Potential Use of Hazelnut Husk in Recycled High-Density Polyethylene Composites

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Hazelnut husk was considered as a potential filler for thermoplastic composites. Different amounts of hazelnut husk flour and the recycled high-density polyethylene (R-HDPE) were used as the filler and polymer matrix, respectively. The composite compounds were produced using single-screw extrusion compounding, and then composite panels were prepared by hot-press compression molding. The morphological, physical, mechanical, and thermal properties, as well as the biological durability of the composites, were evaluated. The flexural and tensile modulus of the composites improved with increasing hazelnut husk filler content, whereas the physical properties, biological durability, and the flexural and tensile strengths were reduced. With the addition of a maleic anhydrite-grafted polyethylene (MAPE), the hazelnut husk filler was more finely dispersed within the polymer matrix and the degree of crystallinity was lower than that of the R-HDPE. This research revealed that hazelnut husk flour has potential for use as a filler in R-HDPE composites.

Keywords: Recycled high-density polyethylene; Polymer composites; Mechanical properties; Differential scanning calorimetry; Scanning electron microscopy

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INTRODUCTION

Thermoplastic composites have attracted significant interest from the building industry in recent years and are being used extensively because of their outstanding properties, such as enhanced strength and stiffness, low cost, effectual recyclability, and high dimensional stability. Therefore, their market share has increased rapidly over the last several years. Polymer composites are made of lignocellulosic (wood or annual plant fiber) and thermoplastic (high density polyethylene (HDPE), polypropylene (PP), and polyvinyl chloride (PVC)) materials (Bledzki *et al*. 2006; Hosseinihashemi *et al*. 2016). Wood fibers are increasingly used for the reinforcement in polymer composites, as they are renewable, nonabrasive, and economical, in addition to exhibiting low density and low carbon dioxide emissions. On the other hand, wood consumption is increasing daily because of rapid population growth. In light of environmental awareness, alternative materials are being considered and evaluated to meet the growing demand for the wood industry and the need for sustainable environmental management. Consequently, various annual plants and agro-waste have been utilized in the manufacturing of polymer composites (Bledzki and Gassan 1999; Chaharmahali *et al*. 2008).

Turkey is the largest hazelnut producer in the world, with an annual production of 660,000 tons. Nearly 70% of the world's hazelnut production is in Turkey, followed by Italy, USA, and Spain (Kilic *et al.* 2009). Accordingly, every year, approximately 260,000 tons of hazelnut husk, the leafy outer covering of the hazelnut, is produced (Tufan *et al.*

2015a). In general, after kernel harvesting, the hazelnut husk stays in the field, is burned in the stove in winter, or is left for biodegradation for soil enrichment.

The use of hazelnut husk in the production of wood-based panels such as particleboard or medium density fiberboard (MDF) was investigated in previous studies (Çöpür *et al.* 2007, 2008). These studies showed that hazelnut husk can be efficiently used in the wood-based panel production. For example, Çöpür *et al.* (2007) reported that the internal bond strength of the particleboards made from hazelnut husk and urea-formaldehyde resin met the requirement for the general purpose particleboard standard, which is European Norm (EN 312, 1996). They concluded that the hazelnut husk was a valuable renewable natural resource for particleboard production and could be utilized as a substitute for wood particles in the particleboard production. In another study, Çöpür *et al.* (2008) reported that MDF panels containing hazelnut husk flour up to 20 wt% had minimum mechanical properties that met general purpose MDF requirements of EN 622-5 (1999) standard. The hazelnut husk could play an important role in the manufacture of thermoplastic composites and may be the most efficient use of the hazelnut husk in the countries which produce hazelnut.

The aim of this study was to determine the dimensional stability, mechanical properties, decay resistance, melting, and crystallization behavior of thermoplastic composites produced from hazelnut husk flour and recycled high-density polyethylene (R-HDPE), with and without the addition of maleic anhydrite-grafted polyethylene (MAPE) as a coupling agent.

EXPERIMENTAL

Materials

The hazelnut husk waste was obtained the agricultural waste left in fields after harvesting from Giresun province in Northeast Turkey. The polymer matrix, R-HDPE, was supplied by Ayan Plastic Co. Ltd., Samsun, Turkey. The coupling agent, MAPE (Clariant Licocene® PE MA4351GR, Muttenz, Switzerland), was obtained from commercial sources. Its viscosity and density were 200 to 500 mPA·s (QM-AA-158 at 140 °C) and 0.98 to 1.00 g/cm^3, respectively. The compositions of various hazelnut husk flour-filled polymer composites are presented in Table 1.

Table 1. Composition of Polymer Composites by Weight

Composite group code	HAZELNUT HUSK (%)	R-HDPE (%)	MAPE (%)
A	30	70	-
B	30	67	3
C	40	60	-
D	40	57	3
E	50	50	-
F	50	47	3
G	60	40	-
H	60	37	3

Note: **R-HDPE:** Recycled high-density polyethylene, **MAPE:** Maleic anhydrite-grafted polyethylene.

Preparation of Polymer Composites

The air-dried hazelnut husk waste was milled using a laboratory type Wiley mill (Fritsch pulverisette 19, Idar-Oberstein, Germany). The flour was screened to 60- and 80-mesh sizes, and these particles were dried for 24 h at 103 ± 2 °C. The hazelnut husk flour was mixed with the R-HDPE and MAPE using a laboratory mixer (Shini SVM-80U, China). This mixture was compounded in a single-screw laboratory extruder (Rondol linear 30, UK, L/D ratio 30:1). The temperature increase in the barrel was 170 °C, 175 °C, 180 °C, and 185 °C, respectively. The screw speed was calibrated at 70 rpm. The extruded samples were cooled and cut into pellets. Finally, the pellets were compressed into 150 (length) mm × 170 (width) mm × 5 (thickness) mm size composites for 3 min at 170 °C.

Methods

Chemical composition of hazelnut husk

The hazelnut husk waste was milled in a Wiley mill. The flour was screened to 60 mesh, and these particles were used for analysis. The ash content was determined according to the TAPPI T-211 om-85 method. The hot water solubility, 1% NaOH solubility, alcohol cyclohexane solubility, and alcohol solubility were determined according to TAPPI methods T-207 om-88, T-212 om-88, and T-204 om 88, respectively. Holocelluloses were prepared using sodium chlorite solution and acetic acid at 75°C according to Wise *et al.* (1946). The acid-insoluble lignin content was estimated according to the method of Runkel and Wilke (1951), using a mixture of 72% sulfuric and 40% hydrobromic acid. Each experiment was replicated twice and the results indicate the average values of the replicated experiments.

Physical properties

For the water absorption (WA) and thickness swelling (TS) tests, 50 mm (L) × 50 mm (W) × 5 mm (T) specimens were prepared. The water temperature was 23 ± 2 °C. Seven replicate specimens of each formulation were tested. The polymer composite test specimens were immersed in a container of water at room temperature for 1, 7, 14, and 28 days. At the end of each immersion time, the specimens were taken out of the container and all surface water was removed using a clean dry cloth. The specimens were then immediately weighed and measured.

Mechanical properties

The flexural and tensile properties of all samples were determined according to ASTM D790-10 (2010) and ASTM D683-10 (2010) standards, respectively, using a Zwick 10-kN universal testing machine (Zwick Inc., Germany). In the three-point flexural test, specimens with dimensions of 150 (L) mm × 12.7 (W) mm × 3.5 (T) mm were used at a crosshead speed of 2 mm/min. For the tensile test (dogbone, type III), the crosshead speed was set at 5 mm/min. The Izod impact strength of the specimens was determined according to ASTM D256-10 (2010) using a HIT5.5P Testing Machine manufactured by Zwick Inc. All the samples were notched in the centre according to the ASTM standard. Seven replicate specimens of each polymer composite group were tested to determine their flexural and tensile properties.

Scanning electron microscopy

The surface morphology of the polymer composite samples of ID groups E and F were observed using a Zeiss scanning electron microscope (SEM) (Zeiss Evo/LS10, Germany). The samples were first dipped in liquid nitrogen and then broken through the middle. All of the samples were coated with gold (Cressington Sputter Coater 108, Ted Pella Inc., USA) under the 50 mbar vacuum for 1 second to eliminate electron charging.

Decay test

A decay test, using part of the moulded samples, was performed in accordance with the European Standard BS EN 113 (1997). One white rot fungus, *Trametes versicolor* (L.) Pilat (Mad-697), and one brown rot fungus, *Postia placenta* (Fr.) M.J. Larsen and Lombard (Mad-698-R), were used for the decay tests (USDA Forest Service, Madison, Wisconsin, USA). The samples were exposed to the fungi for 16 weeks. For each type of sample, four replications were conducted, and the mass loss data were collected after the end of the test.

Differential scanning calorimetry (DSC) analysis

The thermal analyzer (STA 8000, PerkinElmer, USA) was used for the differential scanning calorimetry (DSC) analysis of the samples. The heating rate was 10 °C/min, at a nitrogen flow rate of 20 mL/min, from room temperature to 250 °C. The corrected crystallinity levels, X_c, of the R-HDPE samples were calculated using Eq. 1,

$$X_c = (\Delta H_{exp} / \Delta H) \times (1/W_f) \times 100 \tag{1}$$

where ΔH_{exp} is the experimental heat determined from the DSC results, ΔH is the assumed heat of the R-HDPE (293 J/g), and W_f is the weight fraction of the R-HDPE. The second melting enthalpy values were used for the calculation of X_c.

Statistical analyses

The mechanical, physical, and decay tests were evaluated with analysis of variance. All means were compared using the Duncan multiple comparison test with a 95% confidence interval using Statistical Package for the Social Sciences statistical program (SPSS Version 19, 2010).

RESULTS AND DISCUSSION

Chemical Composition of Hazelnut Husk

The chemical composition of the hazelnut husk particles is presented in Table 2. The amounts of average holocellulose, α cellulose, and lignin of hazelnut husk were found to be 54.51%, 30.59%, and 32.65%, respectively. The average holocellulose and lignin contents of softwoods and hardwoods are reported as 64.5% to 28.8% and 71.7% to 23.0% in the literature, respectively (Rowell 2013). As compared to rice husk (holocellullose: 46.3%, lignin: 37.1%) or wheat husk (holocellulose: 63.0% and lignin: 28.3%), which is widely used in manufacture of thermoplastic composites, the hazelnut husk had higher holocellullose and lignin contents (Thakur 2014). As compared to the softwoods or hardwoods, higher lignin content of hazelnut husk shows that higher hydrophobicity and stiffness. Primarily, lignocellulosic fillers contain holocellulose (cellulose and hemicellulose) and lignin. The properties of each constituent contribute to the overall properties of the lignocellulosic fillers.

Table 2. Chemical Composition of Hazelnut Husk

Property	Min. value (%)	Max. value (%)	Average value (%)
Ash content[a]	6.57	6.59	6.58
Hot water solubility[a]	22.06	22.60	23.36
% 1 NaOH solubility[a]	55.37	57.50	56.59
Alcohol cyclohexane solubility[a]	4.95	5.13	5.05
Alcohol solubility[a]	1.49	1.60	1.22
Lignin content[b]	32.37	31.72	32.65
Holocellulose content[b]	54.39	54.63	54.51
α cellulose[b]	30.59	31.72	31.15

Note: a: The values are based on the oven-dry material; b: Based on extracted material.

Physical Properties

The water absorption (WA) and thickness swelling (TS) values for polymer composites are presented in Table 3. The WA and TS values increased with increasing hazelnut husk flour content in the composites. The highest WA and TS values, 25.03% and 8.43%, respectively, were determined in composites filled with 60% hazelnut husk flour (group code G), without the coupling agent, after 28 days. The water absorption was more pronounced in the specimens compared to the thickness swelling. The water absorption values were always higher than the swelling values. The swelling and absorption of the specimens were significantly affected by the submersion time. The lignocellulosic material is the hydrophilic component of the composites, while the polymer matrix has hydrophobic properties. Therefore, the WA and TS rates increased as the amount of hazelnut husk flour increased in the polymer composites. Moreover, the HDPE is hydrophobic in nature, and the hazelnut husk flour was not sufficiently encapsulated by the polymer matrix, R-HDPE, as its content increased in the composite. As a result, water molecules could more easily penetrate the interior of the polymer composites (Khanjanzadeh *et al.* 2012). The water absorption of thermoplastics filled with lignocellulosic depends on the gaps and flaws at the interfaces, micro-cracks in the matrix formed during the compounding process, fine pores, and the number of free hydroxyl groups of the lignocellulosic. The presence of voids and defects located in the filler/matrix interface was due to poor dispersion of the filler in the polymer matrix. The number of the voids and defects in the R-HDPE composite increased with increasing content of the filler. The SEM micrographs of the tensile fracture surface of the composites confirmed a loss of interfacial bonding between the filler and the polymer matrix. It is clearly shown in Fig. 1A that there was no a good surface interaction between the filler and R-HDPE matrix in the absence of MAPE. The amounts of voids and defects between the filler and polymer matrix decreased as the compatibilizer MAPE was incorporated in the composite. The strong bond between the filler and R-HDPE is shown in Figure 1B. Different from untreated composites, the fibers of hazelnut in the maleated composites had a rougher fractural surface. It indicated that a maleated copolymer indeed strengthened the interfacial adhesion through chemical bonding.

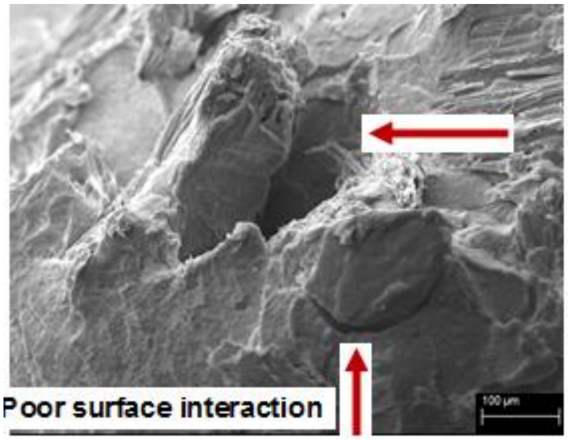

Fig. 1A. The SEM images of the polymer composites produced without MAPE (50 wt% hazelnut husk flour+50 wt% R-HDPE).

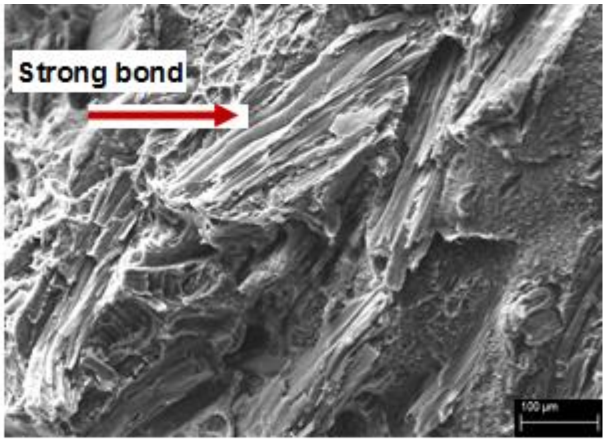

Fig. 1B. The SEM images of the polymer composites with MAPE (50 wt% hazelnut husk flour+47 R-HDPE+wt% 3 MAPE)

Table 3. Physical Properties of Polymer Composites

Group code	Water absorption rate (%)					Thickness swelling rate (%)				
	1 Day	1 Week	2 Weeks	3 Weeks	4 Weeks	1 Day	1 Week	2 Weeks	3 Weeks	4 Weeks
A	1.96 ***ab*** (0.32)	4.38 ***b*** (0.41)	5.68 ***b*** (0.52)	6.80 ***b*** (0.59)	7.88 ***b*** (0.61)	0.75 ***a*** (0.23)	2.10 ***ab*** (0.94)	2.20 ***a*** (1.11)	2.20 ***ab*** (1.62)	2.34 ***a*** (1.28)
B	1.28 ***a*** (0.10)	2.13 ***a*** (0.36)	3.17 ***a*** (0.45)	3.71 ***a*** (0.53)	4.40 ***a*** (0.63)	0.74 ***a*** (0.65)	1.12 ***a*** (0.58)	1.52 ***a*** (1.08)	1.58 ***a*** (1.13)	1.91 ***a*** (1.38)
C	3.17 ***cd*** (0.42)	7.50 ***c*** (1.26)	10.50 ***d*** (1.87)	12.87***d*** (2.58)	15.05 ***d*** (3.01)	1.26 ***a*** (0.46)	2.65 ***bc*** (0.41)	3.42 ***bc*** (1.23)	3.81 ***c*** (0.55)	4.51 ***c*** (0.48)
D	2.53 ***bc*** (0.30)	4.77 ***b*** (1.26)	7.48 ***c*** (0.83)	10.76 ***c*** (0.79)	11.84 ***c*** (0.88)	1.04 ***a*** (0.44)	1.71 ***ab*** (0.27)	2.45 ***ab*** (0.30)	2.69 ***b*** (0.60)	3.31 ***b*** (0.38)
E	5.95 ***e*** (1.60)	10.61 ***d*** (1.06)	15.64 ***f*** (1.44)	18.02 ***e*** (1.18)	21.66 ***f*** (1.99)	2.67 ***bc*** (1.33)	2.81 ***bc*** (1.45)	5.01 ***d*** (1.70)	5.08 ***d*** (0.96)	5.44 ***c*** (0.86)
F	3.48 ***d*** (0.35)	6.92 ***c*** (1.38)	9.99***d*** (0.61)	13.15***d*** (1.71)	17.63 ***e*** (0.77)	2.26 ***b*** (1.50)	3.71 ***cd*** (1.58)	3.97 ***cd*** (1.12)	4.30 ***cd*** (1.10)	4.50 ***c*** (1.09)
G	8.64 ***f*** (1.08)	13.06 ***e*** (0.53)	17.38 ***g*** (0.72)	20.15 ***f*** (0.92)	25.03 ***g*** (1.14)	4.18 ***d*** (0.76)	5.24 ***e*** (0.72)	6.47 ***e*** (0.58)	7.51 ***f*** (0.21)	8.43 ***e*** (0.37)
H	5.74 ***e*** (1.08)	10.03 ***d*** (1.39)	12.83 ***e*** (0.769)	16.89 ***e*** (0.71)	22.12 ***f*** (0.96)	3.37 ***cd*** (0.68)	4.39 ***de*** (1.193)	5.11 ***d*** (0.39)	6.27 ***e*** (0.29)	7.33 ***d*** (0.46)

*Note: The value in parentheses is the standard deviation; each value is the average of seven samples tested; groups with the same letters in the column indicate that there was no statistical difference ($p < 0.05$)

Statistical analysis showed that the physical properties of the composites significantly improved with the addition of the coupling agent. The hazelnut husk flour, having the hydrophilic -OH groups, induced moisture absorption and weakened interfacial adhesion of the lignocellulosic materials with polymer matrices. With addition of the coupling agent, the hydrophilic -OH groups in the lignocellulosic materials reacted with the acid anhydride groups of the MAPE, thus forming ester linkages. This usually results in improved compatibility between the hydrophobic polymeric matrix and the hydrophilic filler, resulting in better dispersion of filler within the matrix. Therefore, after the formation of ester bonds between the hazelnut husk flour and the MAPE, the number of available hydrophilic groups was reduced (Migneault *et al.* 2014).

Mechanical Properties

The tensile properties of polymer composites are presented in Figs. 2 and 3. The tensile strength of the composites decreased with the addition of hazelnut husk flour, whereas the tensile modulus significantly increased, as shown in Fig. 2. The statistical analysis showed that the filler rate significantly affected the tensile properties, $p < 0.05$. The tensile strength of the specimens was reduced by 39.4% when the hazelnut husk flour content increased from 30 wt.% to 60 wt.%. This can be explained by the poor interfacial adhesion between a polar hazelnut husk particle surface and a non-polar polymer matrix surface. This weak interfacial adhesion between the lignocellulosic material and the plastic matrix resulted in a lower tensile strength.

The tensile modulus of the composites increased by approximately 50.3% as the hazelnut husk flour content increased from 30 wt.% to 60 wt.%. Thus, the tensile modulus was enhanced by the incorporation of the hazelnut husk flour addition in the composites. The lignocellulosic material has higher modulus values than the HDPE; thus, adding hazelnut husk flour reduced the ductility of the composites and increased the modulus. Similar results were observed in a previous study, which reported that the addition of lignocellulosic materials into polymer composites enhanced the tensile modulus values (Nourbakhsh *et al.* 2010).

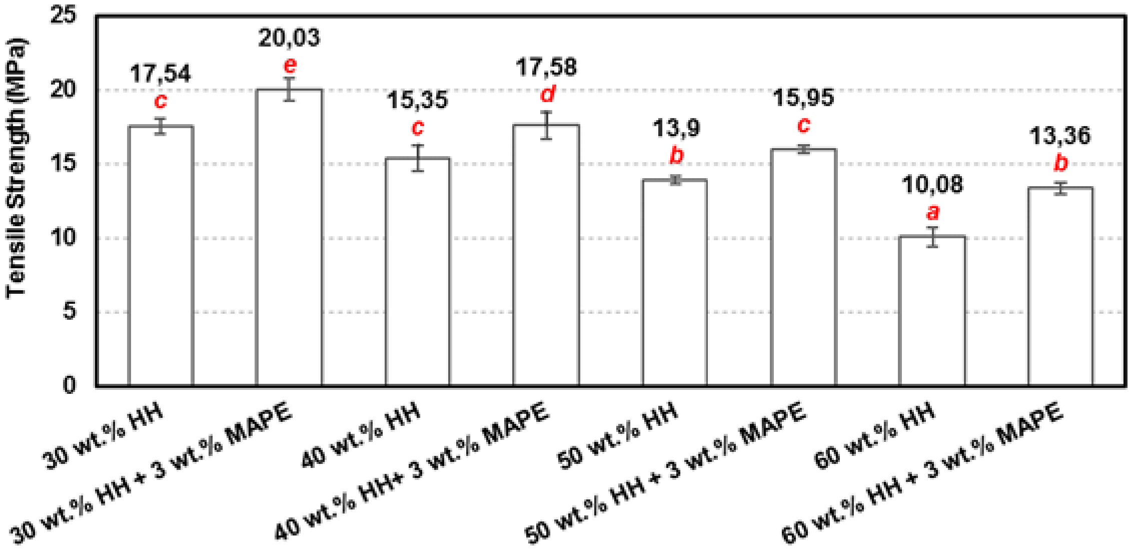

Fig. 2. Averages and standard deviations for the tensile strength of the polymer composites; bars with different letters indicate that the results are significantly different from each other

A statistical analysis showed that the coupling agent addition significantly improved the tensile properties ($p < 0.05$). The tensile strength and modulus values of the composites that were produced with 3 wt.% MAPE were higher than those of the composites produced without MAPE. The maleic anhydride units in the MAPE bonded with the lignocellulosic fibers and improved the compatibility between the lignocellulosic material and the polymer matrix. The higher value of tensile modulus in the coupled composites compared to the uncoupled composites could be attributed to the changes in the molecular morphology of R-HDPE chains near the fiber-polymer matrix interface. The addition of coupling agent has been reported to increase the nucleation capacity of biofibers and alter the crystal morphology of polyolefin around the fiber (Simonsen and Rials 1996).

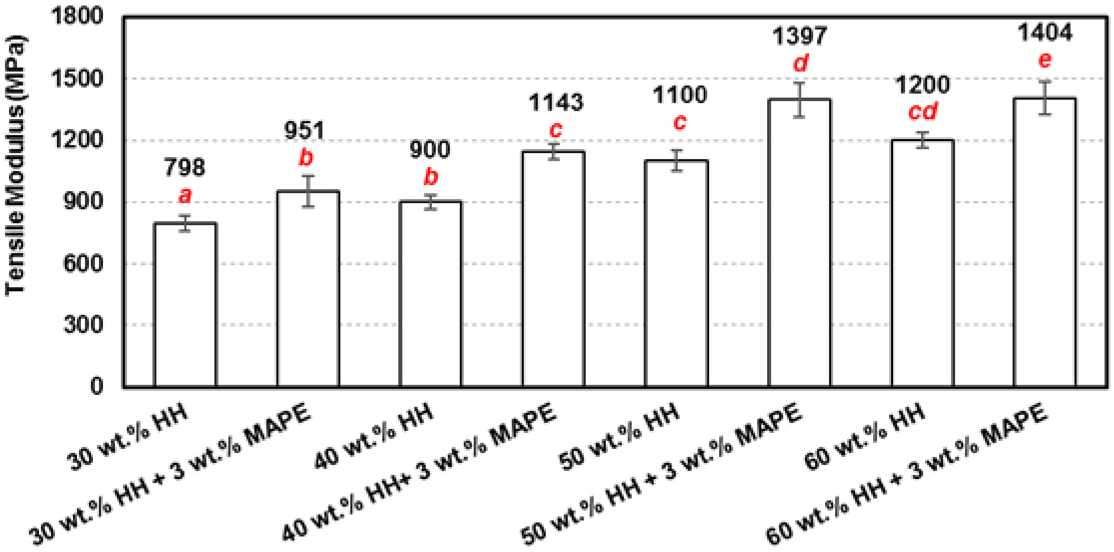

Fig. 3. Averages and standard deviations for the tensile modulus of the polymer composites; bars with different letters indicate that the results are significantly different from each other

The results showed that by modifying the wood flour with MAPE, the compatibility in the interfacial area between the hydrophobic polymer and the hydrophilic hazelnut husk flour was enhanced, leading to the improvement in the mechanical properties (Kord 2012; Tufan *et al.* 2015b). The unfilled spaces and the pulled-out hazelnut husk flour fiber observed in the polymer composite sample (Group code E) are shown in Fig.1(A), while Fig.1(B) shows the well-dispersed hazelnut husk flour in another polymer matrix sample (group code F), indicating good encapsulation of the lignocellulosic material within the matrix.

The flexural strength and modulus values of the composites are presented in Figs. 4 and 5. The results of the flexural strength test were similar to those of the tensile strength test. The tensile strength values decreased with an increase in the hazelnut husk flour content in the composites. For example, the flexural strength values of the composites without the coupling agent decreased by 55.4% as the hazelnut husk flour content was increased from 30 wt.% to 60 wt.%. The poor adhesion between the fillers and the polymer matrix was the main reason for the poor flexural strength (Tufan *et al.* 2016). The weak interfacial regions result in the reduction in the efficiency of stress transfer from the matrix to the reinforcement component (Ayrilmis *et al.* 2013). The flexural modulus values of the specimens without MAPE increased by 57% as the hazelnut husk flour content increased from 30 wt.% to 60 wt.%. It is well known that lignocellulosic materials have a higher modulus than polymer matrices. It is believed that the modulus of elasticity increased with the increasing flexural modulus values of the lignocellulosic material in the polymer composites. Similar results were reported in previous studies (He *et al.* 2015; Pereira *et al.* 2015).

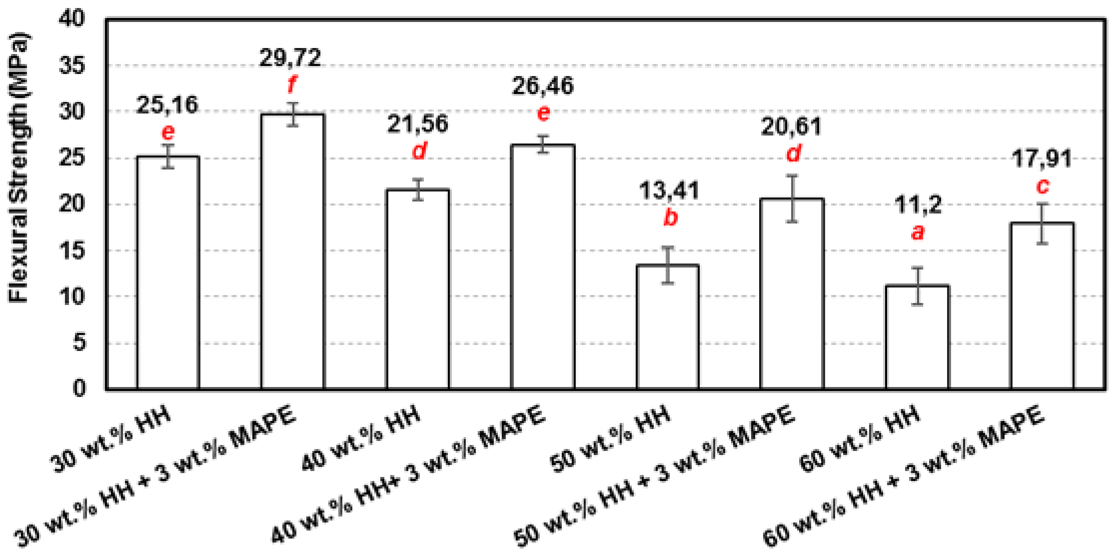

Fig. 4. Averages and standard deviations for the flexural strength of the polymer composites; bars with different letters indicate that the results are significantly different from each other

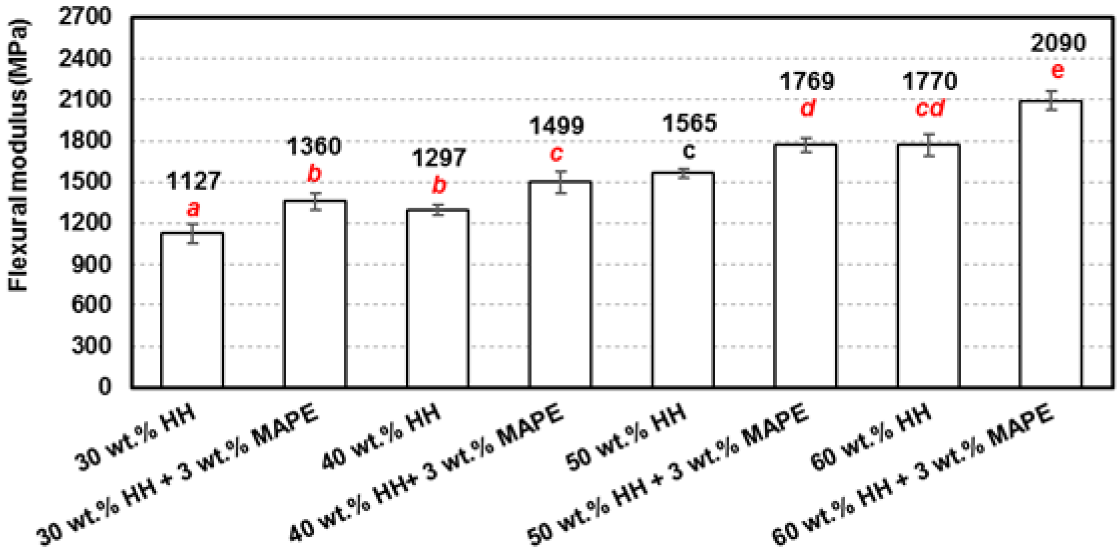

Fig. 5. Averages and standard deviations for the flexural modulus of the polymer composites; bars with different letters indicate that the results are significantly different from each other

Lignocellulosic filled thermoplastic composites usually have been considered as an alternative to the polyolefin-based plastic lumber decking boards. For polyolefin-based plastic lumber decking boards, ASTM D 6662 (2013) standard requires the minimum flexural strength of 6.9 MPa. All the composites produced in this study had flexural strength values in the range 11.20 to 29.72 MPa, which were well over the minimum requirement by the standard. ASTM D 6662 standard requires the minimum flexural modulus of 340 MPa for polyolefin-based plastic lumber decking boards. All composites produced in this study had flexural modulus values (1127-2090 MPa) which is well over required standard.

The impact strength values were reduced in all groups with increasing of hazelnut husk flour content. The impact strength of the without MAPE specimens decreased by 49.81% when hazelnut husk flour content increased from 30 to 60 wt.%. The decrease in the polymer matrix content in the composite as a function of the increase in the hazelnut husk flour content was also responsible for the low tensile strength because when the filler content in the composite increases, the amount of the plastic as the adhesive, decreases.

The poor interfacial bonding between the hazelnut husk flour and polymer matrices increased with increasing of hazelnut husk flour content. The poor interfacial bonding creates micro-cracks. As a consequence, less energy is needed to initiate a crack in the composites, and this cause decreasing impact strength. The composites produced with the MAPE showed lower impact strength values than that of composites without the MAPE. The use of coupling agent enhanced the fiber-matrix interaction thus increasing the brittleness of the composite. Similar findings were reported in other studies (Tascioglu *et al.* 2014; Tufan *et al.* 2016).

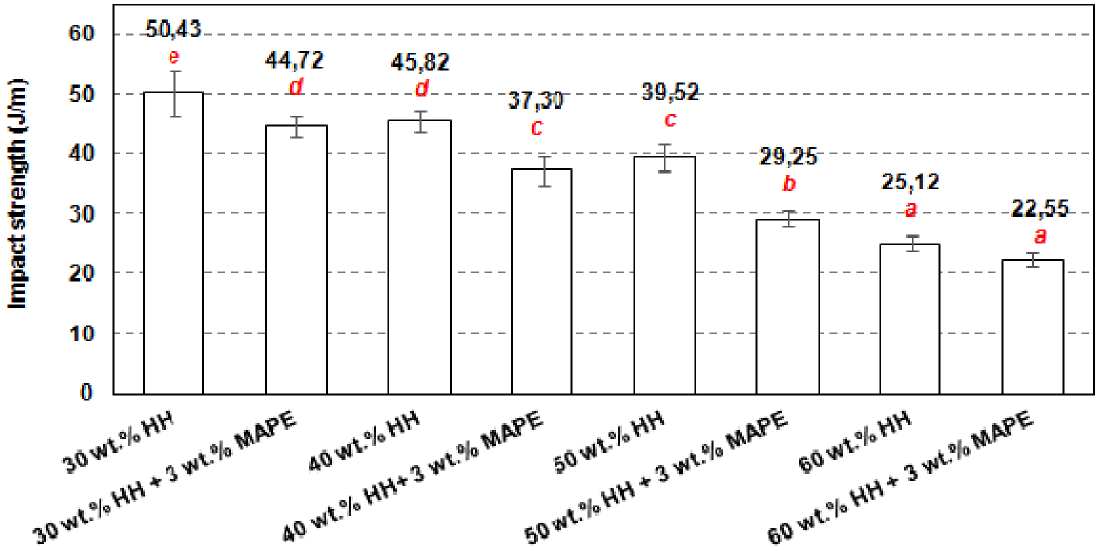

Fig. 6. Averages and standard deviations for the impact strength of the polymer composites; bars with different letters indicate that the results are significantly different from each other

Decay Resistance

The mean mass losses caused by the *T. versicolor* and *P. placenta* fungi on the polymer composites, and the virgin pine wood (the control) samples, are given in Table 3. The highest mass loss rate for the white rot fungus was 40.72%, and for the brown rot fungus, it was 52.56%, both of which were found in the control samples. These results demonstrated the good fungal decay activity on the control species. The results of the fungal tests clearly showed that the polymer composites produced with hazelnut husk flour without MAPE were susceptible to fungal attack, especially when the hazelnut husk flour content was 50% of the total composite weight. A statistical analysis showed that the increase in the mass loss rate significantly affected the mass loss rate of composites without MAPE and with 50% or more hazelnut husk flour loading. In particular, the mass loss rate of the polymer composites significantly increased as the amount of hazelnut husk flour increased from 40 wt.% to 50 wt.%. Furthermore, the white and brown rot fungi caused higher weight losses, 9.77% and 6.49%, respectively, after 16 weeks of exposure.

Table 3. Mean Mass Loss (%) of Polymer Composites after16-Week Exposure to Decay Fungi

Group code	*Trametes versicolor*	*Postia placenta*
A	0.31 ***a*** (0.18)	0.94 ***a*** (0.34)
B	0.23 ***a*** (0.10)	0.47 ***a*** (0.18)
C	1.79***b*** (0.39)	1.95 ***b*** (0.06)
D	1.40***b*** (0.19)	1.41 ***b*** (0.29)
E	4.49 ***c*** (0.40)	2.05 ***bc*** (0.31)
F	3.15 ***c*** (0.37)	3.27 ***c*** (0.37)
G	9.77 ***d*** (0.72)	6.49 ***d*** (0.43)
H	7.16 ***e*** (0.31)	4.49 ***cd*** (0.34)
Scots pine (control)	40.72 ***f*** (11.04)	52.56 ***e*** (9.60)

*Note: The value in parentheses is the standard deviation; each value is the average of the eight samples tested; groups with the same letters in the column indicate that there is no statistical difference ($p < 0.05$) among the composite types

The addition of the coupling agent, at a 3% loading, was effective in reducing the mass loss rate. The biodegradability of the polymer matrix is very limited; thus, the hazelnut husk flour was the predominant fungal nutrient source in the composites. The mass loss rate values of all the polymer composites decreased with the use of the coupling agent because MAPE is known to enhance the interfacial adhesion between wood flour and polymer matrices. Thus, the lignocellulosic material was better encapsulated by the polymer matrix, and the good encapsulation prevented the fungus from reaching the lignocellulosic material (Tascioglu *et al.* 2014; Tufan *et al.* 2015a).

DSC Analysis

The thermal and crystalline properties of polymer composites are given in Table 4. The peak temperatures of the first melting values of all samples with and without MAPE were no better than those of R-HDPE. However, the peak temperatures of the second melting values of the samples were slightly lower than those of the R-HDPE. As the filler content increased from 30 to 60 wt.%, the second melting peak temperature of the composites without the MAPE very slightly decreased (133.61 to 133.22 °C). As the MAPE was incorporated into the composite, the increment in the second melting peak temperature of the composites was negligible (133.69 to 133.40 °C). Similar values were also observed for the first melting peak temperature of the composites (Table 4). The highest second melting enthalpy value was found to be 136.27 J/g for the R-HDPE. The second melting enthalpy of the specimens significantly decreased with increasing content of the hazelnut husk flour (Table 4). The second melting enthalpy of the R-HDPE decreased from 136.27 J/g to 41.03 J/g as the filler content increased from 30 to 60 wt.%. This result indicates that thermal stability of the R-HDPE increased with increasing the filler content.

The reduction in the value of the second melting enthalpy could be explained by the fact that the hazelnut husk flour absorbed more heat energy. It is considerably increased as the MAPE was incorporated into the composite. The addition of the MAPE positively affected the second melting enthalpy values. The crystallization values of the samples were lower than those of the R-HDPE. They decreased as the amount of hazelnut husk filler increased in the composites.

Table 4. Thermal and Crystalline Properties of the Composites

Group code	Peak temperature of first melting (°C)	Peak temperature of crystallization (°C)	Enthalpy of crystallization (J/g)	Peak temperature of second melting (°C)	Enthalpy of second melting (J/g)	Crystallization degree (%)
R-HDPE	131.68	115.90	128.68	134.70	136.27	46.51
A	131.98	119.77	82.62	133.61	86.86	42.35
B	131.38	120.60	100.53	133.69	89.16	43.53
C	131.74	118.64	79.19	133.59	69.08	39.13
D	131.83	119.87	85.45	133.65	74.35	41.99
E	131.30	116.21	64.49	133.26	48.51	33.11
F	131.28	117.88	48.85	133.03	59.96	40.92
G	131.19	116.42	49.42	133.22	41.03	35.00
H	131.37	117.56	79.15	133.40	45.78	39.06

CONCLUSIONS

1. The physical properties of water absorption and thickness swelling of in recycled high-density polyethylene (R-HDPE) polymer composites were negatively affected by the addition of hazelnut husk flour. This was attributed to the poor adhesion between the polymer matrix and the lignocellulosic materials, which was caused by the higher hazelnut husk flour content. A similar trend was observed for the biological durability.
2. The mass loss values of the R-HDPE composites increased with an increase in the hazelnut husk flour content in the composites.
3. The tensile and flexural modulus values of the composites improved with increasing hazelnut husk flour content, whereas the tensile and flexural strength decreased. The tensile and flexural properties were enhanced by the addition of MAPE.
4. All of the polymer composites showed similar first and second melting temperature values. The degree of crystallinity of R-HDPE decreased with the incorporation of hazelnut husk flour.
5. The water absorption, thickness swelling, mass loss rate, and crystallinity degree values were positively affected by the incorporation of the MAPE in the polymer composites.
6. The results revealed that hazelnut husk flour has potential as a filler for polymer composites.

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