

## UTILIZATION OF HAZELNUT SHELLS AS FILLER IN LDPE/PP BASED POLYMER COMPOSITES

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### **Abstract:**

*Polymer based composites manufactured using thermoplastic and lignocellulosic materials are increased recently. Hazelnut shells as lignocellulosic were considered as a potential filler for polymer composites. This study measured the effect of filler loading on the mechanical properties of low density polyethylene (LDPE) and polypropylene (PP) based polymer composites. PP and LDPE were used as thermoplastic polymer. Hazelnut shells flours (HSF) were used as filler. The blends of PP, LDPE and HSF were compounded using single screw extruder and test samples were prepared through injection molding. The tensile, flexural and impact properties of the produced composites were determined in accordance with ASTM D638, ASTM D790, and ASTM D256, respectively. As a result, with increase of filler loading for PP, tensile strength (TS), elongation at break (EatB) and flexural strength (FS) were decreased while tensile modulus (TM) and flexural modulus (FM) were increased. Impact strength (IS) of PP based polymer composites were not changed. Also the addition of filler loading into LDPE matrix reduced TS, EatB, and IS while FS, FM and TM were increased. In this study, manufactured all composites provided flexural properties for the plastic lumber applications by the ASTM D 6662 (2001) standard.*

**Key words:** thermoplastic composite; low density polyethylene; polypropylene; hazelnut shells; mechanical properties.

### **INTRODUCTION**

Polymer composites can be consisted thermoplastic polymers such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and lignocellulosic fillers such as wood flours (pine, poplar, beech, eucalyptus, etc.) and agricultural wastes (wheat straw, rice husk, hemp, kenaf fibers, walnut, hazelnut shells, tea mill waste, etc.). Its low density, low cost, their availability, renewability, high specific properties, low hygroscopicity, high dimensional stability, eco-friendliness and ease of processing can be listed among the advantages of the polymer based composites filled by lignocellulosic materials (Dobrev et al. 2006; Mengeloğlu and Karakus 2008; Kaymakci and Ayrılmış 2014; Donmez Cavdar et al. 2015). Polymer based composites have wide application areas (decks, walkways, automobile industry, house hold applications, fence, door and window frames, music and sports materials, etc.) due to their advantages over both the plastic and wood material (Yang et al. 2004; Muhammed et al. 2015).

The use of fillers in polymer based composites as published in the literature is also summarized. Several studies were conducted to investigate the use of lignocellulosic fillers in polymer based composites. Bamboo was also used as filler in thermoplastic (PLA and PBS) matrix and mechanical properties were

compared (Lee and Wang, 2006). Hamid et al. investigated the physical and mechanical properties of high density polyethylene (HDPE) based reinforced with rice husks and sawdust. Reddy and Yang developed polymer based on mechanical and physical properties of soyprotein-jute and PP-jute composites. There are also some studies on the thermoplastic and lignocellulosic materials. Zhou et al. investigated the mechanical properties of the composites made from ramie filled poly (lactic acid).

There is tremendous amount of forest products industry and agricultural wastes available in Turkey and they are not utilized rationally. It is possible to utilize these wastes in the manufacture of polymeric composites (Mengeloğlu & Karakus 2008). Nutshells are renewable lignocellulosic materials that can be obtained as agricultural byproducts. They are often utilized in relatively low-value applications such as composts, mulches, fertilizers, animal feed, burned or left in the agricultural land after harvest (Sutivisedsak et al. 2012). Annual hazelnut amount is around 768.300 tons per year between 2009-2014. Annual hazelnut husk amount is around 400,000 tons. Turkey is largest hazelnut producer with a supply of 70% followed by Italy, USA and Spain in the world. Nutshell as a filler consist of 25% to 30% cellulose and hemicelluloses and 30% to 40% lignin (Sarica and Cam 2000; Tuik 2010; Salasinska and Ryszkowska 2012; Avci et al. 2013; Boran 2016).

The aim of this study is to investigate the usability of hazelnut shell flour as fillers in polymer based composites. Also, this study measured the effect of filler loading on the mechanical properties of LDPE/PP based polymer composites. The mechanical and physical properties of the polymer composites produced from hazelnut shell flours and LDPE/PP were determined.

## EXPERIMENTAL

### Materials

Low-density polyethylene (LDPE) and polypropylene (PP) were used as thermoplastic matrix. These plastic were used as received from the manufacturer. Hazelnut shell flours (HSF) were used as lignocellulosic filler. The fillers were collected from Trabzon, Turkey. Zinc borate and paraffin wax (K.130.1000) was used as a lubricant.

### Polymer composite manufacturing

The hazelnut shell wastes granulated in Wiley Mill into the flour form. These flours, screened and retained on 60 mesh-size screen (0.25mm), were used in this study. The classified fillers were dried in oven at 103°C (±2) for 24 hours. The experimental design of the study was presented Table 1. Depending on the formulation given LDPE or PP, and HSF and paraffin wax were dry-mixed in a high-intensity mixer to produce a homogeneous blend. These blends were compounded in a single-screw extruder at 40rpm screw speed in the temperatures (barrel to die) of 170-180-185-190-200°C. Extruded samples were cooled in water pool and then granulated into pellets. The pellets were dried in oven at 103°C (±2) for 24 hours. The pellets were injection molded into tensile, flexural test samples using an HDX-88 injection molding machine at a barrel temperature of between 180°C and 200°C (injection pressure: 100 bar, injection speed: 80mm/sec., screw speed: 40rpm., cooling time about 30s.).

Table 1

Manufacturing schedule of composites (%)					
Group ID	Polymer Type (PP) / (PE)	Polymer (%)	Hazelnut shell flours (%)	Zinc borate (%)	Wax (%)
PE-0	PE	96.0	0.0	2	2
PE-1	PE	78.5	17.5	2	2
PE-2	PE	61.0	35.0	2	2
PE-3	PE	43.5	52.5	2	2
PP-0	PP	96.0	0.0	2	2
PP-1	PP	78.5	17.5	2	2
PP-2	PP	61.0	35.0	2	2
PP-3	PP	43.5	52.5	2	2

### Polymer composite testing

Testing of the samples was conducted in a climate-controlled testing laboratory. Densities were measured by a water displacement technique according to the ASTM D 792 standard. Tensile, flexural and impact properties of all samples were determined according to ASTM D 790, ASTM D 638, and ASTM D 256, respectively. The span length of each specimen was 80mm, with the rest left as overhang for flexural testing. The rate of crosshead motion was 2.0mm/min, which is calculated according to the ASTM standard. Tests were performed at a rate of 5.0mm/min. Dog-bone shape samples were used (Type III) for tensile

testing. Ten samples for each group were tested. Flexural and tensile testing were performed on Zwick 10KN while a HIT5,5P by Zwick™ was used for impact property testing on notched samples. The notches were added using a Polytest notching cutter by RayRan™.

**Data analysis**

Design-Expert® Version 7,0,3 statistical software program was used for statistical analysis.

**RESULTS AND DISCUSSION**

LDPE based or PP based polymer composites were produced in the density range of 0,91-1.50g/cm<sup>3</sup>. Mean density values are presented in Table 2. Plastic type and filler amounts were statistically significant. LDPE based composites had higher density values compared to PP based ones due to the density differences of base polymers. Hazelnut shell flours filled composites provided slightly higher density values compared to neat polymers for both LDPE and PP. In addition, density of the composites was increased with filler loading.

Table 2

**Density of the manufactured polymer composites**

Group ID	Density (g/cm <sup>3</sup> )
PE-0	0.96 (0.011)
PE-1	1.27 (0.04)
PE-2	1.36 (0.02)
PE-3	1.50 (0.03)
PP-0	0.91 (0.005)
PP-1	1.20 (0.03)
PP-2	1.27 (0.009)
PP-3	1.38 (0.03)

\* Values in parenthesis are standard deviations.

In this study, tensile, flexural and impact properties of all samples were determined. Mechanical properties of the polymer composites produced with HSF were summarized in Table 3. The arithmetic mean and standard deviation values were given for each group in the table. Two different polymers and three different ratios of filler material (hazelnut shell flours) were used.

Table 3

**Mechanical properties of polymer based composites**

Group ID	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (J/m)
PE-0	9.04 (0.2)*	81.02 (5.72)	103.75 (11.76)	6.07 (0.13)	133.82 (166.13)	436.45 (39.01)
PE-1	8.08 (0.06)	151.51 (23.63)	30.50 (7.55)	10.36 (2.47)	1301.10 (102.82)	135.55 (12.78)
PE-2	6.14 (0.16)	186.06 (21.24)	11.09 (2.30)	10.30 (0.27)	447.18 (41.79)	62.15 (5.94)
PE-3	3.68 (0.45)	263.69 (28.27)	4.68 (0.09)	9.69 (0.18)	786.03 (32.46)	29.97 (3.15)
PP-0	29.01 (0.94)	406.43 (49.25)	465.00 (52.85)	39.52 (1.65)	1077.18 (63.91)	15.21 (2.26)
PP-1	21.58 (0.54)	631.99 (17.69)	8.03 (0.88)	34.02 (1.13)	1307.18 (74.73)	18.85 (3.29)
PP-2	16.27 (0.48)	667.21 (14.37)	5.01 (0.52)	29.89 (1.37)	1660.29 (105.06)	18.22 (1.61)
PP-3	11.52 (0.34)	671.45 (34.26)	3.25 (0.39)	25.02 (0.65)	1917.68 (49.26)	18.22 (2.25)

\* Values in parenthesis are standard deviations.

Tensile properties include tensile strength, tensile modulus and elongation at break. With the increasing of HSF loading tensile strength was significantly reduced in both LDPE and PP based composites. It is thought that the most important reason of decline is lack of bonding between polymer matrix and lignocellulosic fillers (Mengeloglu and Karakus 2008; Donmez et al. 2015). The polymer type was also

effective on the tensile strength of the composite material. PP composites relatively provide better tensile strength compared to the LDPE composites. To mention of tensile modulus, rise of filler loading significantly increased the tensile modulus for both composites. Similar results for other wood flours filled polymer composites were also reported (Lee and Wang 2006). The filler has significant effect on elongation at break values for both composites. Significant reduction by addition of filler in elongation at break values was determined for both polymer matrixes.

Flexural properties include flexural strength and flexural modulus. The results showed that the flexural strengths are significantly affected by filler loading. Similar results were also reported for the flexural strength of other wood flour filled thermoplastic composites (Donmez Cavdar et al. 2015; Boran 2016). With filler loading flexural strength was reduced for PP based composites. PP composites relatively provide better flexural strength compared to the LDPE composites. The results of analysis show that the rate of HSF was effective on flexural strength for PP composites. Compared to control samples, while there is a reduction on the flexural strength for PP based composites, the increase has been observed on flexural strength for LDPE based composites. The polymer type was also effective on the flexural strength of the composite material.

With the increase of filler loading increased the flexural modulus for LDPE and PP based composites.

Lignocellulosic fillers and polymers have different modulus of elasticity from each other. Lignocellulosic fillers have higher modulus of elasticity than polymer. This is caused to have better flexural modulus for composite from pure polymer. Therefore, flexural modulus increased with the rise of lignocellulosic filler loading. Addition of the lignocellulosic filler improves tensile modulus of the thermoplastic composites usually could simply be explained by the rule of mixtures (Matuana et al. 1998; Mengeloğlu and Karakus 2008). PP composites relatively provide better flexural modulus compared to the LDPE composites. In this study, produced polymer composite materials were usually considered as an alternative to the polyolefin-based plastic lumber decking boards. For polyolefin-based plastic lumber decking boards, ASTM D 6662 (2001) standard requires the minimum flexural strength of 6.9MPa. All composites produced in this study provided flexural strength values (9.69-39.52 MPa) that are well over the requirement by the standard. ASTM D 6662 (2001) standard requires the minimum flexural modulus of 340MPa for polyolefin-based plastic lumber decking boards. All composites produced in this study provided flexural modulus values (447-1917MPa) well over required standards.

The results show that pure LDPE has higher impact. Impact strength reduced hazelnut shell flour was added to polymer matrix. There is little difference between impact strength of PP based. With the increase of filler loading decreased the impact strength for LDPE. This usually arises from increasing of brittleness of the composite material (Matuana et al. 1998; Mengelöglu and Karakus 2008).

## CONCLUSIONS

Low density polyethylene (LDPE) and polypropylene (PP) based polymer composites including different ratios of hazelnut shell flour are manufactured by injection moulding. The mechanical properties of the produced polymer composite (tensile strength, tensile modulus, flexural strength, flexural modulus, elongation at break and impact strength) were determined.

Hazelnut shell flours (HSF) flour filled polymer composites were successfully produced and the following conclusions were reached;

1. PP based composites provided better mechanical properties compared to LDPE based composites,
2. Addition of HSF flour into polymeric matrices improved modulus values while reducing strength, elongation and impact values.
3. LDPE and PP based polymer composites provide adequate mechanical properties according to ASTM D 6662 (2001). As a result, HSF flour might be utilized as filler for LDPE and PP based polymer composites.

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