Technological and Thermal Properties of Thermoplastic Composites Filled with Heat-treated Alder Wood

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This study investigated the effect of heat-treated wood content on the water absorption, mechanical, and thermal properties of wood plastic composites (WPCs). The WPCs were produced from various loadings (30, 40, and 50 wt%) of heat-treated and untreated alder wood flours (*Alnus glutinosa* L.) using high-density polyethylene (HDPE) with 3 wt% maleated polyethylene (MAPE) coupling agent. All WPC formulations were compression molded into a hot press for 3 min at 170 ºC. The WPCs were evaluated using mechanical testing, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The mechanical property values of the WPC specimens decreased with increasing amounts of the heat-treated wood flour, except for the tensile modulus values. The heat treatment of alder wood slightly increased the thermal stability of the WPCs compared with the reference WPCs. The crystallization degree (X_c) and the enthalpy of crystallization of the WPCs slightly decreased with increasing content of the heat-treated wood flour. However, all WPCs containing the heat-treated alder wood flour showed a higher crystallinity degree than that of the virgin HDPE.

Keywords: Mechanical properties; Heat-treatment; Thermal stability; Water absorption; Alder wood

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INTRODUCTION

Wood-plastic composites (WPCs) are one of the newest semi-structural composite materials used in thermoplastic and wood composite industries. They have significant advantages compared with solid wood in outdoor applications, such as high dimensional stability and biological durability. Lignocellulosic materials provide several advantages such as being lightweight, having a low density, low cost, high specific properties, low energy consumption, and the absence of production residue or toxic by-products when burnt. Thermoplastics melted and processed below the degradation temperature of lignocellulosic materials, which is around 200 °C, are usually suitable for manufacturing WPCs (Chaharmahali *et al.* 2008; He *et al.* 2014). Mainly five different commercial treatments have emerged, one in Finland (Thermowood), one in Holland (Plato Wood), one in Germany (OHT-Oil Heat Treatment), and two in France (Bois Perdue and Rectification). New heat treatment processes are also emerging in other countries, such as Denmark (WTT) and Austria (Huber Holz) (Esteves and Pereira 2009). For example, the wood species treated by the Finnish method (Thermowood) are essentially Scots pine (*Pinus sylvestris*) and spruce (*Picea abies*), that are used in the exterior applications such as terraces, garden furniture, doors and window, and poplar (*Populus tremula* L.) and birch (*Betula pendula*), that are used in the interior for kitchen furniture, parquets, and pieces of furniture (Esteves and Pereira 2009).

The major drawbacks of WPCs are their susceptibility to fungal attack, their poor interfacial adhesion between the components, and expansion/shrinkage. Biological durability of lignocellulosic materials in WPCs is poor for outdoor applications because they contain sugars, starch, and in particular, hemicellulose, which has the lowest biological durability against fungi. Furthermore, the incompatibility between wood and the polymer matrix leads to low engineering performance and poor interfacial adhesion between the plastic matrix and the filler, which provides pathways for moisture uptake and biological attack. Over time, the swelling and shrinking of WPCs creates microcracks that allow biological degradation by decay fungi, termites, molds, algae, and marine borers (Hosseinaei *et al.* 2012; Samaniego *et al*. 2013; Tascioglu *et al.* 2013). Among the various modification methods used to enhance the biological durability and dimensional stability of wood, heat treatment has recently gained industrial importance (Correa *et al.* 2003; Tschegg *et al.* 2009), but there is very limited information about the heat treatment of alder wood (*Alnus glutinosa* L.). Alder is one of the most important tree species in Turkey; it is a fast growing species that spreads over a wide area of the country (Huş 1962). This study investigated the effect of heat treatment on water absorption as well as the thermal and mechanical properties of WPC produced from heat-treated alder wood flour, using virgin high density polyethylene (HDPE) with a coupling agent.

EXPERIMENTAL

Materials

Heat-treated and untreated alder wood (*Alnus glutinosa* L.) were used as filler materials. The heat-treated wood samples were obtained from Nova Forest Products Industry Trade Inc. (Bolu, Turkey). For the heat-treatment process, the specimens with dimensions of 50 mm x 50 mm x 5 mm were prepared. The Thermo-D heat-treatment method—212 °C for 2 h under saturated steam—was applied to the samples in the Novawood factory located in Bolu, Turkey, as previously described by Navi and Sandberg (2012). Untreated alder wood samples were used as controls. The virgin high-density polyethylene (HDPE, type S 0464) was supplied from Petrokimya Holding Corporation, Aliaga, Turkey. It had a melt flow index range of 0.25 to 0.40 g/10 min (2.16 kg and 190 °C, ASTM D1238-13 (2013)) and a density of 0.959 to 0.963 g/cm^3. Maleated polyethylene (MAPE) was used as the coupling agent (Clariant Licocene® PE MA 4351 granules, Clariant International Ltd., Muttenz, Switzerland). Its viscosity and density were 200 mPA·s to 500 mPA·s (at 140 °C) and 0.98 to 1.00 g/cm^3, respectively.

Preparation of Compression-Molded Wood Plastic Composites

The air-dried, heat-treated and untreated alder wood samples were ground into small particles using a Wiley mill (Fritsch, Pulverisette 19, Idar-Oberstein, Germany). The wood flour retained on an 80-mesh size sieve was dried in a laboratory dryer (Termal, A11680T, Istanbul, Turkey) to a moisture content of 0 to 1% at 103 ± 2 °C (about 24 h). The samples were mixed with the HDPE in a high-intensity laboratory mixer (Shini SVM-80U, Guangdong, China). This mixture was compounded in a single-screw laboratory extruder (Rondol linear 30, Stoke-on-Trent, UK, L/D, with a ratio of 30:1). The temperature profile was set at the die end for 170 °C to 175 °C to 180 °C to

185 °C. The screw speed was calibrated at 60 rpm. The extruded samples were collected and cut into pellets. Finally, the pellets were compressed into 150 mm × 170 mm × 5 mm WPC panels for 3 min at 170 °C. The formulations of the WPCs are given in Table 1.

Table 1. Composition of Hot-Press Molded WPCs

WPC Code	Treated Alder Wood (TAW) (wt%)	Untreated Alder Wood (UAW) (wt%)	HDPE (wt%)	MAPE (wt%)
A	-	30	67	3
B	30	-	67	3
C	-	40	57	3
D	40	-	57	3
E	-	50	47	3
F	50	-	47	3

Methods

Water absorption

The long-term water absorption (WA) behavior of the WPC specimens was tested according to the ASTM D570-98 (2010) standard. Before testing, specimens with dimensions of 50 mm × 50 mm × 5 mm were conditioned at 20 °C and 50% relative humidity to a constant weight according to ASTM D618-13 (2013). Seven replicates from each WPC group were placed into beakers filled with distilled water at a temperature of 23 ± 2 °C. The water was replaced with fresh water after 1, 2, 3, and 4 months.

Scanning electron microscopy

The fractured surface of each WPC sample was examined with a scanning electron microscope (ZEISS EVO LS10, Germany). The specimens were first dipped in liquid nitrogen and snapped in half. The specimens were then coated with gold under vacuum prior to the scanning.

Flexural and tensile properties

The modulus of rupture (MOR) and modulus of elasticity (MOE) were determined specimens with dimensions of 150 mm × 13 mm × 5 mm with a three-point bending test (ASTM D790-10 (2010)). Tensile tests were performed according to ASTM D638-14 (2014). The specimens were tested with a crosshead speed of 5 mm/min. The dog-bone shape specimens (type III) were tested on a Zwick 10KN universal testing machine (Ulm, Germany). Seven samples for each WPC group were used in the tensile and flexural tests.

Thermogravimetric analysis (TGA)

A Perkin Elmer TGA-6000 (Waltham, MA, USA) thermal analyzer was used for the thermogravimetric analysis (TGA) of the samples. The test was performed in the temperature range of room temperature to 600 °C, with a heating rate of 10 °C/min under nitrogen with a 20 mL/min flow rate.

Differential scanning calorimetry (DSC) analysis

A Perkin Elmer DSC 8000 (Waltham, MA, USA) was used for DSC analysis. 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 (χ_{corr}) of the HDPE samples were calculated using Eq. 1,

$$\chi_{corr} = (\Delta H_{exp} / \Delta H) \times (1/W_f) \times 100 \quad (1)$$

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

Fourier transform infrared (FTIR) spectroscopy

A Shimadzu IR Prestige-21 FTIR spectrometer (Tokyo, Japan) equipped with attenuated total reflectance (ATR) was used to characterize wood samples and WPCs. Spectra were recorded between 600 cm^{-1} and 4000 cm^{-1}, with 16 scans per experiment and a resolution of 8 cm^{-1}. The spectra for each group were transformed into absorbance spectra, which were averaged before the baseline correction and normalization.

Statistical analysis

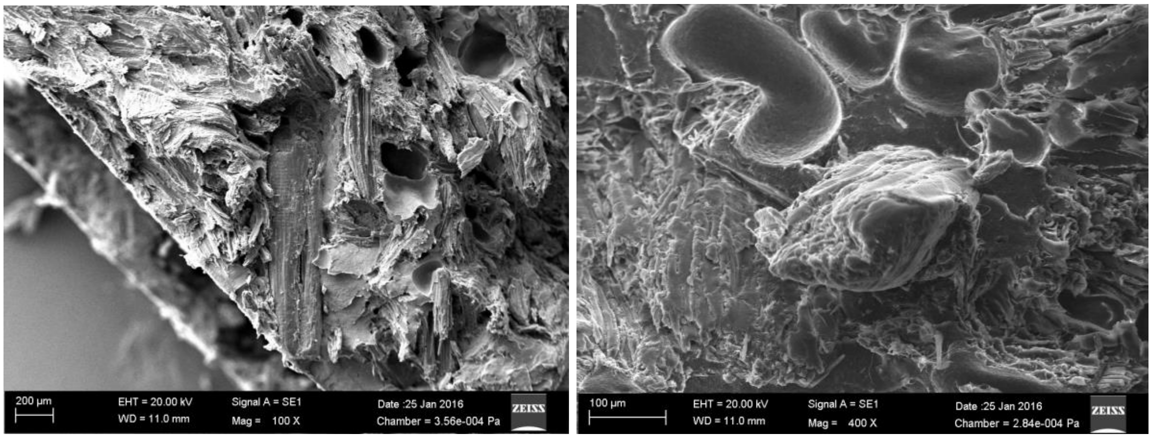
A non-parametric one-way ANOVA was performed using SPSS software (SAS Institute Inc., Cary, NC, USA) and was used to compare the difference in average values of the various parameters at a 95% confidence level.

RESULTS AND DISCUSSION

Water Absorption

The WPCs produced with heat-treated alder wood flour had significantly lower WA values compared with WPCs produced with the untreated alder wood flour (Table 2). The WA values of the specimens significantly decreased with increasing amounts of heat-treated wood flour. Significant differences, where $p < 0.05$, are shown as different letters in Table 2. For 30 wt% wood flour content, there was no significant difference in the WA values between the WPC specimens produced with untreated wood and treated wood flour. However, when the wood flour content was above 30 wt%, significant differences between the WPC groups were observed. These differences were attributed to the thermal degradation of hemicelluloses, which were hydrolyzed during the heat-treatment (Winandy and Krzysik 2007; Ashori and Sheshmani 2010).

The WA results showed that the number of micro gaps and voids in the WPC decreased with increasing amounts of the heat-treated wood flour. The presence of voids and defects in the interface between wood fillers and the polymer matrix was mainly attributable to poor dispersion of the filler in the polymer matrix. The lower WA values of the WPCs produced with heat-treated wood flour revealed that the voids and gaps in the WPC were decreased by the incorporation of the heat-treated wood flour, which enhanced the compatibility between the matrix and filler. The interfacial bonding between the filler and polymer matrix in the WPC specimen is presented in Fig. 1. The unfilled spaces and pulled out the fiber observed WPC specimen produced from untreated wood flour (Fig. 1A). The WPC sample produced with heat treated wood flour exhibited better adhesion between the particles and the polymer matrix. The reduction of the voids and better surface adhesion resulting from the addition of heat treated wood is shown in Figure 1B.



A. B.

Fig. 1. The SEM images of the WPC specimens produced with untreated (A) and heat-treated wood flour (B)

Table 2. Water Absorption Values of the WPCs*

	Water Absorption (%)			
WPC Code	1 month	2 months	3 months	4 months
A	2.49 *a* (0.65)	3.59 *ab* (0.81)	3.81 *a* (0.50)	4.27 *a* (0.33)
B	2.00 *a* (0.44)	2.69 *a* (0.34)	3.05 *a* (0.25)	3.43 *a* (0.29)
C	4.51 *c* (0.18)	5.70 *c* (0.34)	7.05 *c* (1.65)	8.15 *c* (1.97)
D	3.63 *b* (0.35)	4.67 *b* (0.49)	5.72 *b* (0.64)	6.75 *b* (0.80)
E	9.03 *e* (1.27)	11.16 *e* (1.11)	12.77 *e* (1.11)	14.38 *e* (1.11)
F	5.93 *d* (0.78)	8.11 *d* (1.12)	9.88 *d* (1.16)	11.55 *d* (1.22)

*Note: Groups with the same letters in a column indicate no statistical difference ($p < 0.05$); the values in parenthesis are the standard deviations.

Mechanical Properties

The flexural and tensile properties of WPCs produced with heat-treated and control wood flour are given in Table 3. Except for the tensile modulus, the flexural properties of the WPCs decreased with increasing heat-treated wood flour content. The tensile modulus of the WPC specimens increased with increasing amounts of the heat-treated wood flour, while the tensile strength decreased. Compared with control WPCs, the heat-treated wood led to decreases of 13.1%, 7.2%, and 44.2% for the tensile strength at 30 wt%, 40 wt%, and 50 wt% wood flour content, respectively, and increases of

88.3%, 57.2%, and 93.8% for the tensile modulus. Heat treatment led to reductions of 11.0%, 8.8%, and 14.9% for the flexural strength at 30 wt%, 40 wt%, and 50 wt% wood flour content, respectively. Similarly, the flexural modulus decreased by 13.7%, 5.2%, and 6.9%, respectively.

Table 3. Flexural and Tensile Properties of WPCs*

WPC Code	Flexural Modulus (MPa)	Flexural Strength (MPa)	Tensile Modulus (MPa)	Tensile Strength (MPa)
A	2073.75 *b* (188.30)	33.95 *e* (2.24)	231.25 *a* (57.82)	19.33 *e* (0.87)
B	1788.75 *a* (112.69)	30.19 *d* (0.91)	435.88 *bc* (50.33)	16.80 *c* (0.77)
C	2208.75 *b* (155.05)	30.34 *d* (1.81)	269.00 *a* (56.17)	16.76 *c* (0.77)
D	2092.50 *b* (252.29)	27.64 *c* (0.50)	423.25 *b* (36.10)	15.54 *b* (0.80)
E	2753.75 *d* (197.77)	26.00 *b* (1.68)	245.00 *a* (37.72)	17.61 *d* (0.91)
F	2562.50 *c* (93.01)	22.11 *a* (1.13)	475.50 *d* (43.12)	9.83 *a* (0.68)

* Note: Groups with the same letters in a column indicate no difference statistically ($p < 0.05$), the values in parenthesis are the standard deviations

As a hydrophobic substance, HDPE is not compatible with hydrophilic wood material. The resultant poor adhesion between the polymer matrix and the wood filler creates weak interfacial regions in WPCs (Kaboorani *et al.* 2008). The mechanical tests showed that heat treatment made alder wood more compatible with HDPE, leading to an improvement in the tensile modulus. Heat treatment degrades hemicellulose and reduces the polymerization degree. These effects could decrease the flexural strength and flexural modulus of WPCs, as previously reported (Mohebby *et al.* 2008; Ayrilmis *et al.* 2011). The incorporation of the coupling agent (MAPE) in the raw material formulation also affects the mechanical properties of the WPCs. Stronger interfacial bonding between the wood filler and the polymer matrix is caused by the coupling agents. The coupling agent chemically bonds with the OH groups in the lignocellulosic filler and improve the mechanical properties of the WPCs. The anhydride groups in the coupling agent, MAPE, enter into an esterification reaction with the surface hydroxyl groups of wood fibers and covalently bond to the hydroxyl groups. The decrement in the OH groups of hemicelluloses due to heat-treatment can reduce the efficiency of the MAPE for the interfacial bonding between wood flour and polymer matrix, which decreases the mechanical properties of the WPCs produced with the heat-treated wood (Adhikary *et al.* 2008).

Thermogravimetric Analysis

The TGA and derivative TGA of the WPCs produced with the heat-treated wood or the untreated alder wood and pure HDPE are presented in Figs. 2 and 3, respectively. The thermal degradation of HDPE started around at 470 to 500 °C, and the degradation rate was much higher than that of the wood after this point. At first, the degradation temperatures of the heat-treated and untreated wood and the WPCs were much lower than that of the HDPE, but the degradation rate was much slower. The WPC produced with the heat-treated alder wood flour was more thermally stable than the WPC produced with the untreated alder wood flour as it was expected.

Heat treatment of wood produces intensively degraded hemicellulose. In addition, heat treatment either removes or changes the structure of the most sensitive components of wood (Kaboorani 2009; Xing and Li 2014). The first decomposition peak temperature of heat-treated wood and WPCs produced with the untreated wood flour was around 220 °C and 200 °C, respectively. The second decomposition peak temperature was at 480 °C, reflecting the decomposition of HDPE at this temperature (Cavdar *et al*. 2015).

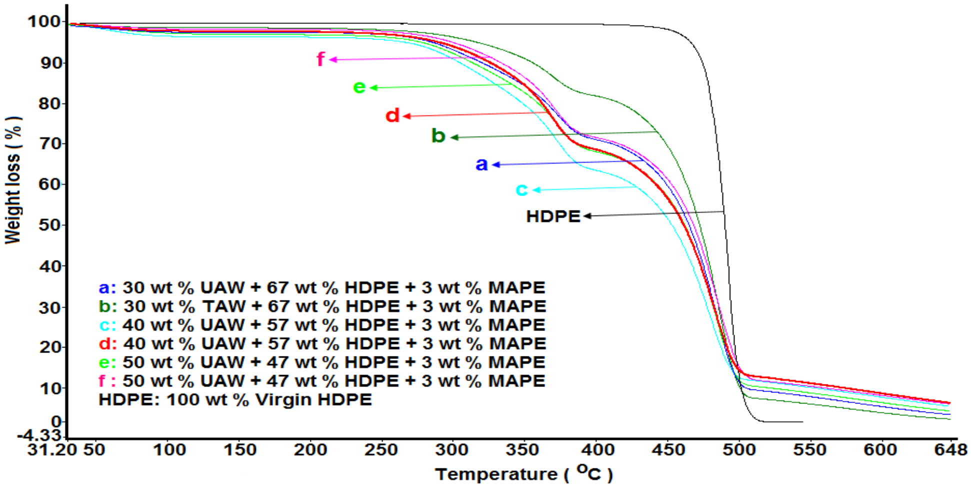


Fig. 2. TGA results of WPCs

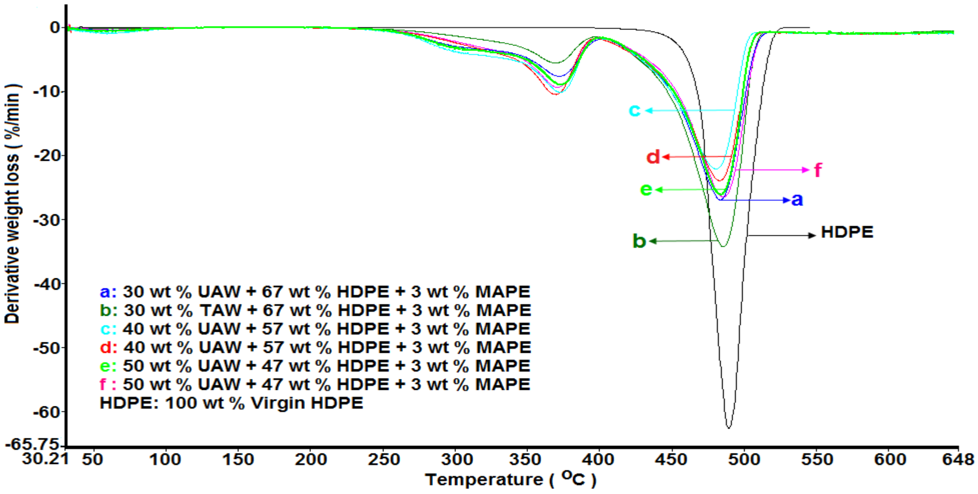


Fig. 3. Derivative TGA results of WPCs

Differential Scanning Calorimetry

In data from the DSC analysis, there were unremarkable changes in the first and second melting peak temperature of the polymer composites (Table 4). The second melting enthalpy (ΔH_m) values decreased with increased filler content in the polymer composites. Similar values were observed for the second crystallization enthalpy (ΔH_c) values. Heat-treated or untreated alder wood-containing HDPE composites had higher crystallinity degree (X_c) values than virgin HDPE. The X_c values increased with increasing wood filler content, which could be due to the nucleation effect of wood flour (Lei *et al.* 2007; Rodrigues *et al.* 2013).

Table 4. Differential Scanning Calorimetry Analysis*

WPC Code	T_m^1 (°C)	T_c^1 (°C)	T_c^2 (°C)	ΔH_c (J/g)	T_m^2 (°C)	ΔH_m (J/g)	X_c (%)
HDPE	130.75	119.45	115.35	128.68	134.95	137.63	43.7
A	133.68	121.52	118.83	103.15	135.48	110.97	50.3
B	132.50	121.34	119.20	95.17	134.45	95.52	46.4
C	132.85	121.58	119.07	103.73	134.85	106.43	59.0
D	133.11	121.51	119.13	98.20	135.23	103.88	55.9
E	133.07	121.24	118.50	98.16	135.43	103.89	67.0
F	132.46	121.38	119.03	87.35	134.93	84.37	59.5

*Notes: T_m^1: Peak temperature of first melting, T_c^1: Onset temperature of crystallization,
T_c^2: Peak temperature of crystallization, ΔH_c: Enthalpy of crystallization,
T_m^2: Peak temperature of second melting, ΔH_m: Enthalpy of second melting,
X_c: Crystallization degree

Compared with the untreated alder wood-filled HDPE composites, the heat-treated alder wood-filled HDPE composites had a lower crystallinity degree. Thus, heat treatment positively affected the WPC crystallization properties. Previously, it was shown that short-term heat treatment of wood has a positive effect on its crystallinity, while long-term treatment decreases crystallinity (Bhuiyan and Hirai 2005; Phetkaew *et al.* 2008). Here, the results suggested that heat treatment negatively effected the crystallinity degree (X_c). The crystallinity degree of the virgin HDPE was considerably lower than that of the HDPE composites filled with untreated or heat-treated alder wood flour.

FTIR Spectroscopy Analysis

The FTIR-ATR spectra of the heat-treated and untreated alder wood are presented in Fig. 4. In the spectral region of 1100 cm^{-1} to 1800 cm^{-1}, the absorption increased after heat treatment. The intensity of the aromatic skeletal vibration increment located at 1602 cm^{-1} after heat-treatment could be caused by cleavage of the propyl groups in lignin (Ucar *et al.* 2005). The intensified peak at 1454 cm^{-1} denoted the formation of new conjugated double bounds due to the heat treatment (Chen *et al.* 2012). The carbonyl absorption peak at 1720 cm^{-1} to 1740 cm^{-1} decreased after the heat treatment. The change in this peak confirmed the cleavage of acetyl side chains in hemicellulose (Kocaefe *et al.* 2008). The benzene ring of stretching vibrations was observed in the band from 1505 cm^{-1} to 1515 cm^{-1}. The hardwood lignin (guaiacyl-G and syringyl-S) and the softwood lignin (guaiacyl-G) were denoted in the bands of 1505 cm^{-1} and 1515 cm^{-1}, respectively (Faix 1991). After the heat treatment, the peak intensity increased at 1515 cm^{-1} but decreased at 1505 cm^{-1}. This result reflected the loss of syringyl units; this unit is condensed less by C-C bonds than the guaiacyl monomer. A syringyl monomer is more likely to be released by thermal degradation (Faix *et al.* 1990). Moreover, the band of 1240 cm^{-1} showed the lignin syringyl monomer and the C-O in xylan (Nuopponen *et al.* 2004; Temiz *et al.* 2007). The peak intensity at 1240 cm^{-1} decreased after the heat treatment.

The FTIR-ATR spectra of the heat-treated and untreated alder wood-filled HDPE composites and virgin HDPE are presented in Fig. 5. The C-O stretching in cellulose and hemicellulose at the 1031 cm^{-1} band, the syringyl lignin and C-O in xylan located at the 1240 cm^{-1} band, and the C-O-C asymmetric band in the cellulose and hemicellulose peak at the 1161 cm^{-1} band (Temiz *et al.* 2007) were observed in the heat-treated and untreated alder WPCs. The intensity of the peaks of the HDPE composites filled with the heat-treated wood flour decreased at 1162 cm^{-1}, 1240 cm^{-1}, and 1740 cm^{-1} but was higher than those of the HDPE composites filled with untreated wood flour and virgin HDPE.

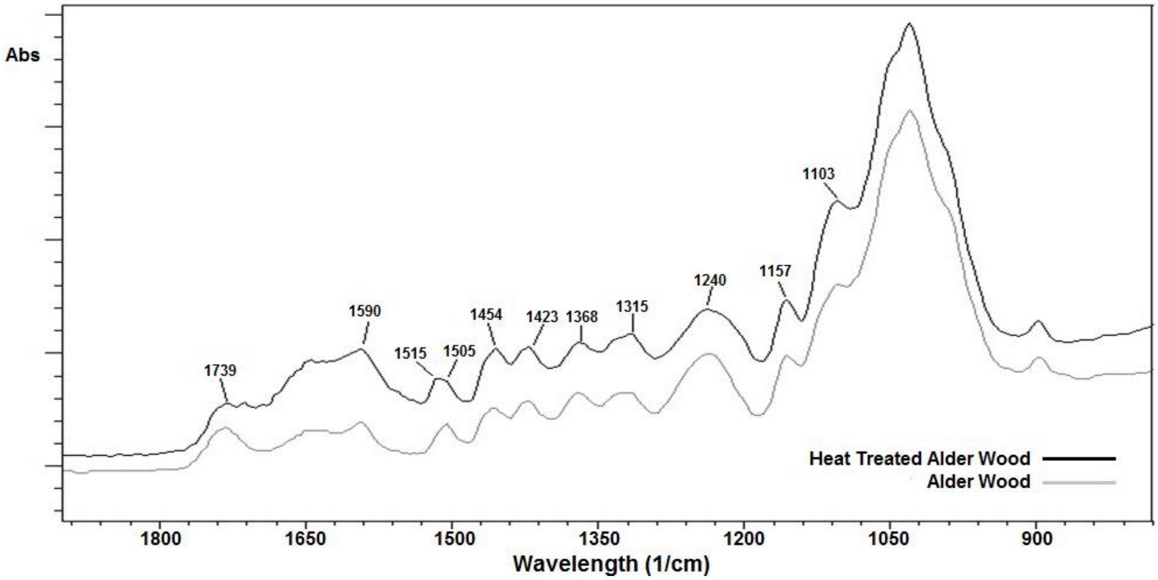


Fig. 4. FTIR-ATR spectra of heat-treated and untreated alder wood

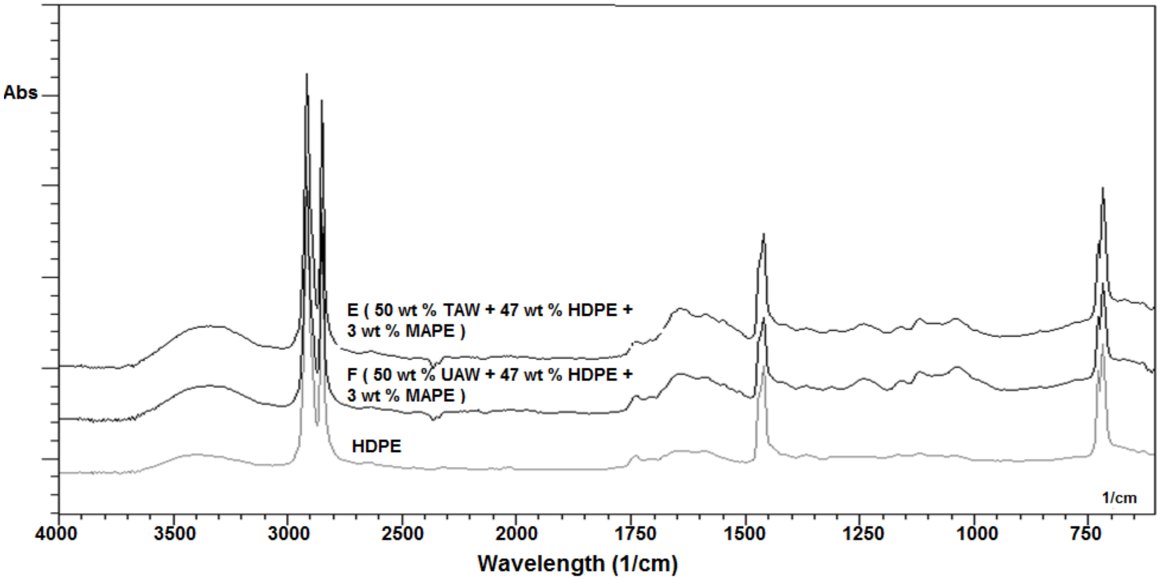


Fig. 5. FTIR-ATR spectra of heat-treated and untreated alder wood-filled HDPE composites and virgin HDPE

CONCLUSIONS

1. Compared to the control specimens, the WPC specimens produced with heat-treated wood showed a significantly higher tensile modulus but lower tensile strength.
2. WPC flexural properties decreased with increasing heat-treated wood flour content.
3. FTIR spectra showed that the heat treatment removed hemicellulose and lignin from alder wood.
4. WPCs produced with heat-treated alder wood had a higher initial temperature and a lower rate of thermal decomposition than the composite filled with untreated wood.
5. Based on the DSC analysis, heat treatment of alder wood had no effect on the melting behavior of the WPC.
6. The crystallization degree and enthalpy of crystallization of the WPC decreased with increasing heat-treated wood content.

ACKNOWLEDGEMENTS

This study was supported by the Directory of Scientific Research Projects of Artvin Çoruh University (BAP) grant number 2014.F11.02.03.

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Article submitted: December 3, 2015; Peer review completed: January 14, 2016; Revised version received and accepted: February 2, 2016; Published: February 10, 2016.
DOI: 10.15376/biores.11.2.3153-3164