Research Article

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Effect of coupling agents on the olive pomace-filled polypropylene composite

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Abstract: The effect of the olive pomace flour (OPF) addition on the mechanical, water uptake, morphological, and thermal properties of polypropylene (PP) with and without the use of two coupling agents was investigated. A higher percentage of a coupling agent yielded a greater impact strength of 141 J/m. Tensile and flexural properties of the OPF/PP composite were improved with the two coupling agents. The addition of OPF to pure PP had reduced these properties, thus proving the utility of the coupling agents. While the addition of the OPF to PP increased the water uptake property by 1.36%, the subsequent addition of a coupling agent decreased it to 0.78%. For the neat PP, the enthalpy of melting ($\Delta H_m = 123$ J/g), the enthalpy of crystallization ($\Delta H_c = 133$ J/g), and the percent of crystallinity ($X_c = 59\%$) values showed a declining trend down to 91, 103 J/g, and 44%, respectively, when the filler and coupling agents added to the composite. The results of this study demonstrated that the OPF could be used as a viable reinforcement for the PP, providing good mechanical and morphological properties, as long as an appropriate coupling agent proportion is added to the composite.

Keywords: coupling agent, olive pomace, polypropylene, mechanical and thermal properties

1 Introduction

The waste products of olive oil production are the residue of the skins and seeds, i.e., the pulp and the stones (1). However, these can now be used as fillers for the polymer material giving rise to desirable products (2). In recent years, the use of the olive pomace as a natural reinforcement agent

in polymer composites has been growing significantly. Its desirable properties including low density, renewability, and biodegradability make it comparable to tough wood (3,4). Farag et al. (5) used olive stone waste in polyester to produce particleboard for interior design. The results showed a competitive physical, mechanical, and biological behavior. Hamida et al. (6) found that the hydrophilic nature of the added OPF to polystyrene caused a matrix swelling that embrittled the composite due to the volume occupied by the OPF. La Mantia et al. (7) studied OPF filled with recycled tri-polymer matrix from low-density polyethylene, linear low-density polyethylene, and poly(ethylene-co-vinylacetate). They observed that the tensile strength and the elongation at break showed a decrease with increasing the OPF content. The observed stiffness of the OPF-filled composite was evident by the low stress at break value, leading to a more brittle material. Moreover, the impact strength was found to decrease with the OPF loading due to the poor adhesion with the nonpolar polymer matrix. OPF dispersed into polylactic acid composite was studied by Koutsomitopoulou et al. (8). The bending properties and the tensile strength of the composite material decreased with the addition of the OPF due to the weak interfacial bonding between the OPF and polylactic acid matrix. OSF-filled polyvinylchloride was studied by Naghmouchi et al. (9). They showed that the water absorption increased with the filler loading. The hydrophilic character of the OPF led to creating cavities, pores, and splits in the filler/matrix interface that assists the diffusion of water. Olive pit-filled polypropylene (PP) composite was investigated by Tasdemir (10,11). They observed a reduction in tensile strength and elongation at break values with the increase of the olive pit content because of the agglomeration and poor dispersion of the OPF into the PP matrix. Moreover, they observed that the impact strength was highly reduced when compared with the neat PP due to the stiffness of the filler and the poor interfacial adhesion between the filler and PP matrix.

The balance between strength and durability of the semi-end product should come through the optimum mixing ratios of the polymer and OPF with the chemical additives, such as UV stabilizer and fire retardant, in case

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of outdoor applications (2). The composites of thermoplastics are generally susceptible to environmental changes causing alterations in their mechanical properties. In real-world applications, these composites are often subject to changes in temperature and moisture (12). Another disadvantage of OPF natural fibers involves their hydrophilic properties. This tends to reduce their compatibility with the materials containing hydrophobic polymeric matrices. Additionally, their poor dimensional and environmental stability limits the applicability of the OPF composites (13). The poor interfacial adhesion of the OPF in thermoplastic polymers is caused by insufficient dispersion of the bio-fillers. The strong hydrogen bonding between the molecules of the OPF bio-fillers limits their diffusion causing them to agglomerate instead (14). To enhance the adhesion and compatibility of the polar OP fiber with the non-polar polymer matrices, coupling agents (CA) or compatibilizers are used. These agents promote chemical bonds to be established between the fiber and the polymer matrix (15,16). The enhancement of the interfacial adhesion between OPF and PP by the addition of 5% maleated PP as a coupling agent with respect to the OPF, which was reported by Naghmouchi et al. (17) There are over 40 coupling agents in production or under research (13). The most commonly used coupling agent is maleic anhydride-modified polypropylene (MAPP) (18,19).

Recently, OPF-filled polymer composites were extensively reviewed by Valvez et al. (20). They strongly recommended that future studies have to give priority to functionalization agents to achieve competitive composite structural properties.

In the present study, we introduced two types of polymer modifiers, as coupling agents to improve the compatibility between the two moieties of the OPF hydrophilic phase and PP hydrophobic phase, at three different loading levels into the OPF-filled PP composite. The type and the amount of the coupling agent were optimized for better composite performance. Mechanical properties, water uptake, morphological, and thermal behavior of the OPF-filled PP composite, without and with the coupling agents, were investigated herein.

2 Materials and experimental procedure

2.1 Materials

The composites were prepared using PP that was purchased from TASNEE, Saudi Arabia, (H4120 PM2371202)

as the polymer matrix. This PP has a density of 0.90 g/cm^3 with a melt flow rate of 12 g/10 min . Olive pomace flour was obtained from an olive oil manufacturing facility located in the Jarash region of Jordan and was conditioned for use as a filler. Two types of coupling agents, under the Fusabond category, commercial products of Dow Inc., USA, were used in these experiments: P353 (chemically modified polypropylene copolymer) and P613 (anhydride-modified polypropylene). The physical and thermal properties of the two coupling agents are summarized in Table 1 (21).

2.2 Experimental procedure

2.2.1 Olive pomace flour (OPF) preparation

The olive pomace used in this research was obtained from the waste remains after the olive oil production. It is the pulp, skin, and pit of the olive that comprises the solid residue. No additional processing was performed on the olive pomace other than grinding it into flour. The grinding was performed with a Pulverisette 9 vibrating cub mill (Fristch Germany). To reduce the moisture content of the flour particles to 1.5% or below, they were oven-dried for 24 h at $103 \pm 2^\circ\text{C}$. The bulk density of the OPF was 0.436 g/cm^3 and the average particle size used in this study was in the range of $63\text{--}106 \mu\text{m}$. Dried olive pomace flour was then kept for further processing.

2.2.2 Composite sample preparation

The dried OPF was compounded with the PP and the coupling agent using a parallel co-rotating twin-screw

Table 1: The physical and thermal properties of Fusabond P353 and P613

The physical and thermal properties (21) ^a	P353	P613
Density	0.904 g/cm^3	0.903 g/cm^3
Melt flow rate ($160^\circ\text{C}/325 \text{ g}$)	22.4 g/10 min	49 g/10 min
Melting point (DSC)	132°C	162°C
Freezing point (DSC)	92°C	
Vicat softening point	112°C	
Maximum processing temperature	300°C	300°C

^a Data according to Dow Chemical Company (2019).

extruder (TSE 20, L/D: 40:1, diameter 22 mm, $8 \times 78 \text{ mm}^2$ flat die) having seven temperature zones: (195°C, 220°C, 220°C, 215°C, 215°C, 210°C, 220°C). The feed rate and screw speeds were 3 kg/h and 50 rpm, respectively. The formulation, i.e., the weight percentages, of the input PP, the coupling agent, and the olive pomace flour are listed in Table 2.

By using an aluminum mold, with 20 cells of the following measurements (L: $63.5 \pm 2 \times$ W: $6.4 \pm 0.2 \times$ T: $12.7 \pm 0.2 \text{ mm}$), the impact toughness test samples were prepared. Multiple sheets (L: $30 \times$ W: $20 \times$ T: 2 mm) from each formulation were obtained by using a stainless-steel mold in a thermal press machine XH-406B (Dongguan Xihua Testing Machine Co., Ltd., China). With an ASTM D-638 type IV specimen die, the tensile test samples of standard dumbbell shape were cut out from the composite sheets. The flexural test samples were prepared by using an iron mold with 10 cells of the following measurements (L: 200 ± 2 , W: 10 ± 0.2 , T: $4 \pm 0.2 \text{ mm}$).

2.2.3 Mechanical characterization

The composite samples were examined using a computer control electrical universal testing machine (WDW-5; DongGuan HongTuo Instruments Co., Ltd., Guangdong, China). It was operated at the rate of 1 mm/min using a 5 kN load cell. Tensile strength and Young's modulus were analyzed using dog-bone specimens according to ISO 257. The flexural test samples were measured according to BS EN ISO 178:2003. Un-notched IZOD impact strength was measured according to ASTM: D256 using a digital display Izod impact testing machine (FI-68; Forcome group Ltd. China) at an impact speed of 3.5 m/s. The results were obtained from an average of no less than five samples.

Table 2: Formulation of the composites

Sample	Weight percent (%)		
	PP	OPF	CA
Pure PP	100	0	0
PP + OPF	80	20	0
PP + P353	79	20	1
PP + P353	75	20	5
PP + P353	70	20	10
PP + P613	79	20	1
PP + P613	75	20	5
PP + P613	70	20	10

2.2.4 Water absorption test

The water absorption tests of the composite sample disks, each measuring 50 mm diameter and 3.4 mm thick, were conducted following the standard ASTM D570. The composite samples were immersed in distilled water at 25°C. Afterward, the samples were removed from the water and weighed on a digital balance scale. The water absorption uptake was recorded on daily basis for 45 days, after which the water absorption percent was calculated according to Eq. 1:

$$\text{Water absorption (\%)} = [(M_t - M)/M] \times 100\% \quad (1)$$

where M and M_t stand for the dry weight of the sample and the weight of the immersed sample at any specific time, respectively.

2.2.5 Scanning electron microscopy (SEM)

To characterize the morphological nature of the specimens, scanning electron microscopy (SEM) photomicrographs were taken of their fractured surfaces. This allowed a study of the physical distribution of the olive pomace flour and the effect of the various coupling agents on the OPF/PP composite. The fractured surfaces were made conductive by sputter-coating for 7 min at a beam current of 38–42 mA with a 100 Å layer of gold/palladium alloy in a vacuum chamber. The prepared samples were examined by a scanning electron microscope (Quanta 600) at an acceleration voltage of 25 kV. Representative micrographs were taken at certain magnification.

2.2.6 Differential scanning calorimetry (DSC)

In accordance with ASTM E 473-85, differential scanning calorimetry (DSC) on the specimens was performed in a NETZCH DSC 204 Phoenix[®] ASC device. In an aluminum crucible, the test specimens weighing 11–15 mg were heated to 200°C with a heating rate of 10°C/min. They were maintained at this temperature for 3 min to remove their thermal history. Next, they were cooled to –50°C at a cooling rate of 10°C/min and again kept at this temperature for 3 min. Once more, the specimens were heated to 200°C with a heating rate of 10°C/min. Note that all the heating and cooling procedures were performed in a nitrogen (N₂) atmosphere at a flow rate of 50 mL/min to prevent oxidation of the specimens. Using Eq. 2, the degree of crystallinity (X_c) was determined from the normalized melting enthalpy values:

$$X_c = (\Delta H_m / \Delta H_0) \times 100\% \quad (2)$$

where ΔH_m is the normalized melting enthalpy of the specimens (J/g) and ΔH_0 is the enthalpy value of the melting of a 100% crystalline of PP (207 J/g) (22).

3 Results and discussions

3.1 Mechanical characterization of the OPF/PP composites

3.1.1 Un-notched izod impact strength

Impact strength by definition is the amount of energy that a material can withstand when stress is suddenly applied (23). It is determined by the nature and distribution of filler, the coupling agents, the polymer matrix, the bonding, and the shape of the material (24). Figure 1 shows the impact strength (J/m) of the composite samples of PP with OPF and different percentages of two coupling agents. OPF was consistently added as 20 wt% fraction in all samples.

Pure PP has the lowest impact energy, 21 J/m. When the OPF was added, impact strength raised to 43 J/m. Additional improvements were seen when 1%, 5%, and 10% P353 coupling agent was added. These increases yielded 51, 103, and 141 J/m, respectively. The greatest impact strength of all composites was seen at 10% P353. Coupling agent P613 gave only minor impact strength

improvement even as its percentage increased in the composites. These were 53, 57, and 62 J/m at 1%, 5%, and 10%, respectively. For impact strength, it was consistently seen that a greater amount of coupling agent was correlated with greater impact strength, and the highest value was always achieved with 10% of the agent. P353 improved the impact strength more than P613; due to the presence of the ethylene–propylene copolymer with a high content of homo-polyethylene segment contributes to high impact strength compared to neat PP (25). The obtained result was in good agreement with the study carried out by Tan et al. (26) who reported that the impact strength can be significantly improved by increasing crystalline ethylene–propylene copolymer content, due to the better adhesion between the ethylene–propylene copolymer and the PP matrix. A higher impact strength indicates a greater ability to absorb energy, i.e., it has greater toughness. Adding the OPF without coupling agents increased the impact strength of pure PP two folds. This was caused by the good dispersion of the OPF within the PP matrix.

The coupling agent improves the impact strength of the sample by establishing either ester bonds or hydrogen bonds, or both, with the filler. The bonds are established when the maleic anhydride-modified polymer and polypropylene interact with the fillers. The results agreed well with Sobczak et al. (19) works, where the dependence of the impact strength on the interfacial behavior was explained by using crack initiation and plastic deformation mechanisms. Where crack initiation is dependent on defects' size introduced by the fillers. The possibility of a

Figure 1: Impact strength of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

Figure 2: Tensile stress at yield of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

filler particle initiating cracks is decreased by enhanced interfacial adhesion. Thus, impact strength can be increased by improved coupling action.

3.1.2 Tensile properties

Tensile strength is a measure of the ability of a material to tolerate tensile stress without failure when it is stretched or pulled. Tensile stress at yield is a measure of the ability of a material to return to its original dimensions after applied stress is removed (27). Figure 2 showed the tensile stress at yield of the composite samples of the PP with OPF and different percentages of two coupling agents. As the data reveals, the coupling agents gave a marginal improvement to tensile stress at yield as their percentage increased except in the case of 10% addition of P613

where the yield stress showed a significant improvement. Jancar et al. (28) developed a descriptive model for the stress at yield boundary values of particulate-filled polymer composite. They found that the filler content, with and without surface adhesion promotor, and the matrix ductility are the main elements in controlling the brittle fracture of the polymer composites. The increased upper limit to the stress that can be applied without causing permanent deformation may have attributed to strain hardening from 10% addition of anhydride PP coupling agent.

Tensile stress at rupture is the maximum stress a plastic can tolerate before it breaks (27). Figure 3 showed the tensile stress at rupture of the composite samples of the PP with OPF and different percentages of two coupling agents.

While adding OPF to PP significantly reduced tensile stress at rupture, because the filler content increases the

Figure 3: Tensile stress at rupture of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

degree of heterogeneity and thus the loss of mechanical properties (29), adding a coupling agent improved it. Moreover, the improvement increased as the percentage of added coupling agents was raised. The addition of P353 to PP/OPF had a relatively minor impact on the tensile stress at rupture at levels of 1% and 5%. But at 10%, the increase to 35 MPa was significant where the coupling agent increases the tensile stress at rupture by postponing the failure between the filler and the PP. The results for P613 showed very small increases with higher amounts of the coupling agent. Researchers such as Yang et al. (30) and Silva et al. (31) observed that further addition of fibers into polymer matrix led to fiber aggregation and even clusters formation, which means that the filler is not uniformly distributed. The existence of fiber aggregation has a negative result on the tensile stress at rupture of composites. The surfaces of the filler when chemically activated it would adhere with the polymer matrix, transfer force, and contribute to the reinforcing effect of the tensile strength of composites as clearly seen in the case of 10% P353 addition to PP matrix.

The change in the physical dimensions of the material relative to its unstressed dimensions is defined as the strain. By convention, tensile stress (σ) causes tensile strain (ϵ) (27). Figure 4 showed the tensile strain at a yield of the composite samples of the PP with OPF and different percentages of two coupling agents.

While adding OPF to PP significantly reduced tensile strain at yield, adding a coupling agent P353 marginally improved it. Moreover, the improvement slightly increased as the percentage of added coupling agent was raised. For pure PP, the highest value of the tensile strain at a yield 21% was measured. When the OPF was added, the tensile strain at yield dropped noticeably to 11%. Adding P353 had

a negligible impact on the tensile strain at yield whereas P613 had shown improvement to strain values. Where the anhydride-based coupling agent P613 increased the flexibility and the mobility of the polymer chains in the vicinity of the reversible elastic deformation region.

Tensile strain at break is a measure of the resistance to a change in the shape of a plastic specimen under stress (27). Figure 5 showed the tensile strain at break (%) of the composite samples of the PP with OPF and different percentages of two coupling agents. Tensile strain at break for pure PP was 20%. When the OPF was added, the tensile strain at break dropped appreciably to 12%. While adding OPF to PP significantly reduced tensile strain at break, adding P613 coupling agent improved it. The improvement increased as the percentage of added coupling agents was raised. At 10% P613, the tensile strain at break nearly approached the performance of pure PP. Tensile stress and strain at break values were found to decrease as OPF was added to the composites without coupling agents. The decrease of the stress as explained by Pérez et al. (32) indicates that filler particles debonded from the matrix before plastic deformation. The inclusion of the coupling agent allowed retaining the composite tensile stress and strain which led to the recovery of ductility especially in the case of P613. These results agreed well with the previously published work by Li and Li (33) and have been attributed to the enhancement in filler dispersion and interfacial interaction promoted by a coupling agent.

As shown in Figures 2–5, the following key results were noted, all four measured stress and strain characteristics of the samples decreased with the addition of OPF. These characteristics included the following: tensile stress at yield, tensile stress at rupture, tensile strain at yield, and tensile strain at break. All these decreases can

Figure 4: Tensile strain at yield of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

Figure 5: Tensile strain at break of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

be attributed to the relative lack of significant interfacial interaction between the OPF and the polymer matrix of PP. The strong hydrogen bonding between the molecules of the OPF limits their ability to diffuse to the hydrophobic polymer part. This causes them to agglomerate rather than diffuse and the filler interaction with the polymer matrix is thereby limited. There is thus an interruption in the transfer of stress along an applied force, thereby decreasing the measured tensile stress and tensile strain (14,34,35). When any of the used coupling agents were added to the OPF/PP composite, all the measured characteristics of the tensile stress and tensile strain demonstrated a similar behavior: The initial addition of 1% coupling agent generally increased the measured stress and strain characteristics. Increasing the percentage of coupling agent to 5% and then 10% gave a further increase. The increase in all four stress and strain

measured characteristics with the addition of coupling agent can be attributed to the improved dispersion of the OPF filler caused by the coupling agent. This improved dispersion enhances the interfacial adhesion between the filler and the polymer matrix of the polypropylene. In addition to that, the coupling agents establish either ester bonds or hydrogen bonds between the OPF and the polymer matrix (16,19).

Young's modulus is the ratio of stress to strain and is a measure of the stiffness of an elastic material (27). Figure 6 shows Young's modulus of the composite samples of PP with OPF and different percentages of two coupling agents.

Pure PP showed Young's modulus of 681 MPa. When OPF was added Young's modulus dropped to 242 MPa. The results for P353 were 389 MPa with 1%, 636 MPa with 5%, and 933 MPa with 10%, showing significant

Figure 6: Young's modulus of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

increases with higher amounts of the coupling agent. A notable result is that adding P353 can match and exceed Young's modulus of pure PP. The results for P613 were showing somewhat smaller increases with higher amounts of P613 coupling agent. As shown in Figure 6, Young's modulus showed a behavior similar to the stress and strain characteristics. It decreased with the addition of OPF alone and increased when a coupling agent was added to the OPF/PP composite. As the percentage of coupling agent increased, Young's modulus also increased. A particularly great increase was seen with 10% of coupling agent P353. The obtained results justified by Chow et al. (36) where the increase in modulus with the increase in coupling agent percentage may be traced to the compatibilizing and toughening contributions of the modified polypropylene copolymer to the composite matrix. The increase in Young's modulus noted with coupling agents resulted in the greater rigidity of the composite (35,37).

3.1.3 Flexural properties

The flexural strength of a material measures its resistance to deformation under load. Flexural strength specifies how much force is required to break a test sample of a given diameter (38). Maximum flexural stress is the highest point in the stress-strain curve of a material. It is a measurement widely used to predict the failure of composite materials (39). Figure 7 shows maximum flexural stress (MPa) of the composite samples of PP with OPF and different percentages of two coupling agents.

The pattern here is similar to what was seen previously. Adding OPF to PP decreases the maximum flexural stress considerably. Then adding a coupling agent

increases it; although the magnitude of the increase is relatively small for P613 and large for P353, at 10% coupling agent, the maximum flexural stress 23 MPa slightly exceeds that of PP 22 MPa.

The decrease in flexural stress of the composite compared to the neat PP polymer can be related to insufficient wetting of the OPF filler with the PP matrix, poor dispersion of OPF, presence of agglomerates, and poor adhesion between the filler and matrix (40,41).

The increase in flexural stress with the increase in coupling agent percentages may be attributed to the improvement in the interfacial interaction of the OPF with the PP especially in the presence of the chemically modified polypropylene copolymer P353. This is believed to be associated with the degree of dispersion and the interfacial interaction of the OPF and the PP matrix. This trend resembles that of the tensile properties. However, the flexural strength is almost one-half of the tensile stress due to the difference in the deformation mode (36).

A flexural strain of maximum force (in %) of the composite samples of PP with OPF and different percentages of two coupling agents is shown in Figure 8. Again, we see a similar pattern. Adding OPF to the PP decreases the flexural strain of maximum force. Then adding a coupling agent increases it, and a greater percentage of coupling agent gives a higher flexural strain of maximum force.

What is notable here, however, is that the effect of adding a coupling agent is significantly greater on the flexural strain of maximum force than on the maximum stress. In several cases, adding a coupling agent gave a higher flexural strain of maximum force that was seen on pure PP. In summary, as shown in Figures 7 and 8, the measured maximum flexural stress and strain of OPF/PP

Figure 7: Maximum flexural stress of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

Figure 8: Flexural strain of the maximum force of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

composite samples decreased with the addition of OPF. The decrease can be attributed to the increased phase incompatibility of the polymer composite with the addition of OPF causing reduced mobility of the polymer chains (15). Adding either coupling agent then reverses the loss. A higher percentage of coupling agents further increases maximum flexural stress and strain. This occurs due to the improved dispersion of the OPF filler. It is the enhanced interfacial adhesion between the filler and the polymer matrix that results from the greater dispersion, thus raising the maximum flexural stress and strain. Where the coupling agents establish either ester bonds or hydrogen bonds between the OPF and the polymer matrix (16,39,42).

The flexural modulus is defined as the ratio of stress to strain when a material is subject to flexural deformation. It is a measure of the ability to resist bending (43). Figure 9

shows the flexural modulus of the composite samples of PP with OPF and different percentages of two coupling agents.

PP had a relatively high flexural modulus and adding OPF decreased it. For P353, a small increase was noted at 1% and 5%, followed by a large increase at 10%. P613 showed large increases in flexural modulus at 5% and 10% P. The basis for these behaviors can be elucidated by using the same reasons as formerly mentioned earlier. Moreover, the results seen suggest that the degree of backbone polymer similarity with the matrix that includes the coupling agents and filler may be an important factor in this behavior (19). P353, a chemically modified polypropylene copolymer, and P613, another anhydride-modified polypropylene showed increases in flexural modulus as the percentage of coupling agent increased. The similarity of the backbones of P613 with that of the polymer matrix is

Figure 9: Flexural modulus of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

a likely reason. Moreover, some superiority was observed for flexural modulus in the case of using P353 due to the toughening behavior of the modified polypropylene copolymer.

3.2 Water absorption properties

The water absorption test is a necessary evaluation tool for the durability of the WPC. An increase in water absorption of the lignocellulosic composite material may be associated with biological activity and the loss of some mechanical properties that would limit the product end-use (44). Water absorption percentage as a function of immersion time of OPF/PP composite material without any coupling agent as well as with two coupling agents in the following percentage 1%, 5%, and 10% are shown in Figure 10. Small incremental water absorption increases were often observed in the first days of immersion in water. Absorption then regularly slowed down until saturation was reached after about 36 days in most cases.

Pure PP showed a very small maximum water absorption of 0.17%. The addition of olive pomace without any coupling agent showed the highest water absorption of 1.36%. P353 and P613 at 1%, 5%, and 10% showed maximum water absorption values between 0.62% and 1.08%. It was thus observed that the water absorption increased measurably with the addition of the hydrophilic OPF filler to the polymer. The insignificant water absorption in PP confirms its hydrophobic nature. The highest increase in water absorption was seen when OPF was added to PP, due to the numerous hydroxyl groups of the lignocellulosic

filler available for interaction via hydrogen bonding with water molecules (45). This addition causes the development of microvoids. It was consistently seen that the use of coupling agents reduces the water absorption of the polymer matrix. It is the reaction between the hydroxyl group of filler and the polar group in coupling agents that lower the water absorption (4,34).

3.3 Scanning electron microscopy (SEM)

The SEM fractured surfaces of the polymer composites are presented in Figure 11. It is visually evident that the specimen with the filler at loading level 20% (Figure 11b) morphologically differs significantly from that of pure PP polymer (Figure 11a). The former surface appears relatively smooth under the SEM, while the latter shows large ridges.

In Figure 11b, it is evident that voids and cavities exist on the surface of the specimen. This indicates that during the fracture, particles of OPF were separated from the PP matrix. It is notable that adding OPF to PP increases the impact strength. The impact strength of PP/OPF 20 wt% (without any coupling agent) was measured at double that of pure PP. This increase in impact strength can be attributed to the good dispersion of OPF filler within the PP polymer matrix as observed in Figure 11b. The opposite however was seen regarding tensile strength and flexural strength. For these parameters, PP/OPF showed lower values than the pure PP. These decreases can be attributed to the relative lack of significant interfacial interaction and are likely due to

Figure 10: Water absorption of the pure PP, uncoupled, and coupled 20% OPF/PP polymer composite with two coupling agent types of different weight percentages.

Figure 11: SEM micrographs of the fractured surface: (a) pure PP, (b) PP/OPF composite without coupling agent, (c) PP/OPF composite with 10% P353, (d) PP/OPF composite with 10% P613.

poor adhesion between the OPF and the polymer matrix of PP. This causes OPF to hardly diffuse, and the filler interaction with the polymer matrix is thereby limited (35,37). The mechanical and physical parameters of the composites are changed by the addition of coupling agents. The agents lower the interfacial tension of the composites, altering their internal structure by reducing agglomeration and voids. This is observed in the improved physical and mechanical properties of the composites (15,35). Their effect on the OPF/PP at 10% coupling agents is seen in Figure 11c and d. As the data previously discussed indicate, the adherence of the coupling agent at 10% with the polymer matrix in all cases improved the impact, tensile, and flexural parameters of the composites relative to their values at 0%, 1%, and 5%.

3.4 Differential scanning calorimetry (DSC)

By definition, differential scanning calorimetry (DSC) is a measure of the change in the heat flow rate to a given sample relative to a reference sample when they are subjected to a controlled temperature program (46). DSC was used to study the thermal properties of OPF/PP composites. It was observed that the melting temperature T_m of the OPF/PP composites slightly decreased with the initial addition of OPF. Noteworthy is the minor change in T_m caused by the subsequent addition of the two coupling agents to the composite polymer matrix (Table 3). This small change is likely caused by the coupling agent's enhancement of the intermolecular forces in the filler-polymer matrix, which limits the reduction of melting temperature, unlike what occurs in an uncompatibilized polymer composite (47).

While the melting enthalpy of neat PP was 123 J/g, the normalized melting enthalpy (ΔH_m) of the 20% OPF/PP composition, 99 J/g, decreased with the initial addition of OPF due to the decrease in polymer crystallinity. Likewise, the subsequent addition of the coupling agent P353 decreased

Table 3: Thermal parameters of the OPF/PP composites extracted from DSC thermographs

Composite type	ΔH_c (J/g)	T_c (°C)	ΔH_m (J/g)	T_m (°C)	X_c
Pure PP	133	116.6	123	166.4	59
OPF/PP	109	116.6	99	165.8	48
P353 (10%)	103	116	91	166.1	44
P613 (10%)	112	117.9	102	166.8	49

the melting enthalpy to 91 J/g, but the addition of the coupling agent P613 increased the melting enthalpy to 102 J/g, due to the structural differences between the two coupling agents. Table 3 clarifies that the degree of crystallinity (X_c) of pure PP, 59%, which is directly proportional to the melting enthalpy, decreased with the addition of OPF to the polymer matrix. Thus, the addition of PP to OPF diminishes both the crystallinity of PP and phase continuity. It was found that when crystallinity decreases the mechanical properties may decrease unless interfacial adhesion compensates for the loss of crystallinity (48). OPF is a wood and lignocellulosic material. These are complex substances consisting mostly of cellulose, hemicellulose, and lignin. Cellulose is the crystalline structure of wood whereas hemicelluloses and lignin are amorphous structures (49). The subsequent addition of coupling agents caused further decreases in PP crystallization especially when P353 was added, because of the polypropylene copolymer structure that differs from the PP in the composite matrix. However, the decrease in polymer matrix crystallinity may be attributed to the coupling effect that limited the polymer chain mobility. The crystallization temperatures of PP (117°C) slightly changed after the addition of OPF and the subsequent addition of two coupling agents. The normalized crystallization enthalpy (ΔH_c) of PP decreased significantly after the addition of OPF and P353. Minor change in ΔH_c was caused by the subsequent addition of the coupling agent P613 to the composite polymer matrix due to the structural similarities between the coupling agent and the polymer matrix in the composite. In summary, DSC analysis showed that the melting temperature (T_m) and crystallization temperature (T_c) did not significantly change on the addition of filler and coupling agents. On the other hand, normalized melting, crystallization enthalpies (ΔH_m , ΔH_c), and the degree of crystallinity (X_c) of OPF/PP composites decreased with the initial addition of the filler and coupling agent P353. Furthermore, the subsequent addition of the coupling agent P613 had a small effect on melting and crystallization enthalpies and the degree of crystallinity.

4 Conclusion

The addition of the 20 wt% OPF alone as well as with the addition of two different coupling agents with 1%, 5%, and 10% weight fractions significantly improved the impact strength of OPF/PP composite materials. The measured tensile and flexural stress and strain characteristics decreased with the addition of OPF. These include tensile and flexural

stress at yield, stress at rupture, strain at yield, and strain at break. All these decreases can be attributed to the relative lack of significant interfacial interaction between the OPF and the polymer matrix of PP. When either of the coupling agents was added to the OPF/PP composite, all the measured characteristics of tensile and flexural stress and strain, as well as modulus, demonstrated increases. These increases can be attributed to the improved dispersion of the OPF filler caused by the coupling agent. This improved dispersion, which has been seen in SEM micrographs, enhances the interfacial adhesion between the filler and the polymer matrix of the PP. In particular, coupling agents permit the use of the OPF as a viable reinforcement to PP, resulting in a usable bio-based composite. Thermal properties related to T_m and T_c values of the modified composites did not show significant change compared to the neat PP. However, ΔH_m , ΔH_c , and X_c values showed a declining trend when filler and coupling agents were added to the composite material compared to the neat PP matrix. The addition of OPF to pure PP did result in a significant increase in its water absorption. However, the subsequent addition of either of the tested coupling agents reduced the water absorption property of the composite. A coupling agent based on chemically modified polypropylene copolymer, P353, provided the OPF/PP composite material with better tensile and flexural performance, lesser water uptake, lower percent crystallinity, and slightly lower melting but higher crystallization temperature compared to the coupling agent based on the anhydride-modified polypropylene, P613. Finally, the addition of OPF and coupling agents to PP makes it a somewhat more environmentally friendly product. In particular, this composite can be viewed as a partially green alternative to conventional polymers in the production of packaging materials.

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References

- (1) Lammi S, Barakat A, Mayer-Laigle C, Djenane D, Gontard N, Angellier-Coussy H. Dry fractionation of olive pomace as a sustainable process to produce fillers for biocomposites. *Powder Technol.* 2018;326:44–53. doi: 10.1016/j.powtec.2017.11.060.

- (2) Kaya N, Atagur M, Akyuz O, Seki Y, Sarikanat M, Sutcu M, et al. Fabrication and characterization of olive pomace filled PP composites. *Compos B Eng* 150:277–83. doi: 10.1016/j.compositesb.2017.08.017.
- (3) Gümüş BE, Yağci Ö, Erdoğan DC, Taşdemir M. Dynamical mechanical properties of polypropylene composites filled with olive pit particles. *J Test Eval*. 2019;47(4):2551–61. doi: 10.1520/JTE20180198.
- (4) Ayırlmis N, Buyuksari U. Utilization of olive mill sludge in manufacture of lignocellulosic/polypropylene composite. *J Mater Sci*. 2009;45(5):1336–42. doi: 10.1007/s10853-009-4087-2.
- (5) Farag E, Alshebani M, Elhrari W, Klash A, Shebani A. Production of particleboard using olive stone waste for interior design. *J Build Eng*. 2020;1(29):101119. doi: 10.1016/j.jobbe.2019.101119.
- (6) Hamida B, Ahmed M, Nadia N, Samira M. Mechanical properties of polystyrene/olive stone flour composites. *Res J Pharm Biol Chem Sci*. 2015;6(3):127–32.
- (7) La Mantia F, Dintcheva NT, Morreale M, Vaca-Garcia C. Green composites of organic materials and recycled post-consumer polyethylene. *Polym Int*. 2004;53(11):1888–91. doi: 10.1002/pi.1614.
- (8) Koutsomitopoulou AF, Bénétet JC, Bergeret A, Papanicolaou GC. Preparation and characterization of olive pit powder as a filler to PLA-matrix bio-composites. *Powder Technol*. 2014;255:10–6. doi: 10.1016/j.powtec.2013.10.047.
- (9) Naghmouchi I, Mutjé P, Boufi S. Polyvinyl chloride composites filled with olive stone flour: Mechanical, thermal, and water absorption properties. *J Appl Polym Sci*. 2014;131(22):41083–92. doi: 10.1002/app.41083.
- (10) Tasdemir M. Effects of olive pit and almond shell powder on polypropylene. *Key Eng Mater*. 2017;733:65–8. doi: 10.4028/www.scientific.net/KEM.733.65.
- (11) Tasdemir M. Polypropylene/olive pit & almond shell polymer composites: wear and friction. *IOP Conf Ser Mater Sci Eng*. 2017;204(1):012015. doi: 10.1088/1757-899X/204/1/012015.
- (12) Azwa ZN, Yousif BF, Manalo AC, Karunasena W. A review on the degradability of polymeric composites based on natural fibres. *Mater Des*. 2013;1(47):424–42. doi: 10.1016/j.matdes.2012.11.025.
- (13) Lin Q, Zhou X, Dai G. Effect of hydrothermal environment on moisture absorption and mechanical properties of wood flour-filled polypropylene composites. *J Appl Polym Sci*. 2002;85(14):2824–32. doi: 10.1002/app.10844.
- (14) Islam MR, Beg MDH. Effect of coupling agent on mechanical properties of composite from kenaf and recycled polypropylene. In *National Conference in Mechanical Engineering Research and Postgraduate Studies, Faculty of Mechanical Engineering UMP Pekan, Pahang Malaysia 2010*; 2010. p. 871–75.
- (15) Kim HS, Lee BH, Choi SW, Kim S, Kim HJ. The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled polypropylene composites. *Compos A Appl Sci Manuf*. 2007;38(6):1473–82. doi: 10.1016/j.compositesa.2007.01.004.
- (16) Poletto M. Polypropylene-based wood-plastic composites: effect of using a coupling agent derived from a renewable resource. *Maderas Ciencia y Tecnología*. 2017;19(3):265–72. doi: 10.4067/S0718-221X2017005000022.
- (17) Naghmouchi I, Mutjé P, Boufi S. Olive stones flour as reinforcement in polypropylene composites: A step forward in the valorization of the solid waste from the olive oil industry. *Ind Crop Prod*. 2015;15(72):183–91. doi: 10.1016/j.indcrop.2014.11.051.
- (18) Karmarkar A, Chauhan SS, Modak JM, Chanda M. Mechanical properties of wood-fiber reinforced polypropylene composites: effect of a novel compatibilizer with isocyanate functional group. *Comp A Appl Sci Manuf*. 2007;38(2):227–33. doi: 10.1016/j.compositesa.2006.05.005.
- (19) Sobczak L, Welsner R, Brüggemann O, Haider A. Polypropylene (PP)-based wood polymer composites: Performance of five commercial maleic anhydride grafted PP coupling agents. *J Thermoplast Compos Mater*. 2014;27(4):439–63. doi: 10.1177/0892705712447806.
- (20) Valvez S, Maceiras A, Santos P, Reis PN. Olive stones as filler for polymer-based composites: a review. *Materials*. 2021;14(4):845. doi: 10.3390/ma14040845.
- (21) Dow Chemical Company. Technical data sheet. Midland, Michigan, United states: Dow Chemical Company; 2019. <http://www.dow.com>
- (22) Gee DR, Melia TP. Thermal properties of melt and solution crystallized isotactic polypropylene. *Die Makromolekulare Chemie Macromol Chem Phys*. 1970;132(1):195–201. doi: 10.1002/macp.1970.021320117.
- (23) Swallowe GM, editor. Mechanical properties and testing of polymers: an a–z reference. Dordrecht, The Netherlands: Springer Science & Business Media; 1999. doi: 10.1007/978-94-015-9231-4.
- (24) Bax B, Müssig J. Impact and tensile properties of PLA/Cordenka and PLA/flax composites. *Compos Sci Technol*. 2008;68(7–8):1601–7. doi: 10.1016/j.compscitech.2008.01.004.
- (25) Rungswang W, Saendee P, Thitisuk B, Pathaweeisariyakul T, Cheevasrirungruang W. Role of crystalline ethylene-propylene copolymer on mechanical properties of impact polypropylene copolymer. *J Appl Polym Sci*. 2013;128(5):3131–40. doi: 10.1002/app.38495.
- (26) Tan H, Li L, Chen Z, Song Y, Zheng Q. Phase morphology and impact toughness of impact polypropylene copolymer. *Polymer*. 2005;46(10):3522–7. doi: 10.1016/j.polymer.2005.02.088.
- (27) Davis JR, editor. Tensile testing. USA: ASM International; 2004.
- (28) Jancar J, Dianselmo A, Dibenedetto AT. The yield strength of particulate reinforced thermoplastic composites. *Polym Eng Sci*. 1992;32(18):1394–9. doi: 10.1002/pen.760321809.
- (29) Mbarek TB, Robert L, Hugot F, Orteu JJ. Mechanical behavior of wood-plastic composites investigated by 3D digital image correlation. *J Compos Mater*. 2011;45(26):2751–64. doi: 10.1177/0021998311410466.
- (30) Yang Q, He X, Liu X, Leng FF, Mai YW. The effective properties and local aggregation effect of CNT/SMP composites. *Compos Part B Eng*. 2012;43(1):33–8. doi: 10.1016/j.compositesb.2011.04.027.
- (31) Silva J, Lanceros-Mendez S, Simoes R. Effect of cylindrical filler aggregation on the electrical conductivity of composites. *Phys Lett A*. 2014;378(40):2985–8. doi: 10.1016/j.physleta.2014.08.011.

- (32) Pérez E, Famá L, Pardo SG, Abad MJ, Bernal C. Tensile and fracture behavior of PP/wood flour composites. *Compos B Eng*. 2012;43(7):2795–800. doi: 10.1016/j.compositesb.2012.04.041.
- (33) Li TQ, Li RKY. Impact behavior of sawdust/recycled-PP composites. *J Appl Polym Sci*. 2001;81(6):1420–8. doi: 10.1002/app.1567.
- (34) Butylina S, Martikka O, Kärki T. Properties of wood fibre-polypropylene composites: effect of wood fibre source. *Appl Comp Mater*. 2011;18(2):101–11. doi: 10.1007/s10443-010-9134-2.
- (35) Amar B, Salem K, Hocine D, Chadia I, Juan MJ. Study and characterization of composites materials based on polypropylene loaded with olive husk flour. *J Appl Polym Sci*. 2011;122(2):1382–94. doi: 10.1002/app.34084.
- (36) Chow WS, Bakar AA, Ishak ZM, Karger-Kocsis J, Ishiaku US. Effect of maleic anhydride-grafted ethylene-propylene rubber on the mechanical, rheological and morphological properties of organoclay reinforced polyamide 6/polypropylene nanocomposites. *Eur Polym J*. 2005;41(4):687–96. doi: 10.1016/j.eurpolymj.2004.10.041.
- (37) Banat R, Fares MM. Olive oil waste filled high density polyethylene bio-composite: mechanical, morphological and water absorption properties. *Int J Compos Mater*. 2015;5(5):133–41. doi: 10.5923/j.cmaterials.20150505.05.
- (38) Ashby M. *Materials selection in mechanical design*. London: Butterworth-Heinemann; 2011. p. 40. doi: 10.1051/jp4:1993701.
- (39) Feng NL, Malingam SD, Irulappasamy S. Bolted joint behavior of hybrid composites. In *failure analysis in biocomposites, fibre-reinforced composites and hybrid composites*. Sawston, Cambridge: Woodhead Publishing; 2019. p. 79–95. doi: 10.1016/B978-0-08-102293-1.00004-8.
- (40) Shumigin D, Tarasova E, Krumme A, Meier P. Rheological and mechanical properties of poly(lactic) acid/cellulose and LDPE/cellulose composites. *Mater Sci*. 2011;17(1):32–7. doi: 10.5755/j01.ms.17.1.245.
- (41) Reyes JEP. Effect of surface treatment and particle loading on the mechanical properties of CFB fly ash reinforced thermoset composite. *Int J Chem Eng Appl*. 2015;6(1):6–11. doi: 10.7763/IJCEA.2015.V6.441.
- (42) Ashori A, Nourbakhsh A. Preparation and characterization of polypropylene/wood flour/nanoclay composites. *Eur J Wood Wood Prod*. 2011;69(4):663–6. doi: 10.1007/s00107-010-0488-9.
- (43) Zweben C, Smith WS, Wardle MW. Test methods for fiber tensile strength, composite flexural modulus, and properties of fabric-reinforced laminates. In *Composite materials: testing and design (fifth conference)*. USA: ASTM International; 1979. doi: 10.1520/STP36912S.
- (44) Ibach RE, Gnatowski M, Sun G. Field and laboratory decay evaluations of wood-plastic composites. *Forest Prod J*. 2013;63(3–4):76–87. doi: 10.13073/FPJ-D-12-00115.
- (45) Nachtigall SM, Cerveira GS, Rosa SM. New polymeric-coupling agent for polypropylene/wood-flour composites. *Polym Test*. 2007;26(5):619–28. doi: 10.1016/j.polymertesting.2007.03.007.
- (46) Höhne G, Hemminger WF, Flammersheim HJ. *Differential scanning calorimetry*. Berlin Heidelberg: Springer Science & Business Media; 2003. doi: 10.1007/978-3-662-06710-9.
- (47) Banat R, Fares MM. Thermo-gravimetric stability of high density polyethylene composite filled with olive shell flour. *Am J Polym Sci*. 2015;5(3):65–74. doi: 10.5923/j.ajps.20150503.02.
- (48) Sharma R, Maiti SN. Effects of crystallinity of polypropylene (PP) on the mechanical properties of PP/styrene-ethylene-butylene-styrene-g-maleic anhydride (SEBS-g-MA)/teak wood flour (TWF) composites. *Polymer Bull*. 2015 Mar;72(3):627–43. doi: 10.1007/s00289-014-1296-x.
- (49) Ndiaye D, Tidjani A. Effects of coupling agents on thermal behavior and mechanical properties of wood flour/polypropylene composites. *J Compos Mater*. 2012;46(24):3067–75. doi: 10.1177/0021998311435675.