Utilization of Walnut Shells as Filler in Polymer Composites

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Abstract:

In this study, the utilisability of Walnut Shell (WS) flour in polypropylene (PP) and high density polyethylene (HDPE) matrix composites are investigated due to its relative hardness and availability. The WS flour was compounded with PP and HDPE at 50% (weight) content with and without coupling agent in a single screw extruder. Then, granulated compositions were manufactured by press moulding process. Some mechanical properties (Tensile, impact, flexural strength), TGA and DSC were performed on the polymer composites samples. When WS flour were added 3% coupling agent bending properties of the HDPE and PP samples increased to 1340 MPa and 1514 MPa, respectively. However, WS2 samples which HDPE composites type was added 3% coupling agent in the form showed 26% lower impact factor than WS1. The addition of coupling agents improved the properties of polymer composites. MAPE coupling agents performed better in HDPE while MAPP coupling agents were superior in PP based composites. According to mechanical properties of the composites groups, the lowest strength was in the WS3 which content 50% PP without couple agent. All produced composites provided mechanical properties required by the ASTM D662 standard for plastic lumber decking boards. The analysis showed that MAPE didn't affect to thermal degradation of 47% WS filled HDPE composites samples. Melting temperature was around WS1 and WS2 130 °C while WS3 and WS4 around 165 °C. The second melting peak temperature of WS2 composites with 3% coupling agent was around 170 °C. As a result Walnut shell which was considered agricultural waste can be utilized in polymer composite production.

Key words: Polymer composites, walnut shell, mechanical properties, DSC and TGA

Introduction:

There is currently worldwide interest in manufacturing composite materials from waste industrial and agricultural materials due to increasing demands for environmentally friendly material. However technology is evolving that holds promise for using waste lignocellulosic materials and plastic to make an array of high performance composite products that are themselves potentially recyclable (Rowell et all. 1991; Bolton 1995; Najafi and Eslam 2011; Nitin and Singh 2013a).

Polymer composites might consist of various species wood and organic fillers such as corncobs, nutshell, pepper stem, cereal straw and even cellulose wastes, and polymers such as polyethylene, polypropylene, and polyvinyl chloride. Its low density, high specific properties, low hygroscopicity and high dimensional stability can be listed among the advantages of the polymer-composites filled by organic materials (Clemons 2002; Mengeloglu and Matuana 2003; Panthapulakkal et al. 2006; Mengeloglu and Karakus 2008; Nitin and Singh 2013b). That is why the usage of several agricultural wastes in polymer composites as fillers and reinforcer were investigated.

In this study investigated the potential utilization of walnut shell as fillers in polymer composites. Walnut (*Juglans regia* L.) is an important crop that is cultivated throughout the world's temperate regions for its edible nuts (Pirayesh et al. 2012; Ayrilmis et al. 2013). Worldwide walnut production was approximately 2.55 million tons from a total of 834 thousand ha in 2010. Turkey produces annually 178,142 tons walnut and ranking 4th place after China (1,060,000 tons), USA (458,000 tons), and Iran (278,300). Since walnut shell comprises 67% of the total weight of the walnut kernel, around 1.5 million tons of walnut shell is left behind each year all over the world (URL 1; Pirayesh et al. 2012). Walnut shells are renewable lignocellulosic materials that can be obtained as agricultural products. Walnut shell abrasive is used to blast clean and polish soft metals, fiberglass, wood, plastics and stone. Also they are often utilized in relatively low-value applications such as burning and fertilizer (Srinivasan and Viraraghava 2008).

Materials and Methods:

Walnut shells were supplied by a manufacturer in Artvin, Turkey. Polypropylene (PP) and high density polyethylene (HDPE) were used as polymer matrix and provided by PETKİM (Petrokimya Holding A.Ş.). First air dried walnut shells (WS) were grinded into small particles using a Willey mill. Then grinding WS flour was screened to 40 mesh size particles and dried to oven-dry moisture. Maleic anhydrite grafted polyethylene (MAPE: Clariant Licocene PE MA 4351 GR)/polypropylene (MAPP: Clariant Licocene PP MA 6452 TP) was also used as coupling agent. The experimental design of the study is presented in Table 1.

Table 1. Composition of the Polymer Composites.

Composite Type	Composite Composition				
	WS flour	Polymer Type		Coupling Agent Type	
		PP	HDPE	MAPP	MAPE
WS1	50	-	50	-	0
WS2	50	-	47	-	3
WS3	50	50	-	0	-
WS4	50	47	-	3	-

This blend was then compounded in a laboratory-scale single extruder. The temperature profile set toward the die end for 180-190-195-210 °C. Screw speed calibrated at 50 rpm. Extruded samples were collected, and granulated into pellets. Finally, pellets were compressed into 5 × 150 × 170 mm size composites for 5 min at 175 °C.

Testing of the manufactured composites was conducted in a climate-controlled testing laboratory. Flexural, tensile and impact properties of all boards were determined. The flexural tests were conducted in accordance with ASTM D 790. Test samples were cut in the dimensions of 4 × 13 × 150 mm. The span length of each specimen was 80 mm, with the rest left as overhang. Samples were tested on Zwick 10 KN. The rate of crosshead motion was 2.0 mm/min, which was calculated according to the ASTM D 790 standard. The tensile tests were conducted according to the ASTM D 683. Samples were tested on Zwick 10 KN. Test were performed at a rate of 5.0 mm/min. The tensile modulus of the samples was taken as the slope of the curve a stress levels between 0.05% and 0.2%, while the tensile strength was the maximum stress experienced by each specimen. The impact tests were performed according to ASTM D 256. Impact samples for each group were cut from the manufactured composites. The notches were added using a Polytest notching cutter by RayRan™ and notched samples were tested on a HIT 5.5 P impact testing machine, manufactured by Zwick™.

The PerkinElmer STA 6000 thermal analyzer was used for the thermogravimetric analysis (TGA) of the samples. The test samples, each weighing 3-5 mg were heated in an aluminum crucible up to 600 °C with the heating rate of 10 °C min under nitrogen 29 ml/min^2 flow rate and kept at this temperature for 2 min to monitor thermal history.

Differential scanning calorimetry (DSC) analysis was performed in Shimadzu DSC-60 using 10 °C/min heating rate under nitrogen with 30 ml/min^2 flow rate, from room temperature to 200 °C.

Statistical analysis based on non-parametric one-way ANOVA was used to compare the difference in average values of the various parameters considered at the 99% confidence level.

Results and Discussion:

The effects of filler loading and coupling agent on the specific mechanical and thermal properties of the composites were studied. Most of physical and mechanical properties polymer composites depend on mainly on the interaction developed between lignocellulosic filler and the thermoplastic material. One way to improve this interaction is incorporating a coupling agent as additive. In general, the additives help the compatibility between hydrophilic wood and hydrophobic plastic allowing the formation of single-phase composite (Wechsler and Hiziroglu 2006).

Four different groups of polymer composites were produced, flexural, tensile, and impact properties were determined. The mechanical properties were summarized in Table 2. Statistical analysis showed that MAPE significantly affected the tensile strength of the polymer-composites ($P < 0.01$). Average Flexural Modulus value of the samples containing 50% WS without having any coupling agent was found 1280 MPa and 1461 MPa. When these samples were added 3% coupling agent bending properties of the samples increased to 1340 MPa and 1514 MPa. However, WS2 samples which HDPE composites type was added 3% coupling agent in the form showed 26% lower impact factor than WS1. Notched impact strength reduced with the MAPE coupling agent. This result was expected since the use of the coupling agent enhanced the interaction between filler and polymer resulting in increased brittleness of the composite (Selke and Childress 1993). This might have changed the mode of failure from "fiber pull-out" to "fiber breakage". Former one requires a larger amount of energy during the crack propagation compared to fiber breakage where the crack goes through the brittle wood-fiber (Matuana and Balatinecz 1998; Mengeloglu et. al. 2000).The addition of coupling agents improved the properties of polymer composites. MAPE coupling agents performed better in HDPE while MAPP coupling agents were superior in PP based composites. All produced composites provided flexural properties required by the ASTM standard for plastic lumber decking boards.

Table 2. Mechanical Properties of WS Filled Composites.

Composite Type*	Mechanical Properties				
	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (J/M)
WS1	8,24 c (0,96)	998,71 a (33,96)	17,87 c (0,99)	1280 a (119)	41,90 a (4,15)
WS2	9,36 b (0,33)	1012,14 a (93,27)	19,00 b (1,24)	1340 a (160)	30,73 b (2,41)
WS3	6,00 d (0,97)	996,71 a (81,14)	14,85 b (1,97)	1461,4 a (351,30)	14,25 c (1,13)
WS4	11,30 a (0,984)	1088,86 a (118,84)	23,50 a (1,98)	1514,29 a (77,43)	20,34 d (1,73)

Note:
-The numerical value in the parenthesis is standard deviation.
-Different letters indicate significantly different groups ($p < 0.01$, $N=10$)
-*See Table 1 for composite formulation

Tensile modulus and Flexural modulus of the specimens increased from 1280 to 1514 MPa as the coupling agent content by 3% in the both PP and HDPE increased. While impact strength decreased from 41.9 to 30.73 J/M both PP and HDPE. Also tensile strength and flexural strength of the specimens increased as the coupling agent content by 3% in the all groups. According to mechanical properties of the composites groups, the lowest strength was in the WS3 which content 50% PP without couple agent. The highest strength value showed in which content 47% PP with 3% coupling agent except for impact strength. The mechanical properties increased as comparable values according to Ayrilmis et al (2013). This could be due to non-homogenous mixture of WS flour and polymers. These results of the polymer composites filled with walnut shell were competitive with the results of thermoplastic composites filled with various agriculture wastes such as olive mill sludge, pine cone, rice husk, and nutshell (Ayrilmis et al. 2010; Safdari et al. 2011). Chemical structure of the lignocellulosic materials may play an important role on the physical and mechanical properties of composites. It has reported that WS observes to have 47.78, 26.51, and 49.18 of holocellulose, cellulose, and lignin, respectively (Guntekin et al. 2008).

Figure 1 and Figure 2 show the TGA and DTGA thermographs of the samples. Initial degradation of WS composites was started around 250 °C. While WS4 samples were founded fast degradable temperature between 250 °C- 450 °C.

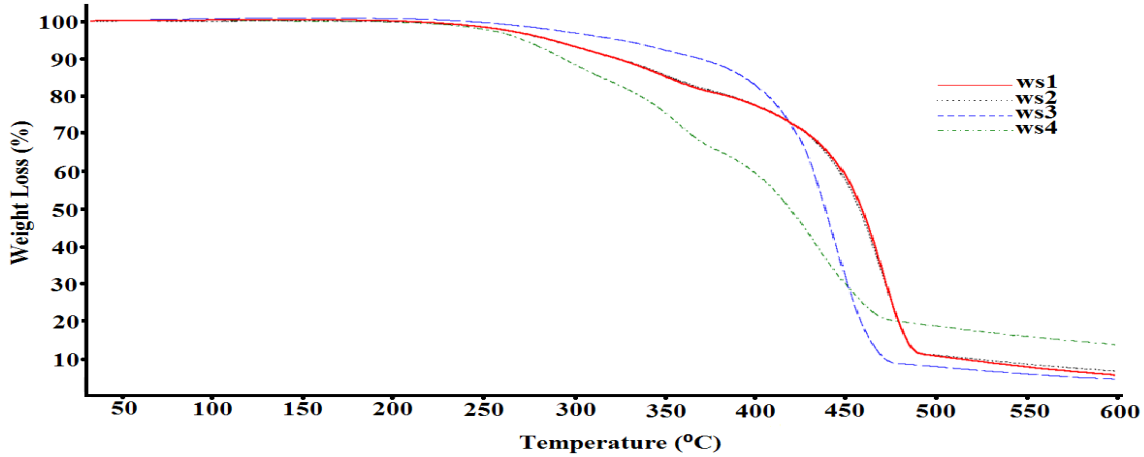

Fig 1. TGA thermograph of composites groups

WS1 and WS2 samples were founded any differences according to TGA thermograph analysis. The analysis showed that MAPE didn't affect to thermal degradation of 47% WS filled polyethylene composites samples.

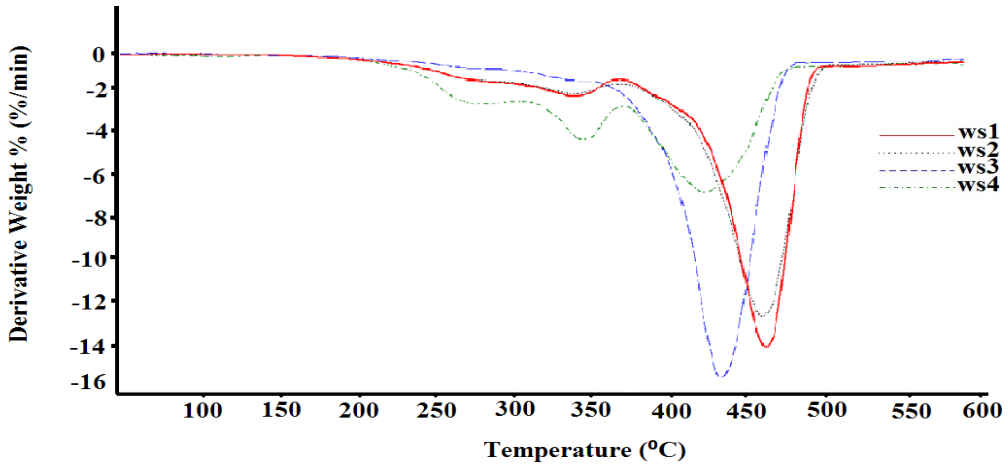

Fig 2. DTGA thermograph of composites groups

The DSC results of WS filled polymer composites are presented in Fig. 3. Melting temperature was around WS1 and WS2 130 °C while WS3 and WS4 165 °C. The second melting peak temperature of WS2 composites with 3% coupling agent was around 170 °C. This result indicates that thermal stability of the polymers increased with MAPP and MAPE (Sutivisedsak et al. 2012; Ayrilmis et al. 2013). Also, we know that melting point of HDPE and PP is around 130 °C and 175 °C, respectively (Klyosov 2007).

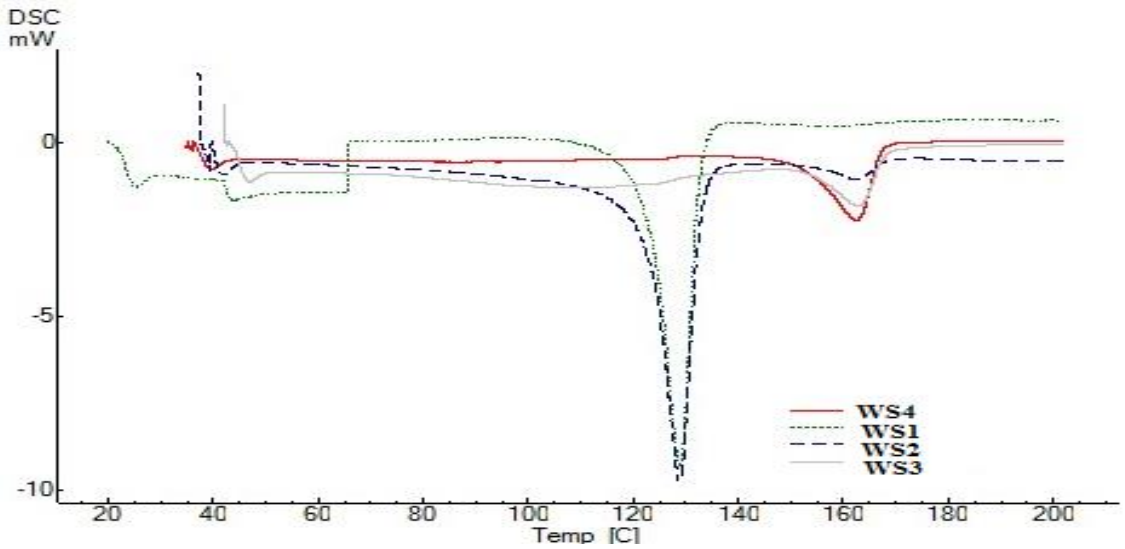

Fig 3. DSC thermograph of composites groups.

During the manufacturing of polymer-composites, melting temperature of the polymer and the degradation temperature of the filler have great importance. Based on the TGA and DSC analysis during the manufacturing of polymer-composites, extruder temperatures should be over 129 °C to facilitate the melting of the polymer matrix and should be less than 220 °C to prevent the WS from degrading. In other studies, initial degradation of natural fibers such as hemp and flax are reported to be 230 °C (Kozlowski and Pryzbylak 2008) while jute and wheat straw flour were 190 °C (Choundhury and Adhikari 2007) and 220 °C (Mengeloglu and Karakus 2008), respectively. It is believed that low temperature degradation is associated with the degradation of hemicelluloses. It should also be noted that residence time of the material in the extruder is also important (Chan and Balke 1997). In this study extruder temperature set up between 180 °C and 210 °C. Higher processing temperature can be set if the component passes through the extruder in a short period of time.

Conclusions

1. Agricultural residue and industrial wastes such as wheat straw, rice straw, hemp fiber, shells of various dry fruits flour, wood sawdust, and sawdust of particleboard could in the future be good reinforcements for recycled polymers. Using of these materials can be a resource for manufacturing of polymer composites. In this study, polymer composites were manufactured using walnut shell flour as filler and polymer matrix via extrusion and compression methods.

2. The final product tested to determine their tensile, flexural, impact strength properties as well as thermal properties. The best results were obtained composites containing respectively 47%-3%-50 formulation of WS flour-MAPP-PP can be used in composites applications requiring mechanical properties.

3. In addition, composites which were produced walnut shell provided the values of ASTM D6662 standard.

4. The use of coupling agent noticeably improved the tensile and flexural strength but did not significantly affect impact strength of WS filled polyethylene based composites.

5. The compatibilizer MAPP was found to be effective in improving mechanical properties.

6. Based on the TGA and DSC studies, thermal stability of the polymers increased with MAPP and MAPE. That's why; processing temperature should be adjusted between 129 °C and 230 °C

for polymer composites utilizing WS and polymers.

7. The data collected in our country which waste a large portion of walnut shell allows for the evaluation of the production polymer composites. As a result walnut shell which was considered agricultural waste can be utilized in polymer composite production.

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