Chemical, Hygroscopic, and Mechanical Properties of Various Wood Species Heat Treated *via* the ThermoWood® Method

Ayhan Aytin,[a,]* Nevzat Çakıcıer,[b] and Turgay Birtürk [c]

Fourier-transform infrared spectroscopy (FTIR), energy dissipation spectrometry, dimensional stability, and compressive strength tests were conducted parallel to the fibers on various heat-treated trees, *i.e.*, narrow-leaved ash (*Fraxinus angustifolia* Vahl), aspen (*Populus tremula* L.), Oriental spruce (*Picea orientalis* (L.) Link.), and Uludağ fir (*Abies bornmüelleriana* Mattf.), which grow naturally in forests in Turkey. Panels made from these trees were first heat treated *via* the ThermoWood® method, producing ThermoWood® panels. Then, FTIR, as well as energy dissipation spectrometry analysis, dimensional stability, and compressive strength tests were performed on test samples prepared from the panels. The FTIR data showed that the hemicelluloses were degraded in the ThermoWood® test samples and the proportion of cellulose increased. The energy dissipation spectrometry results showed that the amount of carbon increased, the amount of oxygen decreased, while the amount of hydrogen remained approximately the same in the ThermoWood® panels compared to the control samples. It was determined that the proportion of silicon increased in the narrow-leaved ash panels. In addition, among the physical properties, the amount of shrinkage and swelling decreased in all the tested ThermoWood® panels compared to the control samples, whereas the compressive strength values, which are considered a mechanical property, increased.

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*Contact information: a: Interior Design, Department of Design, Duzce Vocational School, Duzce University, Duzce 81100 Turkey; b: Faculty of Forestry, Forest Industrial Engineering Department, Duzce University, Duzce 81100 Turkey; c: Faculty of Forestry, Forest Engineering Department, Duzce University, Duzce 81100 Turkey; *Corresponding author: ayhanaytin@duzce.edu.tr*

INTRODUCTION

Since the 1990s, heat treatment has been accepted as an environmentally friendly production method for wood materials and has begun to be used more frequently in the market. With this application, the dimensional stability of wood materials is improved and resistance to biological degradation is ensured. Furthermore, the wood color is darkened, and it becomes possible to obtain a more homogeneous color. Thus, the positive changes that occur with heat treatment, particularly in the physical properties of the wood materials, bring new opportunities in the use of wood materials (Aytin 2013; Shen *et al.* 2016).

Wood has a complex structure, ranging from low molecular compounds to polymeric compounds. In order to understand the numerous changes that occur in the physical and mechanical structure of wood during the heat treatment process, it is necessary to know the chemical composition of the wood, as well as the basic characteristics and the physical properties of the primary components that make up its structure (Korkut and Kocaefe 2009). In heat-treated wood, the cell wall components exhibit different behavior from each other under the effect of temperature (Sundqvist 2004). For example, while the change in lignins and hemicelluloses begins to be seen at a temperature of approximately 120 °C, cellulose begins to be affected at higher temperature values (ThermoWood 2003).

The changes in the wood material structure due to heat treatment and the results of these changes are worth researching and examining for various reasons, especially in order to benefit from the material more rationally. Numerous studies have been conducted on the chemical structure of wood materials and the effect of heat treatment on the chemical structure, as well as the reflection of this effect on the physical properties and mechanical resistance values, which are important for determining its usage. One of these studies reported that the heat treatment of Eastern beech wood (*Fagus orientalis* L.) at 150, 175, and 200 °C for 1, 3, and 5 h increased the weight and density loss and improved the dimensional stability (DS) at high temperatures (Perçin *et al*. 2016). However, it was reported that there was a small increase in the bending strength and elastic modulus in terms of the bending and hardness values. In addition, an increase was observed in the compressive strength (CS) resistance following treatment at a temperature of 200 °C, except for a treatment time of 5 h, and the mechanical resistance values decreased as the heat treatment temperature increased). Another study examining the bamboo tree found that the cellulose and lignin content increased due to heat treatment and the hemicellulose content decreased (Wang *et al*. 2020). It was observed that the hygroscopicity decreased, and the strength and flexibility increased (at temperatures of 180 and 200 °C and different moisture contents) in heat-treated ash wood (*Fraxinus excelsior* L.) (Roszyk *et al*. 2020). Considering the results that improved the moisture properties and equilibrium moisture content of laminated strand lumber (LSL) and laminated veneer lumber (LVL), which were heat treated at different temperatures, it was stated that it might be possible to obtain products with the desired properties in terms of strength (Aroa *et al*. 2016). Based on the results of Fourier-transform infrared (FTIR) spectroscopy performed after the heat treatment of oak wood *via* the ThermoWood® method at a temperature of 160, 180, and 210 °C, Kubovský *et al*. (2020) stated that hemicelluloses were less stable than celluloses. They emphasized that thermal modification causes chemical changes in the primary components of wood materials, and it is important to consider the changes in terms of mechanical strength, especially in wood structure design. However, Özgenç *et al*. (2017) determined the chemical changes in scotch pine (*Pinus sylvestris* L.), Eastern beech (*Fagus orientalis* L.), and Oriental picea (*Picea orientalis* L.) trees after heat treatment at different temperatures using attenuated total reflection (ATR) FTIR and FT Raman spectrometry. The findings revealed that the effects on the carbohydrate and lignin peaks varied across the tree species. Based on the spectral changes that occurred after the heat treatment, it was emphasized that the hemicelluloses degraded, the free hydroxyl groups decreased, and the crystalline cellulose proportion increased due to the degradation of amorphous cellulose at high temperatures. The FTIR analysis of beech (*Fagus sylvatica* L.) wood after heat treatment *via* the ThermoWood® method revealed that the changes in the chemical structure were related (Timar *et al*. 2016).

When the previous studies are examined, it can be seen that the changes in the chemical structure of heat-treated wood and the physical and mechanical properties that determine its areas of use are related. It is known that the physical, mechanical, chemical, and anatomical properties of tree species that grow in different geographical regions can change. For this reason, it is important to investigate the post-heat treatment properties of tree species that grow naturally in different climatic regions, even for the same tree species.

This study aimed to examine the changes in two hardwoods and two softwoods species growing naturally in Turkey after heat treatment. To this end, the chemical structure changes were investigated using FTIR spectroscopy, and elemental analysis was performed *via* energy dissipation spectrometry (EDS). In addition, the compressive strength parallel to the fibers and the dimensional stability values were determined.

EXPERIMENTAL

Materials

The tree species used in this study were selected among the species that have an important sectoral use and potential, according to TS standard 4176 (1984). Tree species and their geographic growing areas are shown in Fig. 1 and Table 1. The map was obtained from the Internet, and the tree species were marked on the places where they were taken (Google 2020).

Fig. 1. The areas where the tree species used in this study grow

Table 1. Production Areas Where the Trees in the Study were Obtained

Tree species	Abbreviation	Province	Place
Aspen (*Populus tremula* L.)	PT	Düzce	Düzce
Narrow-leaved ash (*Fraxinus angustifolia* Vahl.)	FA	Adapazarı	Hendek
Oriental spruce (*Picea orientalis* (L.) Link.)	OP	Trabzon	Akçaabat
Uludağ fir (*Abies bornmüelleriana* Mattf.)	UF	Düzce	Düzce

Methods

Heat treatment application

Tree samples prepared with dimensions of 26 mm x 100 mm x 600 mm by giving dimensional tolerances from trial trees were subjected to heat treatment at a temperature of 190 °C for 1 h (TW1) and 212 °C for 1 h (TW2) using the ThermoWood® method at the Novawood Forest Products Factory (Gerede/Bolu). The ThermoWood® trees obtained were kept in an air-conditioning room with control samples at an average temperature of 20 °C ± 2 °C and a relative humidity of 60% ± 5% until they reached a constant weight.

Determining the amount of shrinkage and swelling

The amount of shrinkage was determined in longitudinal, radial, tangential, and volumetric terms in accordance with the principles of TS standard 4083 (1984) and TS standard 4085 (1983). According to TS CEN/TS standard 15679 (2010), a total of 120 shrinkage samples, 30 samples for each tree species (10 control samples, 10 samples of 190°C ThermoWood®, and 10 samples of 212°C ThermoWood®), were prepared and kept in water until there was no change in their size. Then, the dimensions of the samples were measured with a precision digital caliper (up to ± 0.001 mm), and their dimensions when they were moist were determined. The samples were kept under normal atmospheric conditions for two weeks and then dried in a drying cabinet at a temperature of 103 °C ± 2 °C until their weight remained constant. The samples were left to cool in a desiccator with $CaCl_2$ and the exact dimensions when they were dry were found by measuring again at the first measurement points, and calculated using Eq. 1,

$$\beta = (R_y - R_0)/R_y \times 100\ (\%) \tag{1}$$

where β is the amount of shrinkage (%), R_y is the wet measurement (mm), and R_0 is the full dry measurement (mm).

The amount of swelling was determined in longitudinal, radial, tangential, and volumetric terms in accordance with the principles of TS standard 4084 (1984) and TS standard 4086 (1983). According to TS CEN/TS standard 15679 (2010), a total of 120 shrinkage samples, 30 samples for each tree species (10 control samples, 10 samples of 190 °C ThermoWood®, and 10 samples of 212 °C ThermoWood®), were prepared. They were dried in a drying cabinet at a temperature of 103 °C ± 2 °C until their weight remained constant. Then, after cooling in a desiccator containing $CaCl_2$, the lengths between the points marked on the two opposite sections were measured with a precision digital caliper (up to ± 0.001 mm). The samples were kept in water until there was no change in their size. Their dimensions at humid conditions were measured with a ± 0.001 mm precision digital caliper. The swelling percentages (α) for the dimensions at moist and fully dry conditions were determined as a % using Eq. 2,

$$\alpha = (R_y - R_0)/R_0 \times 100\ (\%) \tag{2}$$

where α is the amount of swelling (%), R_y is the wet measurement (mm), and R_0 is the full dry measurement (mm).

Determining the compressive strength parallel to the fibers

The compressive strength parallel to the fibers was determined according to the principles of TS standard 2595 (1977). A total of 120 test samples were prepared, 10 for each variation, with a cross-section of 20 mm x 20 mm x 30 mm. Before the experiment, the cross-sectional dimensions of the test samples were measured with a caliper that can measure with an accuracy of ± 0.01 mm. Their weights were measured on a 0.01 g precision scale, and then were placed on a universal testing machine with the force direction parallel to the fiber. The universal testing machine was operated at a speed of 6 mm/min to ensure that the breakage occurred 1.5 min to 2 min after the loading time. The compressive strength parallel to the fibers was calculated using Eq. 3,

$$\sigma_w = P_{max} / A\ (\text{N/mm}^2) \tag{3}$$

where σ_w is the CS (N/mm^2), P_{max} is the maximum force at break (N), and A is the cross-sectional area of the sample (mm^2).

After testing the pressure parallel to the fibers, the humidity values were determined according to TS standard 2471 (1976). The following equation was used to set the values of the CS to 12% for the control samples with humidity values different from 12%, as shown in Eq. 4,

$$\sigma_{W12} = \sigma_R\,[1+\alpha(R\text{-}12)]\ (\mathrm{N/mm^2}) \tag{4}$$

where σ_{W12} is the CS for air-dry fibers (N/mm^2), R is the moisture (%), σ_R is the CS of the measured fibers (N/mm^2), and α is the correction factor (0.05).

Fourier transform infrared (FTIR) spectroscopy analysis

Fourier transform infrared (FTIR) spectroscopy was recorded with an ATR Attached Shimadzu IR Prestige 21 spectrometer. Spectrum analysis was performed between 400 and 4000 nm, with 64 scans (Demirci 2018). The ATR Attached Shimadzu IR Prestige 21 spectrometer is shown in Fig. 2.

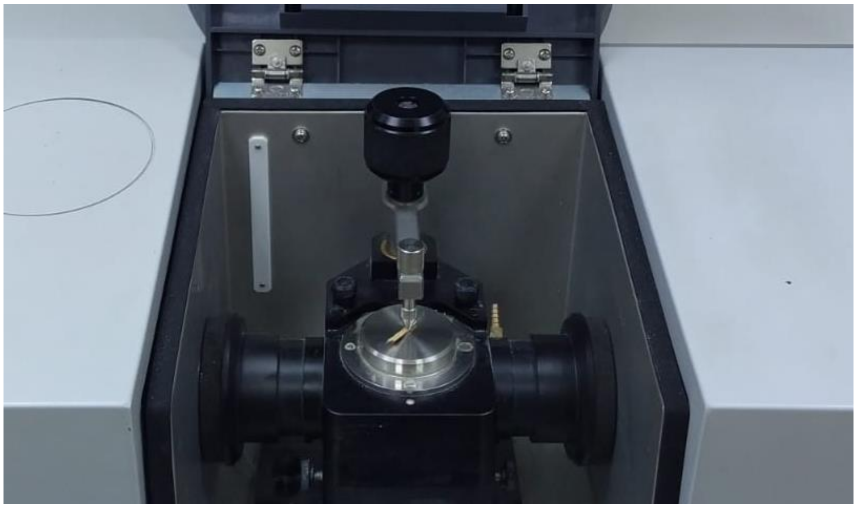

Fig. 2. The ATR Attached Shimadzu IR Prestige 21 spectrometer

Energy dissipation spectrometry (EDS) analysis

The elemental analysis was carried out with a Thermo Scientific Flash 2000 instrument. The device is designed for the unattended and fully automatic determination of CHNS and oxygen in any sample (Thermo Scientific 2021).

Statistical evaluation

The SPSS package program (IBM, SPSS 15.0 for Windows, Armonk, NY) was used for the statistical evaluation of the data. An analysis of variance was used to determine whether the factors were effective for the results obtained, and Duncan's test was used to determine the size of the difference on the factors that were found to be significant.

RESULTS AND DISCUSSION

Results Regarding the Amount of Shrinkage and Swelling

The basic analysis of variance (BVA), statistics, and Duncan test results regarding shrinkage values according to tree species are given in Table 2.

Table 2. Shrinkage Values for Each Tree Species (Basic Analysis of Variance (BVA) Results, Statistics, and Duncan's Test Results)

TS*	D	BVA						STATISTICS			
		VAR	ST	df	SM	F	S	G	M	SD	H
PT	R	BG	30.833	2	15.416	26.57	0.000	COS	4.900	0.520	C
		WG	15.662	27	0.580			TW1	3.474	0.296	B
		TTL	46.495	29				TW2	2.426	1.175	A
	T	BG	84.356	2	42.178	47.48	0.000	COS	7.269	0.623	B
		WG	23.982	27	0.888			TW1	6.787	1.245	B
		TTL	108.337	29				TW2	3.496	0.852	A
	V	BG	209.059	2	104.530	52.46	0.000	COS	12.588	0.769	B
		WG	53.794	27	1.992			TW1	10.437	1.499	C
		TTL	262.853	29				TW2	6.233	1.771	A
FA	R	BG	11.299	2	5.650	36.47	0.000	COS	3.616	0.341	C
		WG	4.182	27	0.155			TW1	3.220	0.295	B
		TTL	15.481	29				TW2	2.162	0.510	A
	T	BG	35.595	2	17.798	14.35	0.000	COS	6.570	1.371	B
		WG	33.480	27	1.240			TW1	6.704	1.297	B
		TTL	69.076	29				TW2	4.329	0.393	A
	V	BG	77.567	2	38.784	24.46	0.000	COS	10.290	1.549	B
		WG	42.796	27	1.585			TW1	9.965	1.485	B
		TTL	120.364	29				TW2	6.731	0.384	A
OP	R	BG	13.732	2	6.866	7.127	0.003	COS	4.768	1.191	B
		WG	26.012	27	0.963			TW1	3.323	0.826	A
		TTL	39.744	29				TW2	3.343	0.886	A
	T	BG	19.868	2	9.934	32.92	0.000	COS	7.148	0.324	C
		WG	8.147	27	0.302			TW1	6.372	0.593	B
		TTL	28.016	29				TW2	5.170	0.669	A
	V	BG	68.756	2	34.378	37.17	0.000	COS	12.47	1.073	B
		WG	24.970	27	0.925			TW1	9.667	0.858	A
		TTL	93.726	29				TW2	8.965	0.940	A
UF	R	BG	35.925	2	17.963	47.03	0.000	COS	4.347	0.518	C
		WG	10.311	27	0.382			TW1	3.028	0.465	B
		TTL	46.236	29				TW2	1.667	0.812	A
	T	BG	37.391	2	18.695	35.05	0.000	COS	7.698	0.980	B
		WG	14.398	27	0.533			TW1	6.909	0.615	B
		TTL	51.789	29				TW2	5.036	0.510	A
	V	BG	169.004	2	84.502	70.218	0.000	COS	12.61	1.404	C
		WG	32.493	27	1.203			TW1	10.11	0.946	B
		TTL	201.497	29				TW2	6.823	0.861	A

Note: *BG: Between groups; WG: Within groups; TTL: Total; TS: Tree species; ST: Total of Squares; df: Coefficient of freedom; SM: Mean of squares; S: Significance; Mean: Mean value; SD: Standard deviation; HG: Homogeneity comparison based on Duncan test result; D: Direction; R: Radial; T: Tangential; and V: Volumetric shrinkage

Table 3. Swelling Values for Each Tree Species (Basic Analysis of Variance (BVA) Results and Statistics)

TS	D	BVA						STATISTICS			
		VAR	ST	df	SM	F	S	G	M	SD	HG
PT	R	BG	60.273	2	30.137	76.136	0.000	COS	5.070	0.937	C
		WG	10.687	27	0.396			TW1	3.448	0.431	B
		TTL	70.961	29				TW2	1.601	0.351	A
	T	BG	260.591	2	130.296	189.581	0.000	COS	10.191	0.958	C
		WG	18.557	27	0.687			TW1	6.488	0.603	B
		TTL	279.148	29				TW2	2.972	0.882	A
	V	BG	620.635	2	310.317	307.438	0.000	COS	16.338	1.134	C
		WG	27.253	27	1.009			TW1	10.456	0.931	B
		TTL	647.888	29				TW2	5.203	0.933	A
FA	R	BG	34.628	2	17.314	15.279	0.000	COS	4.835	1.218	B
		WG	30.597	27	1.133			TW1	4.107	1.280	B
		TTL	65.224	29				TW2	2.281	0.524	A
	T	BG	113.782	2	56.891	35.507	0.000	COS	8.783	1.497	C
		WG	43.261	27	1.602			TW1	6.954	1.046	B
		TTL	157.043	29				TW2	4.053	1.212	A
	V	BG	252.768	2	126.384	58.384	0.000	COS	13.870	1.548	C
		WG	58.447	27	2.165			TW1	11.452	1.727	B
		TTL	311.215	29				TW2	6.871	1.053	A
OP	R	BG	30.298	2	15.149	34.750	0.000	COS	5.863	0.362	B
		WG	11.770	27	0.436			TW1	3.698	0.771	A
		TTL	42.068	29				TW2	3.766	0.762	A
	T	BG	37.278	2	18.639	12.026	0.000	COS	8.104	1.898	B
		WG	41.846	27	1.550			TW1	6.335	0.720	A
		TTL	79.124	29				TW2	5.418	0.724	A
	V	BG	137.201	2	68.600	33.317	0.000	COS	14.623	1.823	B
		WG	55.593	27	2.059			TW1	10.571	1.100	A
		TTL	192.794	29				TW2	9.721	1.281	A
UF	R	BG	74.964	2	37.482	83.867	0.000	COS	5.836	0.873	B
		WG	12.067	27	0.447			TW1	2.872	0.683	C
		TTL	87.031	29				TW2	2.197	0.331	A
	T	BG	108.627	2	54.313	32.533	0.000	COS	9.307	1.728	B
		WG	45.076	27	1.669			TW1	6.322	1.312	C
		TTL	153.703	29				TW2	4.715	0.545	A
	V	BG	442.684	2	221.342	83.369	0.000	COS	16.107	2.232	B
		WG	71.684	27	2.655			TW1	9.569	1.630	C
		Total	514.368	29				TW2	6.977	0.569	A

Note: *BG: Between groups; WG: Within groups; TTL: Total; TS: Tree species; ST: Total of Squares; df: Coefficient of freedom; SM: Mean of squares; S: Significance; Mean: Mean value; SD: Standard deviation; HG: Homogeneity comparison based on Duncan test result; D: Direction; R: Radial; T: Tangential; and V: Volumetric shrinkage

The highest volumetric shrinkage value was determined as 12.61 in the UF control samples, and the lowest volumetric shrinkage value was 6.23, from the PT 212 °C ThermoWood® samples. In all ThermoWood® samples, the amount of volumetric shrinkage in the control samples decreased. The maximum decrease in the volumetric shrinkage was 50.47% in the PT 212 °C ThermoWood® test samples, and the lowest decrease was 28.14% in the OP 212 °C samples.

The BVA results and statistics regarding the swelling values of each tree species are given in Table 3. The highest volumetric swelling value was 16.33, which was in the PT control samples, and the lowest value was 5.20, which was in the PT 212 °C ThermoWood® samples. The volumetric swelling amount increased in all the ThermoWood® samples compared to the control samples. The maximum increase in volumetric swelling was 68.15% in the PT 212 °C ThermoWood® samples, and the lowest was in the OP 212°C samples, with an increase of 33.51%.

The shrinkage and swelling results obtained in the study are compatible with the results found in previous literature. Boonstra (2008) states that dimensional stability increases as a result of decreasing shrinkage and swelling in heat-treated wood material. Bak and Nemeth (2012) found that the dimensional stability of poplar wood, which they heat treated at different temperatures ranging from 160 to 200 °C, considerably improved. Li *et al*. (2011) reached similar results in their study, in which they investigated the effect of high temperature on some physical properties of Douglas fir wood by applying heat treatment at a temperature of 160, 180, 200, and 220 °C for 1, 2, 3, or 4 h. In their study with Eastern beech, Kol *et al*. (2017) found that the amount of shrinkage was higher in the heat-treated samples compared to the control samples as the heat treatment temperature increased. The results of the study show that the shrinkage difference of 14.31% at a temperature of 170 °C compared to the control samples increased to 54.28% at a temperature of 212 °C. Şahin and Güler (2018) stated in their study on ash wood that the dimensional stability value could be improved up to 58.4% by increasing the heat treatment temperature to 210 °C. İçel *et al*. (2015) revealed in their study that up to a 58% improvement in the dimensional stability in European spruce and 52% in Scotch pine can be achieved with heat treatment.

Findings regarding compressive strength (CS) parallel to the fibers

The BVA results and statistics regarding the CS values for the PT, FA, OP, and UF samples are given in Table 4. Out of all the ThermoWood® products in all tested tree species, the highest percentage increase was 17.37% and 21.1% in PT and UF, respectively, when compared to the control samples. In the narrow leaf ash tree and OP samples, the CS value was determined as 7.83 and 4.42, respectively, compared to the control samples.

In their study with Eastern beech (*Fagus orientalis* Lipsky) wood, Perçin *et al*. (2016) revealed that the compressive strength increased with heat treatment. Özçifçi *et al*. (2009) and Sefil (2010) found that compressive strength parallel to the fibers increased as the heat treatment temperature increased. In another study, it is stated that the strength in wood material is related to the covalent and hydrogen polymer bonds (Çalıova 2011). The increase in the amount of bound water and the weakening of the hydrogen bonds between the polymeric compounds of the cell wall decrease the strength properties. However, it is also emphasized that the increase in compressive strength parallel to the fibers is due to the decrease in the amount of equilibrium humidity in heat treated trees. Thus, it is stated that heat treated wood is less hygroscopic, and since the maximum amount of bound water is reduced, heat treatment can positively contribute to its strength properties (Aytin 2013).

Table 4. Basic Analysis of Variance (BVA) Results and Statistics Regarding the Compressive Strength Values

	BVA						STATISTICS			
TS	VAR	ST	df	SM	F	S	G	M	SD	HG
PT	BG	324.571	2	162.285	4.591	0.019	COS	45.42	1.91	B
	WG	954.508	27	35.352			TW1	47.95	2.46	BA
	TTL	1279.079	29				TW2	53.31	9.81	A
FA	BG	134.491	2	67.246	2.152	0.136	COS	57.52	6.03	A
	WG	843.786	27	31.251			TW1	62.01	5.84	A
	TTL	978.277	29				TW2	62.02	4.81	A
OP	BG	27.188	2	13.594	0.347	0.710	COS	50.14	7.50	A
	WG	1056.583	27	39.133			TW1	52.36	7.50	A
	TTL	1083.771	29				TW2	51.87	2.17	A
UF	BG	945.012	2	472.506	14.966	0.000	COS	50.17	7.24	B
	WG	852.455	27	31.572			TW1	59.48	4.59	A
	TTL	1797.467	29				TW2	63.59	4.59	A

Note: *BG: Between groups; WG: Within groups; TTL: Total; TS: Tree species; ST: Total of Squares; df: Coefficient of freedom; SM: Mean of squares; S: Significance; Mean: Mean value; SD: Standard deviation; HG: Homogeneity comparison based on Duncan test result; D: Direction; R: Radial; T: Tangential; and V: Volumetric shrinkage

Fourier-transform infrared (FTIR) spectroscopy and energy dissipation spectrometer (EDS) analysis

The FTIR analyses for the PT are given in Fig. 3, and the frequency reactions and EDS results of the functional groups are given in Table 5.

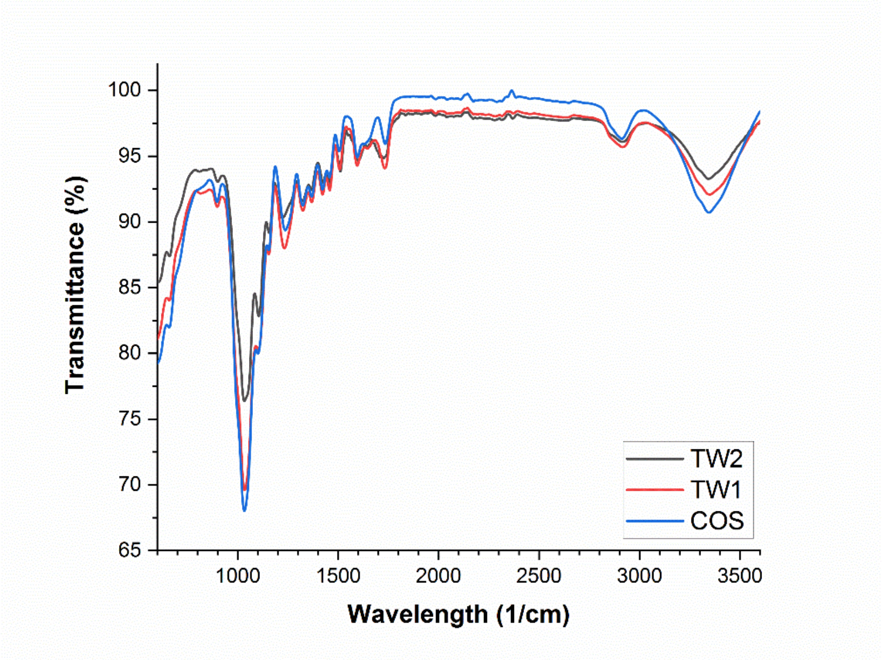

Fig. 3. FTIR analysis of the PT samples

Table 5. Reactions in the Aspen (PT) Bond Structure and the Energy Dissipation Spectrometry (EDS) Results

Frequency	Functional Group	Elemental Analysis (%)*				
896 cm^{-1}	β-glycosidic bonds, C-H cellulose deformation		N	C	H	O
1031 cm^{-1}	Aromatic C-H deformation, C-O deformation	COS	0.01	44.95	6.04	49.00
1157 cm^{-1}	Vibration in C-O-C Cellulose and Hemicellulose	TW1	0.12	46.86	6.14	46.88
1234 cm^{-1}	C= resistance and syringyl ring in lignin and xylan	TW2	0.01	48.66	5.88	45.45
1319 cm^{-1}	C-O vibration in syringyl derivatives and C-H vibration in cellulose					
1421 cm^{-1}	Aromatic ring vibration combined with CH in deformation					
1452 cm^{-1}	CH- deformation, asymmetric in CH_2 and CH_3					
1593 cm^{-1}	Aromatic ring vibration, plus C=O tension					
1670 cm^{-1}	C=O tension in unconjugated ketone, carbonyl, and ester groups					
Note: *N: nitrogen; C: carbon; H: hydrogen; and O: oxygen						

The changes between the peaks of the wood carbohydrates and lignins in the neighborhoods of 1730 and 650 cm^{-1}, which are the characteristic peaks of the wood structure in the ThermoWood® PT samples (as shown in the spectrum in Fig. 3). The presence of peaks at 1105, 1030, and 892 cm^{-1}, which are the primary lignin peaks according to the spectrum, indicated that the cellulose structure has started to deteriorate in the ThermoWood® samples. However, the peaks observed at wavelengths of 1028 and 3077 cm^{-1}, representing hemicelluloses, indicated that the intensity of the peak decreased, and the structure was less converted to a cellulose structure.

The FTIR analyses for the FA samples are given in Fig. 4, and the frequency reactions and EDS results of the functional groups are given in Table 6.

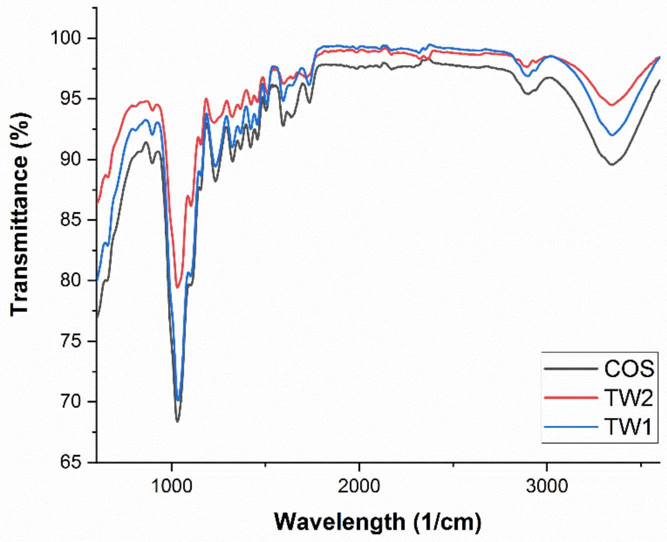

Fig. 4. FTIR analysis of the FA samples

The changes in the lignin peaks and wood carbohydrate peaks between 1800 cm^{-1} and 650 cm^{-1}, which are the characteristic peaks of the wood structure in the ThermoWood® FA samples, are given in the spectrum in Fig. 4. According to the spectrum, the presence of peaks at 1105, 1030, and 892 cm^{-1}, which are the primary lignin peaks, shows that the cellulose structure deteriorated in the TW1 and TW2 samples. However, the peaks observed at wavelengths of 1028 and 3077 cm^{-1} are the peaks representing the hemicellulose found in the wood structure.

Table 6. Reactions in the Narrow-leaved Ash (FA) Bond Structure and the Energy Dissipation Spectrometry (EDS) Results

Frequency	Functional Group	Elemental Analysis (%)*					
896 cm^{-1}	β-glycosidic bonds, C-H cellulose deformation		N	C	H	O	Si*
1032 cm^{-1}	Aromatic C-H, C-O deformation	COS	0.11	45.30	5.84	47.40	1.36
1155 cm^{-1}	Vibration in C-O-C Cellulose and Hemicellulose	TW1	0.05	47.17	5.87	44.54	2.37
1232 cm^{-1}	C= resistance and syringyl ring in lignin and xylan	TW2	0.08	49.75	6.18	41.66	2.32
1327 cm^{-1}	C-O vibration in syringyl derivatives and C-H vibration in cellulose						
1417 cm^{-1}	Aromatic ring vibration combined with CH in deformation						
1454 cm^{-1}	CH- deformation, asymmetric in CH_2 and CH_3						
1593 cm^{-1}	Aromatic ring vibration, plus C=O tension						
1732 cm^{-1}	C=O tension in unconjugated ketone, carbonyl, and ester groups						
Note: *N: nitrogen; C: carbon; H: hydrogen; and O: oxygen							

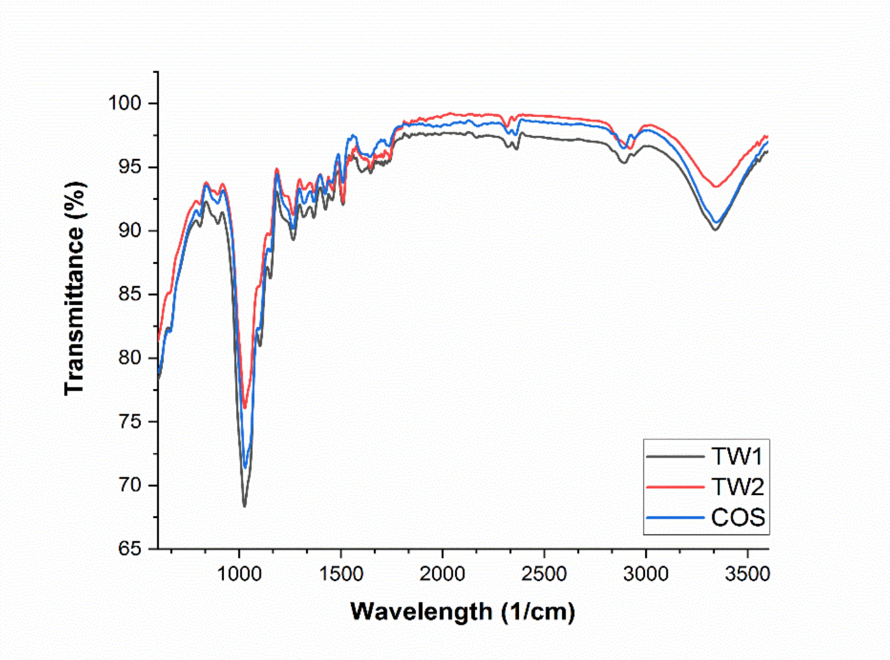

Fig. 5. FTIR analysis of the OP samples

The FTIR analysis for the OP samples is given in Fig. 5, and the frequency reactions and the EDS results of the functional groups are given in Table 7. According to the spectrum of the wood structure of the ThermoWood® PO samples, the presence of the primary peaks of lignins, *i.e.*, 1105, 1030, and 892 cm^{-1}, indicated that the TW1 and TW2 cellulose structures of the samples had started to deteriorate. However, the peaks observed at wavelengths of 1028 and 3077 cm^{-1} are the peaks that representing the hemicellulose in the wood structure. In addition, it was observed that the intensity of the peaks decreased at TW2, but the intensity of the peaks of the structure increased at TW1 and the structure started to transform into a cellulose structure.

Table 7. Reactions in the Oriental Picea (OP) Bond Structure and the Energy Dissipation Spectrometry (EDS) Results

Frequency	Functional Group	Elemental Analysis (%)*				
896 cm^{-1}	β-glycosidic bonds, C-H cellulose deformation		N	C	H	O
1032 cm^{-1}	Aromatic C-H deformation, C-O deformation	COS	0,03	46,11	6,00	47,87
1143 cm^{-1}	Vibration in C-O-C Cellulose and Hemicellulose	TW1	0,04	47,06	5,99	46,91
1226 cm^{-1}	C= resistance and syringyl ring in lignin and xylan	TW2	0,65	49,50	6,21	43,63
1327 cm^{-1}	C-O vibration in syringyl derivatives and C-H vibration in cellulose					
1417 cm^{-1}	Aromatic ring vibration combined with CH in deformation					
1458 cm^{-1}	CH- deformation, asymmetric in CH_2 and CH_3					
1588 cm^{-1}	Aromatic ring vibration, plus C=O tension					
1653 cm^{-1}	C=O tension in unconjugated ketone, carbonyl, and ester groups					

Note: *N: nitrogen; C: carbon; H: hydrogen; and O: oxygen

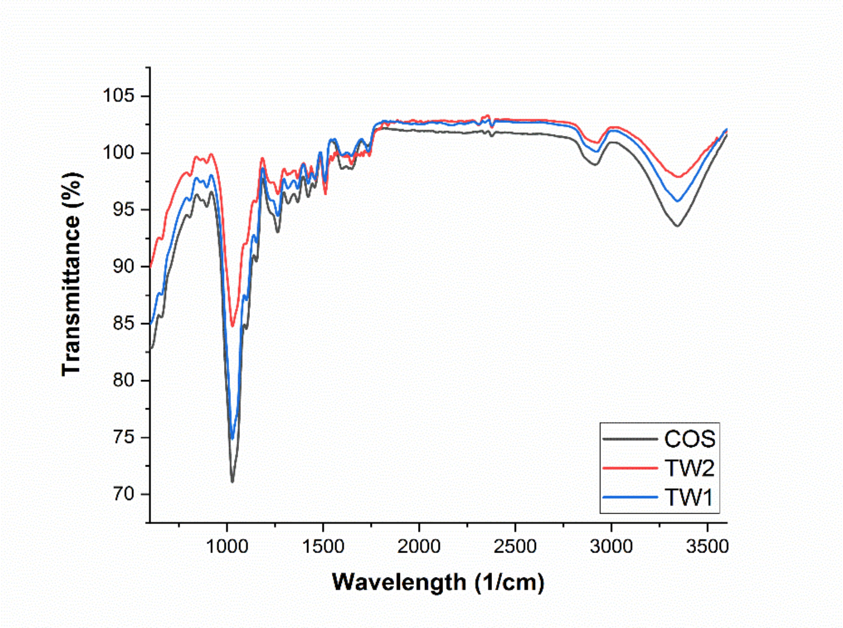

Fig. 6. FTIR analysis of the UF samples

The FTIR analyses for the UF samples are given in Fig. 6, and the frequency reactions and the EDS results of the functional groups are given in Table 8. Considering the spectrum of the wood structure in the ThermoWood® UF samples, the primary peaks of lignins, *i.e.*, 1105, 1030, and 892 cm^{-1}, show that the cellulose structure deteriorated in TW1 and TW2. However, it was observed that the peaks observed at wavelengths of 1028 and 3077 cm^{-1} are the peaks representing the hemicellulose found in the wood structure. In addition, it was found that the intensity of the peaks of the structure in the TW1 and TW2 samples decreased, and that the structure turned into a lower amount of cellulose.

Table 8. Reactions in the Uludağ Fir (UF) Bond Structure and the Energy Dissipation Spectrometry (EDS) Results

Frequency	Functional Group	Elemental Analysis (%)*				
896 cm^{-1}	β-glycosidic bonds, C-H cellulose deformation		N	C	H	O
1029 cm^{-1}	Aromatic C-H deformation, C-O deformation	COS	0,01	44,87	5,96	49,16
1157 cm^{-1}	Vibration in C-O-C Cellulose and Hemicellulose	TW1	0,05	48,35	5,81	45,79
1265 cm^{-1}	C= resistance and syringyl ring in lignin and xylan	TW2	0,08	49,90	5,86	44,17
1369 cm^{-1}	C-O vibration in syringyl derivatives and C-H vibration in cellulose					
1423 cm^{-1}	Aromatic ring vibration combined with CH in deformation					
1457 cm^{-1}	CH- deformation, asymmetric in CH_2 and CH_3					
1508 cm^{-1}	Aromatic ring vibration, plus C=O tension					
1602 cm^{-1}	C=O tension in unconjugated ketone, carbonyl and ester groups					
Note: *N: nitrogen; C: carbon; H: hydrogen; and O: oxygen						

The results of the elemental analysis revealed that the proportional amount of carbon increased in all ThermoWood® products compared to the control samples, and the highest increase was in UF, with a 10% increase. In contrast to the carbon content, the oxygen content decreased in all the ThermoWood® samples compared to the control samples, and it was revealed that the highest decrease was in the FA samples. It was emphasized that the changes in the physical properties were caused by the important changes in the structure and chemical composition of the wood material during the modification process.

According to Hill (2006), the heat treatment of wood considerably reduces its water adsorption. The presence and/or accessibility of free hydroxyl groups in wood carbohydrates play an important role in water adsorption and desorption. It is obvious that there is a decrease in the accessibility to the free hydroxyl groups as a result of the heat treatment application. A reason for this is the depolymerization of the carbohydrates, especially hemicellulose, which leads to a decrease in the total amount of free hydroxyl groups. Another reason is the increase in the relative ratio of crystalline cellulose, where hydroxyl groups cannot easily reach water molecules, and the cross-linking of the lignin network, which prevents the access of free hydroxyl groups to water.

According to the results of Niemz *et al*. (2010), in which some physical, mechanical, and chemical properties of various industrially important hard and soft woods were measured and evaluated after heat treatment in a N_2 atmosphere, the chemical changes affecting the physical properties could be investigated and monitored by establishing correlations between the physical and chemical properties. It was also emphasized that the correlation between the hard wood samples was stronger than between the soft woods.

CONCLUSIONS

1. Within the scope of the study, after the heat treatment of aspen (*Populus tremula* L.), narrow-leaved ash (*Fraxinus angustifolia* Vahl), Oriental spruce (*Picea orientalis* (L.) Link.), and Uludağ fir (*Abies bornmüelleriana* Mattf.) trees, which naturally grow in the forests of Turkey, the dimensional stability (as a physical property), compressive strength parallel to the fibers (as a mechanical property), and bond structure (as a chemical property) were investigated with Fourier transform infrared (FTIR) and elemental analysis and it has been understood that the results obtained are in accordance with the literature on the subject.

2. The dimensional stability test results revealed that the amount of shrinkage and swelling decreased in all the heat-treated tree species compared to the control (COS) samples. The greatest change was found in the COS samples, while the lowest change as found in TW2 test samples (heated at 212 °C for 1 h). The volumetric shrinkage values of TW2 samples occurred in the *Populus tremula* (PT), *Fraxinus angustifolia* (FA), *Picea orientalis* (OP), and *Abies bornmüelleriana* (UF) trees, 50.48, 34.58, 28.10, and 56.46%, respectively, being lower than COS samples; the volumetric swelling values of TW2 samples occurred in the PT, FA, OP and UF trees, 68.15, 50.46, 33.52, and 56.85%, respectively, being lower than COS samples. The chemical analysis results clearly support the reasons underlying the increase in dimensional stability. Similarly, the conversion of the wood structure to a cellulose structure via heat treatment, the increase in free hydroxyl groups, and the increase in crystalline cellulose support the trend that indicates an increase in the compressive strength parallel to the fibers. The lowest change was found in the COS samples, while the greatest change was found in all the heat-treated test samples. According to compressive strength parallel to the fibers values of heat-treated test samples occurred in the PT, FA, OP and UF trees, 17.37, 7.38, 4.42, and 26.46%, respectively being highest than COS samples.
3. The findings of the study are important in terms of optimizing the existing resources for the use of natural resources. Finding materials that can be evaluated by the heat treatment industry, which is an environmentally friendly production system, and the creation of alternatives are the other option. The scientific contribution of the results should be taken into account.

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