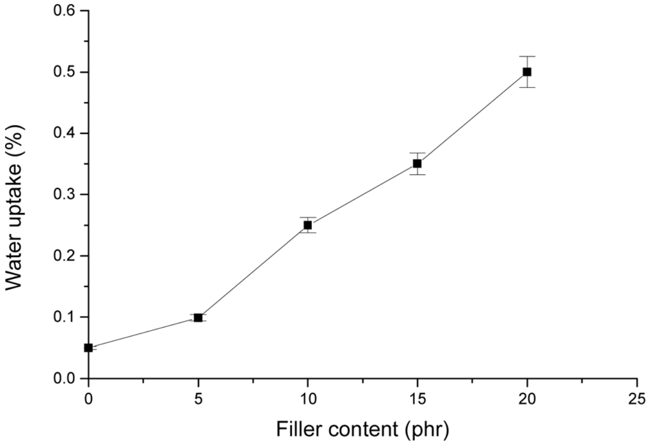

Figure 3: Water uptake as a function of olive husk loading for PVC composites.

the cell walls of the lignocelluloses (OH in this case) (11–13). In this respect, the incorporation of OH has resulted in an increase water uptake for the PVC composites compared to the control. This observation should be traced to the hydrophilic nature of natural fiber. This is expected to enhance the moisture uptake via hydrogen bond formation. In turn this will reduce the physical bonding between the fiber surfaces and PVC composites (14). Hence the water penetration will be facilitated and increased water uptake will take place.

Thermal Properties

The influence of OH loading on the enthalpy of fusion (ΔH_m) of the composites is displayed in Figure 4 as derived from the DSC thermograms. It is obvious that the incorporation of OH has decreased ΔH_m compared to the control. This could be related to the ability of OH to absorb more heat energy in the melting process of the composites. Note that the ΔHm of olive husk-filled PVC is much lower than that of the control sample. On the other hand, it can be noted that the enthalpy of fusion increased with filler loading when considering the filled composites. This is a clue that the thermal stability of the compounds is being enhanced with olive husk content. The rational behind this was the phenolic hydroxyl group of the lignin (4,15,16).

Topography

The topography of fractured tensile surface for PVC composites with and without filler is shown in Figure 5(a and b) respectively. Note that the picture shown in Figure 5(a) revealed a smooth surface with ductile fracture mode

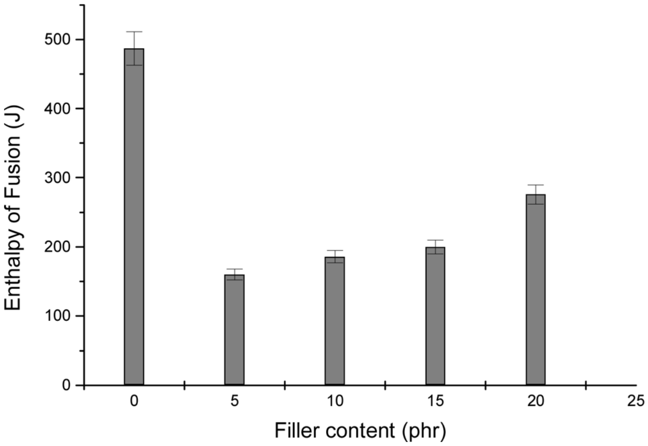

Figure 4: The influence of olive husk loading on PVC enthalpy of fusion as derived from DSC.

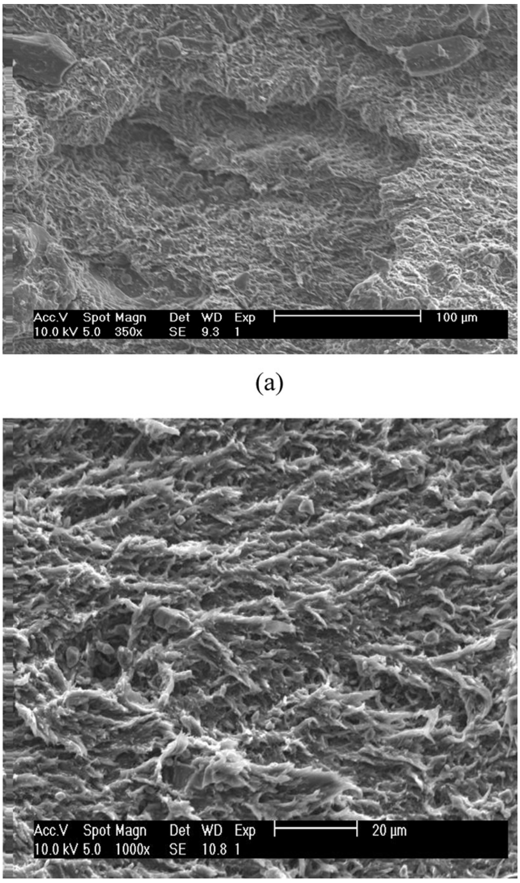

Figure 5: Scanning electron micrographs of fractured tensile specimens for a) PVC compound, b) PVC/olive husk composite.

of the sample. Additionally, the picture shows an increased number of holes shown in the matrix. The ductile fracture mode could be attributed to the impact modifier and stearic acid already involved in the formula acting as internal lubricant. The presence of holes could be related to the pull out of ingredients included with the PVC formula, such as the impact modifier, calcium carbonates and TiO_2 particles. The micrograph of the filled sample is shown in Figure 5(b). It can be seen that the addition of OH resulted in two observations; the former is elongated fibrils on the fractured surfaces with stiff appearance, and the latter is a relatively fewer number of holes on the surface compared to the unfilled counterpart. The formation of such fibrils is a characteristic feature of ductile failure mode as well as improved interaction between the OH and the PVC. The ductility could be related to the oil residue retained within the olive husk, in addition to the internal lubricants already involved in the formula as mentioned earlier. Hence, the filler incorporation is expected to enhance the composite flexibility and the filler dispersion via the plasticization role of the left fatty acids within the OH. Another factor to justify the observed topography of the filled sample is the hydrogen bond being formed between the PVC formula and the OH filler. The conclusions derived from the fractography test could be utilized as further proof to justify the improved tensile properties.

CONCLUSIONS

Based on the aforementioned results the following conclusion could be stated:

The enhanced tensile properties with OH loading up to a certain limit might be due to polar-polar interaction between the PVC and olive husk via the hydrogen bond. Such interactions were examined by ATR-IR spectra. The increment in strain percentage was related to the fatty acid residue during the extraction process of the oil. The enthalpy of fusion detected by the DSC indicated that the filler absorbed heat more than the matrix, which contributes to the thermal stability of the composites. SEM micrographs indicate that the fracture surface has changed with filler loading to a more stiff appearance.

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