INVESTIGATING CHANGES IN THE CHEMICAL CONSTITUENTS AND DIMENSIONAL STABILITY OF HEAT-TREATED HORNBEAM AND ULUDAG FIR WOOD

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Changes in chemical constituents and some physical properties such as swelling and water absorption of hornbeam (*Carpinus betulus* L) and uludag fir (*Abies bornmulleriana* Mattf.) wood were investigated after heat treatment at three different temperatures (170 ^{o}C, 190 ^{o}C, and 210 ^{o}C) for three different durations (4, 8, and 12 hours) by using thermal gravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectrometry. The results of TGA show that there was less weight loss in the main degradation region (300-500 ^{o}C) for the heat-treated samples as compared to untreated (control) samples. In addition, there was greater weight loss of hornbeam wood than of uludag fir wood in a similar degradation region. This difference could be due to the chemical constituents of softwoods and hardwoods. The results of FTIR spectrometry show that the chemical constituents of the hornbeam wood samples were more affected by heat treatment. All heat-treated samples exhibited lower water absorption and swelling compared to control samples. It was found that the relative decrease in swelling and water absorption for uludag fir was higher than for hornbeam. The maximum decrease in water absorption and swelling was found for both species that were heat-treated at 210 ^{o}C for 12 hours.

Keywords: FTIR Measurement; TGA analysis; Heat treatment; Dimensional Thermal Stability

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INTRODUCTION

Wood is a complex composite material, that consists of cellulose (ca. 40 to 45%), hemicelluloses (ca. 20 to 25%), lignin (ca. 20 to 30%), and low-molecular-mass compounds as volatile and non-volatile extractives (3 to 5%) (Wigberg and Maunu 2004). The cellulose component can be characterized as a linear high molecular mass polymer made up of anhydro-D-gluco-pyranose units linked by β-D-l-4 glycosidic linkages. Hemicelluloses, which are a second major component just after cellulose, are comprised of various sugar monomers such as glucose, mannose, galactose, xylose, and arabinose that are linked by various bonds and as a result form a branched polymeric structure. Lignin, the third major chemical in wood, is an aromatic polymer formed of phenyl propane units linked together mainly by aryl ether linkages (Esteves et al. 2008).

Heat treatment of wood modifies the cell wall components. This method has been recognized as an alternative way to improve some physical properties including swelling and shrinkage with moisture (dimensional stability) and biological durability (Militz 2002; Gunduz et al. 2008; Kaygin et al. 2009; Tumen et al. 2010). The influence of heat treatment conditions on wood properties has been intensively investigated during the last decade (Petrissans et al. 2003). Improving biological resistance against fungi was reported to be mostly due to thermal degradation. However, thermal degradation was found to be associated with less ordered polysaccharides, including hemicelluloses and amorphous cellulose (Nguila Inari et al. 2007). Recently, it was reported that decrease in mass due to heat treatment could be a reliable and accurate parameter to predict decay resistance of heat-treated wood (Welzbacher et al. 2007). This decrease is directly proportional to treatment intensity, which is directly related to treatment conditions. When the treatment temperature increases, the weight of the wood is decreased. It was determined that about 4% and 9% mass loss due to thermal degradation occurred after isothermal heating at 180 °C and 200 °C, respectively, for 550 min, which contributed to about 35% and 85% decline in wood stiffness, respectively (Jiang et al. 2009).

According to a widely used practice (Esteves and Pereira 2009), wood is heated slowly up to 200–230 ºC in a humid inert gas environment. This reduces the hydrophilic behavior of the wood by modifying the moisture-sensitive constituents such as carbohydrates and lignin (Raimo et al. 1996; Gailliot 1998). This modification effect lowers the re-absorption of liquids inside the wood; as a result, the heat-treated wood becomes dimensionally more stable compared to untreated wood. However, elimination of hydroxyl groups from wood (e.g. hemicelluloses or less ordered cellulose structure) also reduces the number of potential bonding sites for water (Poncsak et al. 2005). During the heat treatment process, many volatile organic compounds such as alcohols, resins, terpenes, and the acetic acid generated from wood pyrolysis are released from the wood (Manninen et al. 2002; Graf et al. 2003). A significant decrease of hemicelluloses content is also reported in the literature (Bekhta and Niemz 2003). It is well established that the hemicelluloses degrade first from 160 °C to 260 °C, since their low molecular weight and their branching structure facilitates faster degradation compared to the other components present in wood (Fengel and Wegener 1989).

Yorulmaz and Altimtay (2009) used thermogravimetric analysis to determine the thermal behaviors of medium density fiberboard (MDF), particleboard (PB), plywood (PL), and pine wood treated with fire retardants. The largest weight loss was observed in the second region (250 to 400°C) for all samples. Weight losses for the treated samples were smaller in the second region (about 50 to 55%) compared to those of untreated pine samples (average 63%). In the third region, the largest weight losses were seen for the treated waste wood samples (about 31 to 35% for MDF, PL, and PB).

Yang et al. (2007) characterized cellulose, hemicelluloses, and lignin by using thermogravimetric analysis. Great differences were found among the pyrolysis behaviors of the three components. Hemicelluloses started their decomposition easily. Maximum mass loss (0.95 wt.%) occurred at 268 °C, and there was still 20% solid residue left even at 900 °C. Cellulose pyrolysis was focused at a higher temperature range (315 to 400 °C) with the maximum weight loss rate (2.84 wt.%/ °C) attained at 355 °C. When the temperature was higher than 400 °C, almost all of the cellulose was pyrolyzed, with a very low solid residue remaining (6.5 wt.% °C). Among the three components, lignin was the most difficult one to decompose. Its decomposition occurred slowly throughout the whole temperature range (from ambient to 900 °C), at a very low mass loss rate (0.14 wt.% / °C). The solid residue left from lignin pyrolysis (45.7 wt.%) was the highest. The differences in the inherent structures and chemical nature of the three components likely account for the different behaviors observed (McKendry 2002; Rao and Sharma 1998).

The chemical analysis of woods after heat treatment at various temperatures shows relatively good stability of the components up to 100 °C and up to a treating time of 48 h. At higher temperatures the content of polysaccharides (holocelluloses) is further decreased, and the hemicelluloses react more sensitively than cellulose. Alpha-cellulose of softwood contains a relatively high amount of hemicelluloses and residual lignin; the decrease of alpha-cellulose, which begins at 100 °C, can be attributed to the loss of these accompanying compounds, so that the content of pure cellulose remains constant up to 150 °C even in softwood. The lignin content remains constant over a wide temperature range; above 150 to 160 °C the relative lignin content increases (Fengel and Wegener 1989).

The heat effects on the chemical constituents, as well as the mechanical and physical properties of woods have been well defined with various methods. The aim of the current study is to determine the thermal performance, changes in chemical constituents, and dimensional stability of heat-treated hornbeam (*Carpinus betulus* L.) and uludag fir (*Abies bornmulleriana* Mattf.) wood, which are commonly used in Turkey. The data obtained in this study could be used for both scientific and industrial applications.

MATERIALS AND METHODS

Preparation of Experimental Samples

Hornbeam (*Carpinus betulus* L.) and uludag fir (*Abies bornmulleriana* Mattf.) woods were obtained from Bartin City in Turkey. The wood samples were first dried in air, with initial moisture contents from 11% to 13%. The dimensions of the samples were prepared as 20 x 20 x 30 mm (longitudinal, radial, and tangential) pieces.

Heat treatment was then applied on the test samples in an oven capable of controlling the temperatures within a range of ± 1 °C. Treatment was applied at three different temperatures (170, 190, and 210 °C) and three different durations (4, 8, and 12 h) under inert atmosphere. During heat treatment, temperature was increased gradually.

Before chemical analysis, heat-treated, and control samples were ground in a Wiley mill into a homogenous meal according to the TAPPI T257 cm-0221 standard (2002). In this study, 3 replicates were used for TGA and 2 replicates were used for FTIR analysis.

Analysis by Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the coherence of a radiative source, using time-domain or space-domain measurements of electromagnetic or other types of radiation (Kotilainen et al. 2000; Harrington et al. 1964). In this study, oven-dried ground woods obtained from hornbeam and uludag fir wood samples treated by heating were subjected to FTIR analysis. The dried samples (ca. 10 to 15 mg) for each group were embedded in potassium bromide (KBr) pellets and analyzed by using a Perkin Elmer Spectrum One FTIR spectrophotometer model 2000. They were recorded in the absorption mode in the range of 2500 to 800 cm^{-1} with an accumulation of 32 scans, resolution of 2 cm^{-1}, and the data obtained were normalized to the C–O–C band at 2900 cm^{-1}. FTIR analysis was applied to control, 170°C for 4 and 12 hours, and 210°C for 4 and 12 hours for determining the changes between groups.

Analysis by Thermogravimetric Analysis (TGA)

TGA is commonly used to determine thermal performance, degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation (Hsu et al. 2000). In this study, thermal behavior and mass loss of heat treated hornbeam and uludag fir wood were investigated using a Shimatzu TGA-50 thermogravimetric analyzer, which was fully supported by computer–controlled software options for control and data handling. TGA tests were run under a dynamic nitrogen atmosphere flowing at 20 mL/min and at a scanning rate of 10^oC/min. TGA curves were determined in three regions on thermographs. The curves of TGA are interpreted as evaporation of water and extractive mass from the wood (first region is between 100-200 ^oC), degradation of wood’s constituents (second region, between 200 and 400 ^oC), and decomposition (third region, above 400 ^oC). In preparing the samples, each sample weighing approximately 5 to 10 mg was placed in an open experimental sample pan and suspended from a sensitive microbalance. A furnace surrounded the sample to provide accurate heating range from 50 to 850 °C. In order to isolate the decomposition step, all runs were purged in an air atmosphere, at a flow rate of 20 mL/min at 5 °C/min (slow–heating regime) or at 40 °C/min (fast–heating regime). The slow and fast heating regimes were applied to compare differences in thermal properties and char. Three replicates were used for TGA analysis, and the reported results consisted of the averages of those replicated tests. TGA analysis was applied to control, 170 °C for 4 and12 hours, 190 °C for 4 and 12 hours, and 210 °C for 4 and 12 hours.

Determination of Dimensional Stability and Water Absorption

Tests of dimensional stability and water absorption were conducted on the same samples with 20 x 20 x 30 mm dimensions (10 samples were replicated for each group). Measurements on the samples were conducted by caliper with ± 0.01 mm accuracy in three different directions (tangential, radial, and longitudinal) of wood before and after immersion in water for 48 h. The dimensional stability and water absorption values of the samples were determined using ISO 4859 (1982).

In this study, all statistical calculations were based on the 95% confidence level. ANOVA and Tukey's Multiple Range Tests showed that all differences were significant.

RESULTS AND DISCUSSION

Figures 1 and 2 show TGA thermograms of heat-treated samples of hornbeam and uludag fir, respectively. Summary data of TGA for both woods can be found in Table 1. Note that all thermograms represented in Figs. 1 and 2 are similar to each other. According to the TGA results, three regions were determined for the approximate starting and ending points of the thermogravimetric analysis curve, which shows the thermal breakdown of the organic matter and volatiles in the samples (Markova 1998).

The thermal degradation mechanism of woods generally included three regions. The first region (100 to 200 °C) shows evaporation of extractives and water loss in wood. The second region (200 to 400 °C) included the decomposition of major wood chemical constituents (Markova 1998).

The results illustrated in Table 1 show that the samples had a different decomposition temperature (T_d) in the second region. In second region (at 200 °C), the ratio of weight loss for uludag fir and hornbeam were 4.52% and 5.06% for the control samples, 3.54% and 4.70% for the heat treated samples at 170 °C for 12 hours, 3.81% and 5.42% for the heat treated samples at 190°C for 12 hours, and 4.38% and 4.92% for the heat treated samples at 210 °C for 12 hours, respectively.

According to the TGA results, thermal stability of the heat-treated samples increased as compared to the control samples. This increasing for hornbeam wood was higher than uludag fir wood. Temperatures with a maximum rate of decomposition (T_{max}) also differed for the wood samples. The decomposition curves in the second stage of samples were of similar shape, with nearly the same T_d, T_{max}, and weight loss. The third region began around 400 °C with a weight loss for uludag fir and hornbeam of about 75.49% and 70.88% in control samples, 74.79% and 69.85% for heat-treated samples at 170 °C for 12 hours, 71.79% and 68.77% for heat-treated samples at 190 °C for 12 hours, and 64.02% and 65.62% for heat-treated samples at 210 °C for 12 hours, for uludag fir and hornbeam, respectively.

The thermal degradation steps were in agreement with the results reported in the literature for degraded woods (Yorulmaz and Atimtay 2009). When the temperature reached 500 °C, the ratio of weight loss of uludag fir and hornbeam were 97.47% and 95.79% in control samples, 96.82% and 96.85% at 170 °C for 12 hours, 97.03% and 96.85% at 190 °C for 12 hours, and 97.17% and 97.21% at 210 °C for 12 hours, respectively.

As a result, there were differences between samples treated at 210 °C for 12 hours in both uludag fir and hornbeam wood. It was found that the changes in TGA curves for both woods were similar, but there was less weight loss of uludag fir wood than of hornbeam.

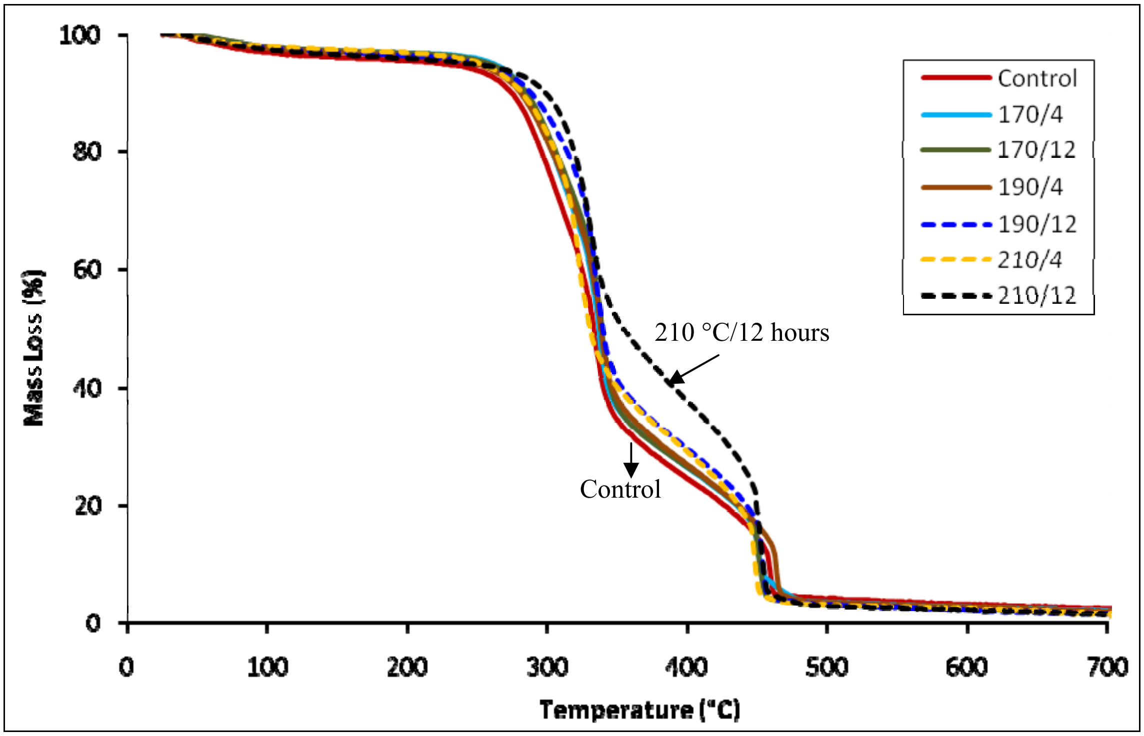

Figure 1. Thermogravimetric analysis of heat-treated and untreated hornbeam wood

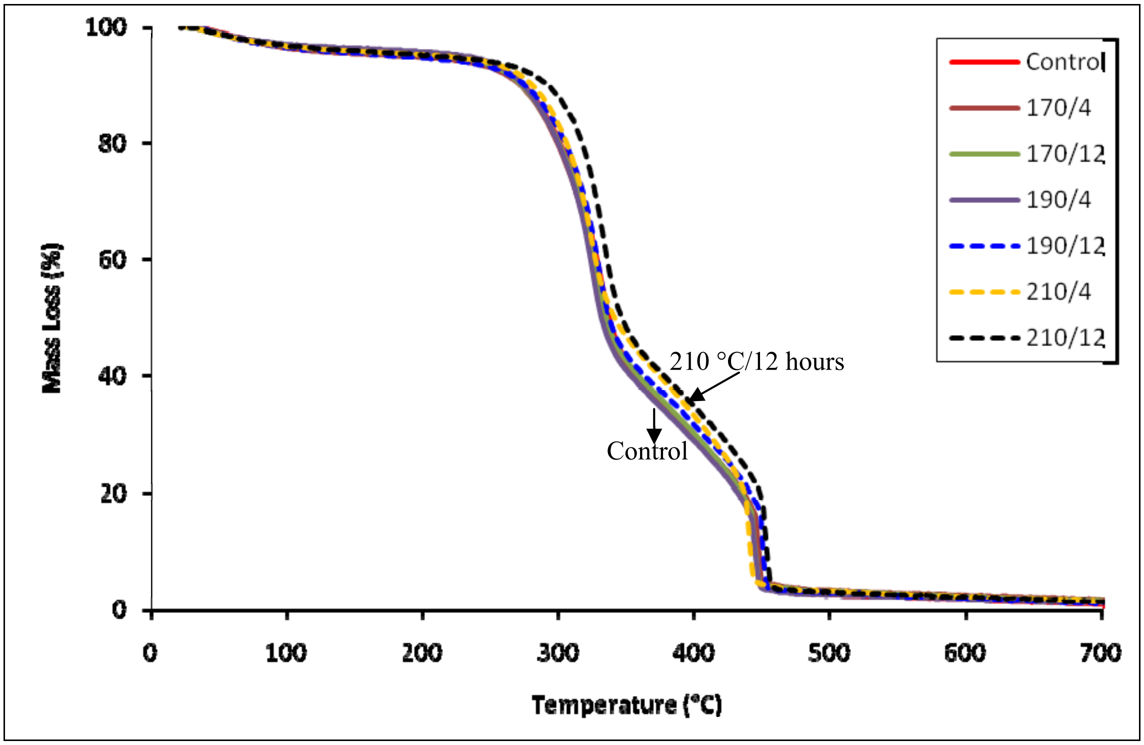

Figure 2. Thermogravimetric analysis of heat-treated and untreated uludag fir wood

Table 1 reveals that the largest weight loss was observed in the second region (200 to 400 °C) for all samples. Weight losses for the treated hornbeam were higher in the second region compared to treated uludag fir samples. In the third region (400 to 500 °C), the largest weight losses were seen for the treated hornbeam wood samples. At temperatures above 500 °C the weight losses of both un-treated and heat treated wood continued quite slowly.

Yang et al. (2007) investigated differences among the pyrolysis behaviors of the main constituents of woods. Hemicelluloses started their decomposition easily, with weight loss mainly occurring within the range 220 to 315 °C. Cellulose pyrolysis was focused at a higher temperature range (315 to 400°C). Lignin was the most difficult to decompose. Its decomposition occurred slowly from ambient temperature to 900 °C; the differences in the inherent structures and chemical nature of the three components likely account for the different behaviors observed (McKendry 2002; Rao and Sharma 1998). Wang et al. (2007) reported that the decomposition of cellulose mainly occurred within the temperature range of 277 to 397 °C, and above 403 °C additional loss of weight continued quite slowly. The results found in this study are consistent with these findings.

Table 1. Temperatures and Weight Loss during Thermal Degradation of Control and Heat-treated Samples

Mass Loss (%)	**200°C**		**300°C**		**400°C**		**500°C**	
	H	**UF**	**H**	**UF**	**H**	**UF**	**H**	**UF**
Control	4.52	5.06	22.86	20.06	75.49	70.88	97.47	95.79
170°C 4 h	3.38	5.30	21.04	22.09	74.41	71.06	96.52	96.43
170°C 8 h	3.39	4.20	20.95	20.67	74.46	70.76	96.55	96.65
170°C 12 h	3.54	4.70	21.02	19.44	74.79	69.85	96.82	96.85
190°C 4 h	3.77	4.20	20.41	17.01	73.95	69.89	97. 52	96.55
190°C 8 h	3.62	4.85	19.68	18.73	72.24	68.40	97.65	96.64
190°C 12 h	3.81	5.42	16.41	18.98	71.79	68.77	97.03	96.85
210°C 4 h	3.56	4.80	14.47	16.37	69.51	66.78	96.86	96.90
210°C 8 h	3.70	3.76	13.11	13.15	67.78	64.32	96.92	97.12
210°C 12 h	4.38	4.92	12.47	12.46	64.02	65.62	97.17	97.21

In this table, abbreviations show H for hornbeam and UF for uludag fir wood.

The straightforward interpretation of the spectral data was difficult due to the complex nature of wood and the multitude of chemical reactions taking place in the wood constituents during heat treatment. Analysis of FTIR spectra was applied to the controls, as well as to the samples treated at 170 °C for 4 to 12 hours and 210 °C for 4 to 12 hours for both woods. FTIR spectra of untreated and treated samples were made between the wavelengths of 2500 cm^{-1} and 800 cm^{-1}. Figures 3 and 4 show the FTIR plots. The FTIR spectra for both woods are documented in Table 2.

The chemical modification of the cell-wall constituents was studied by FTIR spectroscopy, which is appropriate to determine the specific bonds and functional groups within the polymeric structure. It was assumed that cleavage of acetyl groups of the hemicelluloses occurred above 150 °C. However, the FTIR spectra indicated an increase in the specific ester carbonyl peak. The esters that formed during heat treatment were mainly linked to the lignin complex, and the newly formed carbonyl groups were found present in heat-treated wood. Moreover, it was found that FTIR results were similar to each other (170 °C for 4-12 hours and 210 °C for 4-12 hours). As a result, it was found that heat treatment does not cause more change in wood constituents expect for what is defined above.

Kocaefe et al. (2008) found that thermal treatment does not cause any change in C-H bonds of birch and aspen wood treated at 160 °C, 220 °C, and 230 °C for 45 min. This chemical bond, whether it is on cellulose or hemicelluloses, is more stable than C-OH, C-O-C, R-COO-R, or Ar-OCH_3 bonds and can be expected to remain nearly unchanged. In fact, the number of C-H groups can decrease significantly because of the presence of C-H in volatile components. However, those molecules represent only 4% to 6% of the wood mass (Fengel and Wegener 1989; Nishimura et al. 1983).

Hakkou et al. (2005) applied FTIR spectroscopy to samples treated at 160 °C and 260 °C and to untreated samples. The overall FTIR spectra of both treated and untreated samples indicate that a number of spectral modifications appeared after heat treatment, even though the general aspect of the spectra remained unchanged. The diminution of the water IR absorption band at 1640 cm^{-1} compared to the C=C skeletal vibration band observed at 1595 cm^{-1} confirms the drying phase. Compared to the aromatic band at 1595 cm^{-1}, heat treatment at 260 °C led to an important decrease of the carbonyl band at 1730 cm^{-1}, indicating hemicelluloses degradation.

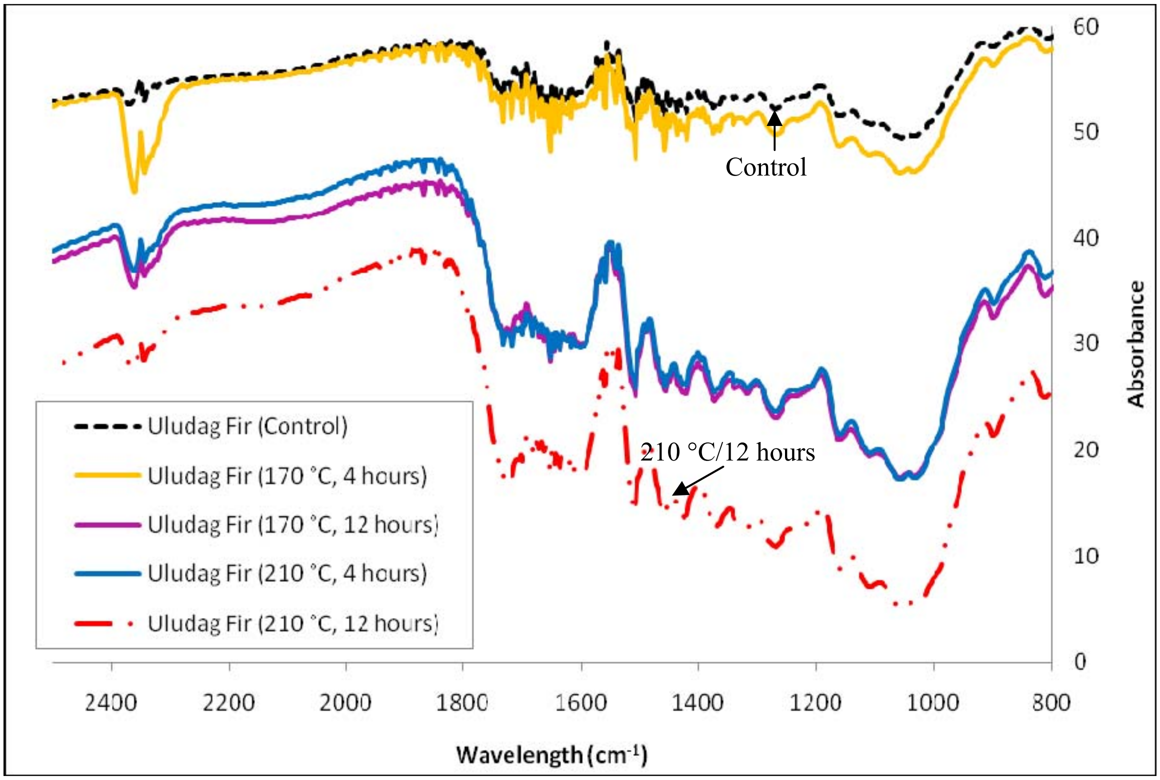

Figure 3. FTIR analysis of heat-treated and untreated uludag fir wood

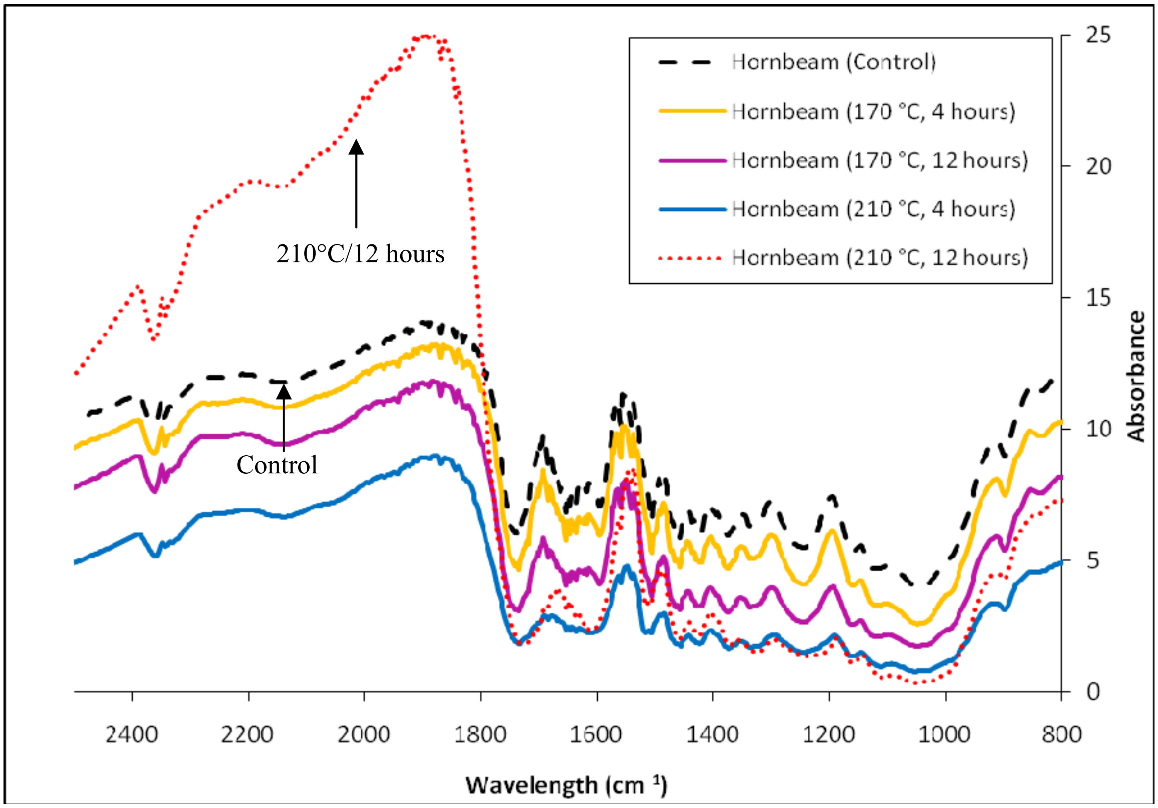

Figure. 4. FTIR analysis of heat-treated and untreated hornbeam wood

Heat treatment improves directional swelling properties of samples in various degrees. It is well known that heat treatment decreases the hygroscopicity of wood and consequently improves its dimensional stability due to chemical modification of the wood polymers. In particular, etherification contributes to wood's dimensional stability. However, cross-linking reactions also occur during thermal treatment of wood.

The changes in the chemical composition mostly affect the sorption relation between water and wood. Wood absorbs less water, and swelling of wood is decreased due to less water absorption. Table 4 shows the changes in water absorption and swelling of wood after heat treatment.

After heat treatment at 170 °C, 190 °C, and 210 °C, the water absorption and swelling of both hornbeam wood and uludag fir wood decreased. The relative decrease was higher for uludag fir than for hornbeam. The maximum decrease in water absorption was found for heat treated species at 210 °C for 12 hours. Water absorption decreased as 44.55% and 42.51% for uludag fir and hornbeam at 210 °C for 12 hours.

The effect of heat treatment on swelling was similar to that for water absorption. The maximum decrease of swelling was found at 210 °C for 12 hours. It was also found to reduce by 54.2%, 44%, and 56.5% for uludag fir and 30.14%, 18.2%, and 48.9% for hornbeam, samples in tangential, radial, and longitudinal directions upon decrease in swelling at 210 °C for 12 hours.

Table 2. Assignments of FT-IR Absorption Bands for Heat-Treated Wood (Kotilainen et al. 2000)

Wavenumber (cm^{-1})	General trend, with an increasing mass loss	Remarks*
809	Decrease	mainly vibration of mannan and C-H out-of-plane bending vibration in lignin (Harrington et al. 1964)
855	Decrease	aromatic C-H out-of-plane deformation (guaiacyl-type lignin) (Faix 1992)
895	Decrease	C_1-farbon in hemicelluloses and in cellulose (pyranoid ring) (Kuo et al. 1988)
1030	Increase	C-O deformation in aliphatic alcohols and ethers, symmetric C-O-C stretching of dialkyl ethers, aromatic C-H deformation in plane (Colthup 1990)
1060	Increase	C-O deformation in aliphatic alcohols and ethers (carbohydrates) (Faix 1992)
1110	Increase	OH association (cellulose) (Kuo et al. 1988)
1160	Increase	C--C symmetric stretching (Faix 1992; Sarkanen and Hergert 1971)
1205-1210	Increase	OH-bending (cellulose), aryl aldehyde, a- and p -unsaturated aldehyde, lactones. phenols, diary ethers (Kemp 1991)
1234	Increase	alkyl-aryl-ether bonds, lactones (Colthup et al. 1990; Kemp 1991)
1268	Increase	Esters, phenols (Colthup et al. 1990)
1330	Increase	Phenol group (Colthup et al. 1990; Sarkanen et al. 1967)
1370	Increase	C-H bending. -CH, (lignin), -CH, (carbohydrates). LCC (lignin carbohydrate complexes) bonds (Kuo et al. 1988; Nagaty et al. 1982)
1426	Increase	aromatic skeletal vibrations (lignin) and C-H deformation in plane (cellulose) (Kuo et al. 1988; Sarkanen and Hergert 1971; Moroshi, 1991)
1450	Increase	C-H bond, extractives, 0-H in plane deformation (cellulose) (Morohoshi 1991).
1510	Increase	aromatic skeletal vibrations (lignin) (Faix 1992)
1600	Increase	aromatic skeletal vibrations, affected by aromatic C-0 stretching mode and by conjugation with u-carbonyl groups (Kuo et al. 1988; Sarkanen and Hergert 1971)
1650	Decrease	Conjugated double bonds (Funako et al. 1990). Adsorbed water (Morohoshi 1991)
1700-1730	decrease increases and the peak broadens to lower wave numbers	carboxyl- and ester groups, nonconjugated aldehyde (Harrington et al. 1964; Cow 1971)
2000-2150	Decrease	overtones of fundamental C-OH stretching at 100-1070 cm^{-1} (cellulose) (Colthup 1990)

* Literature reference was included only in the cases typical for wood constituents.

Table 4. Water Absorption and Swelling of Uludag Fir and Hornbeam Treated at 170 to 210°C

Heat Treatment	Statistical Values	Fir	Hornbeam	Fir			Hornbeam		
		Water Absorption		Swelling (%)					
				Tan.	Rad.	Lon.	Tan.	Rad.	Lon.
Control	x	85.36A	75.67A	11.21A	6.34A	0.69A	10.32A	5.49A	0.47A
	±s	1.25	11.00	0.85	0.81	0.00	0.65	0.20	0.07
170°C 4 hours	x	77.53B	64.00B	9.65AB	5.12AB	0.67B	10.13A	5.21A	0.37B
	±s	1.74	2.65	0.77	0.41	0.04	0.44	0.33	0.01
170°C 8 hours	x	65.84C	52.85C	9.28BC	5.06AB	0.63C	9.08AB	5.13A	0.33
	±s	5.28	11.99	0.62	0.22	0.03	0.50	0.40	0.01
170°C 12 hours	x	58.79F	47.74F	9.08BCD	4.16B	0.53D	8.81AB	5.09A	0.30D
	±s	2.29	6.35	0.18	0.03	0.01	0.48	0.04	0.03
190°C 4 hours	x	63.49D	51.52DC	7.88BCDE	4.05B	0.62C	7.98B	5.26A	0.35C
	±s	3.96	3.02	0.28	0.22	0.02	0.78	0.56	0.01
190°C 8 hours	x	51.33G	49.14E	7.54DEFG	3.85B	0.47E	7.81B	5.15A	0.31DE
	±s	6.25	1.21	0.80	0.33	0.03	1.43	0.37	0.02
190°C 12 hours	x	50.46GH	49.06E	7.32EFG	3.61B	0.45E	7.73B	4.93AB	0.28EF
	±s	1.50	0.59	0.50	0.20	0.01	0.65	0.25	0.01
210°C 4 hours	x	60.65E	50.81ED	6.63FGH	3.91B	0.53D	7.51B	5.14A	0.32DE
	±s	5.82	0.98	0.05	0.27	0.01	0.51	0.07	0.04
210°C 8 hours	x	49.72H	46.64F	5.87FG	3.82B	0.40F	7.38B	5.09A	0.29FG
	±s	8.78	2.23	0.20	0.21	0.02	0.61	0.49	0.02
210°C 12 hours	x	47.33H	43.50G	5.14G	3.55B	0.30G	7.21B	4.47B	0.24H
	±s	2.08	1.29	0.56	0.33	0.03	0.67	0.21	0.02

X: Average, ±s: Standard deviation. Letters such as A, B, C…etc are the results of Duncan test. Ten replicates were used in each test. All data in variance and one-way ANOVA tests were conducted at a confidence level of $p < 0.05$ (95%).

Swelling reductions of the heat-treated wood were lower compared to untreated wood, indicating that swelling in different sections decreased during the heat treatment process. It is well known that heat treatment significantly reduces tangential and radial swelling to very low values (Jamsa et al. 1999; Gunduz et al. 2010; Gunduz and Aydemir 2009).

CONCLUSIONS

Heat treatment, which is a major preservation method for wood, is most popular in Europe. It is important to understand how properties of wood change as a result of heat treatment. Such information was determined using by FTIR and TGA spectroscopy to reveal changes in the chemical constituents and thermal performance of hardwood and softwood during heat treatment. TGA results showed that heat-treated samples had less weight loss than control samples. It was also found that the minimum weight loss was achieved with 170 °C for 4 hours of treatment for both species evaluated at 500 °C. The concentration of hydroxyl groups was reduced after treating at high temperature. Etherification reactions were found to occur in the second treatment step, as indicated by the increase in a specific carbonyl peak (above 150 °C) in the FTIR spectrum of heat-treated uludag fir and hornbeam wood. After heat treatment, the effects of etherification reactions leading to the decreased swelling were found to be moderate compared to the influence of cross-linking. The maximum change in swelling was found in uludag fir samples, especially when treated at 210 °C for 12 hours. The change, depending on the direction of uludag fir (tangential, radial, and longitudinal), was found to be 54.14%, 44%, and 56.52%, respectively.

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