Effect of Heat Treatment Parameters on the Physical, Mechanical, and Crystallinity Index Properties of Scots Pine and Beech Wood

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Effects of heat treatment parameters on the physical properties, mechanical properties, and crystallinity index of Scots pine and beech wood were investigated. Scots pine (*Pinus sylvestris* L.) and beech (*Fagus orientalis* Lipsky) sapwood samples were prepared in 2 cm × 2 cm × 36 cm dimensions by considering the physical and mechanical tests. The samples were heat-treated for 2 h and 4 h at 150 °C, 180 °C, and 210 °C in an atmospheric environment. The shrinking and swelling percentages of all samples were calculated. The compressive strength, bending strength, modulus of elasticity (MOE), and hardness tests were carried out. X-ray diffraction (XRD) was performed to calculate the crystallinity index values. As a result of the study, it was determined that heat treatment generally had a positive effect on the physical properties of Scots pine and beech samples. It was observed that the bending strength of the wood samples decreased up to 180 °C as the temperature increased and then increased. It was determined that the MOE of the Scots pine and beech wood decreased with the heat treatment. As the heat treatment temperature and time were increased, the crystallinity index values initially increased partially and then decreased.

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INTRODUCTION

Wood is a renewable material with high strength properties compared to its density. In addition, wood is biodegradable in places of use, and it can shrink and swell in size with moisture. Various wood protection methods such as impregnation, chemical modification, and heat treatment have been developed to prevent these problems encountered by wood material.

Heat treatment is basically the process of exposing the wood material to a temperature between 150 and 240 °C for certain periods. Heat treatment causes significant changes in the physical and chemical structure of the wood material (Kocaefe *et al.* 2008). During heat treatment, the hemicellulose is the first to degrade in wood. This causes the mechanical properties of the heat-treated wood to partially decrease, and the wood gains biological durability with the partial disappearance of the nutrient medium suitable, especially for fungi. A significant decrease in the number of accessible hydroxyl groups in the cell wall occurs with the depolymerisation of hemicellulose. This situation reduces the hygroscopic feature of the wood and provides dimensional stability to the wood (Yun *et al.* 2015).

Cellulose in the cell wall polymers degrades after the hemicellulose. Cellulose consists of helically wrapped microfibrils, which contain amorphous and crystalline regions. While the crystalline regions are the parts with regular cellulose chains, the amorphous regions refer to the regions of the more irregularly arranged cellulose chains (Andersson *et al.* 2003). The crystallinity of cellulose, which starts to decompose thermally with the temperature, changes (Bhuiyan *et al.* 2002). The highly regular crystalline cellulose ratio increases due to the degradation and/or crystallization of amorphous cellulose as a result of heat treatment (Korkut and Kocaefe 2009). Crystallinity affects the physical and mechanical properties of wood. As the crystallinity increases, the modulus of elasticity (MOE) increases and the elasticity decreases (Lee 1961). X-ray diffraction (XRD) is one of the methods used to determine the crystallinity of wood (Alexander 1971; Balta-Calleja and Volk 1989).

The last polymer to degrade in the cell wall by heat treatment is lignin. During heat treatment, formaldehyde, which is formed by the decomposition of organic acids and phenol units of lignin, takes part in irreversible crosslinking reactions. It is suggested that this situation increases the dimensional stability of the wood and negatively affects its physical and mechanical properties (Tjeerdsma *et al.* 1998; Tjeerdsma and Militz 2005; Obataya and Higashihara 2017). The findings of a study by Bourgois and Guyonnet (1988) on maritime pine (*Pinus pinaster*) showed that longer process durations increased lignin concentration at the same temperature.

The cell wall of wood is composed of cellulose, hemicellulose, and lignin. Approximately 50% of the cell wall consists of cellulose. Therefore, the main component that determines the properties of wood is cellulose. The thermal stability of cellulose is mainly dependent on the crystallinity index (degree of crystallization), the crystallite size, and the degree of polymerization (Nada *et al.* 2000; Kim *et al.* 2010; Poletto *et al.* 2012). The literature shows that the size of the crystallite and the changes in the crystallinity index are almost the same (Bhuiyan *et al.* 2002). The crystalline regions of cellulose can determine the mechanical properties of the cell wall due to their high density and low chemical reactivity (Wei *et al.* 2015a,b; Kong *et al.* 2017). On the other hand, the increase in the crystalline cellulose density in the wood with the heat treatment also affects the hardness of the wood. Changes in the molecular structure of the wood due to the breakdown of long polymers can decrease the elasticity and make the wood more brittle (Gosselink *et al.* 2004; Kocaefe *et al.* 2008; Fengel and Wegener 2011).

In this study, the relationship between the crystallinity index and the heat treatment applied to Scots pine and beech wood at different temperatures and durations was investigated. In particular, the effect of the crystallinity index change on the physical and mechanical properties of wood was investigated.

EXPERIMENTAL

Wood Materials

Scots pine (*Pinus sylvestris* L.) and beech (*Fagus orientalis* Lipsky) sapwood samples were obtained from Kastamonu, Turkey. The samples were prepared in accordance with the TS 4176 (1984) standard. The test samples were cut in 2 cm × 2 cm × 36 cm dimensions considering the physical and mechanical tests planned to be carried out after the heat treatment.

Heat Treatment of Scots Pine and Beech Wood

Samples of Scots pine and beech wood were subjected to heat treatment at 150, 180, and 210 °C for 2 and 4 h according to the experiment matrix in Table 1. The heat treatment was carried out in a laboratory type oven in an atmospheric environment. After the heat treatment, all the samples were kept at a relative humidity of 65 ± 5% and at a temperature of 20 ± 2 °C for 7 d.

Table 1. Heat Treatment Parameters of Scots Pine and Beech Samples

Scots Pine	Beech Wood	Temperature (°C)	Time (h)
SControl	BControl	-	-
S1	B1	150	2
S2	B2	150	4
S3	B3	180	2
S4	B4	180	4
S5	B5	210	2
S6	B6	210	4

Determination of the Physical Properties

A micrometer with an accuracy of 0.001 mm was used to measure the dimensions of the test samples and an assay balance with an accuracy of 0.01 g was used to determine the weight. To determine the shrinking percentage, the weights and dimensions of the air-dried samples were measured. The samples were then completely dried at 103 ± 2 °C and their weights and dimensions were measured again.

To determine the swelling percentage, the air-dried samples were kept in pure water until their dimensions became constant. At the end of this period, the saturated weights and measurements of the samples were determined. The air-dry and oven-dry densities were determined according to the TS 2472 (1976) standard. The radial, tangential, and longitudinal shrinking percentages were calculated according to the TS 4083 (1983) standard, while the swelling percentage was calculated according to the TS 4084 (1983) standard. In addition, the volume shrinking and volume swelling percentages were determined according to the TS 4085 (1983) and 4086 (1983) standards, respectively.

Determination of the Mechanical Properties

The compressive strength parallel to grain was determined according to the TS 2595 standard. The test samples were prepared in 2 cm × 2 cm × 3 cm dimensions. The bending strength was determined according to TS 2474 (1976) standard, and the MOE was determined according to the TS 2478 (1976) standard. The previously prepared samples of 2 cm × 2 cm × 3 cm were used for the bending strength and MOE tests. The radial and tangential hardness measurements were made with a shore D hardness tester. For all physical and mechanical tests, 10 samples were selected and each test was applied 10 times.

Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR analysis of control samples and heat-treated samples were performed with the potassium bromide (KBr) technique. After the wood samples in all the groups were ground, a mixture of 1% was prepared with KBr and turned into a transparent tablet in a mold. The infrared absorption spectra of the tablets were provided with 4 cm^{-1} (40 scans) in Shimadzu FTIR-8400S device (Kyoto, Japan).

Determination of the Crystallinity Properties

Samples of Scots pine and beech were made into wood flour for the XRD analysis. The X-ray powder patterns were measured using a Bruker D8 ADVANCE spectrometer (Billerica, MA, USA). The X-ray diffractometer was rigged with a two circle (θ and 2θ) goniometer housed in a radiation safety enclosure. The X-ray source was a closed 2.2 kW Cu X-ray tube, maintained at an operating current of 40 kV and 30 mA. The goniometer was computer controlled with independent stepper motors and optical encoders for the θ and 2θ circles with the smallest angular step size of 0.0001° 2θ. The samples were scanned in the range of 5° to 60° 2θ. A step size of 0.02° and a step time of 1.0 s were used during the measurements. A Peltier cooled solid-state [Si(Li)] detector (Sol-X) with a useful energy range of 1 to 60 KeV was used as the detector. No correction was made for Kβ radiation. A set of 2° Soller slits were used to lower the horizontal beam divergence.

The crystallinity index peak height ratio was calculated according to the peak height method developed by Segal *et al.* (1959), as seen in Eq. 1,

$$CI = \frac{I_{002} - I_{am}}{I_{am}} x\, 100 \qquad (1)$$

where *CI* is the crystallinity index (%), I_{002} is the intensity of the 002 crystalline peak at 22°, and I_{am} is the height of the minimum (I_{am}) between the 002 and 101 peaks.

RESULTS AND DISCUSSION

Physical Properties

The oven-dry and air-dry densities, the radial and tangential swelling, and radial and tangential shrinking percentages of the heat-treated Scots pine and beech samples are shown in Table 2.

According to Table 2, the air-dry density (D_{12}) and oven-dry density (D_0) decreased in certain rates as the temperature and time increased in all the groups. This decrease was mainly due to the transformation of the wood components, especially hemicellulose, into volatile products during the heat treatment, the evaporation of extractives, and the lower equilibrium moisture content because the wood was less hygroscopic with the application of heat treatment (Korkut and Kocaefe 2009).

The percentages of shrinking (β_v) in the radial (β_r), tangential (β_t), and longitudinal (β_l) directions of the Scots pine and beech wood samples can be seen in Table 2. The heat treatment decreased the percentage of volume shrinking compared to the control group for all the samples (Fig. 1). It was determined that the lowest volume shrinking percentage was observed in the S6 and B6 (210 °C, 4 h) groups, and the highest volume shrinking percentage was observed in the SControl and BControl groups. When the effect of heat treatment temperature on volume shrinking was examined, it was observed that the percentage of volume shrinking in the samples of Scots pine and beech wood decreased as the temperature increased. As the heat treatment time increased, the percentage of volume shrinking decreased for all the groups.

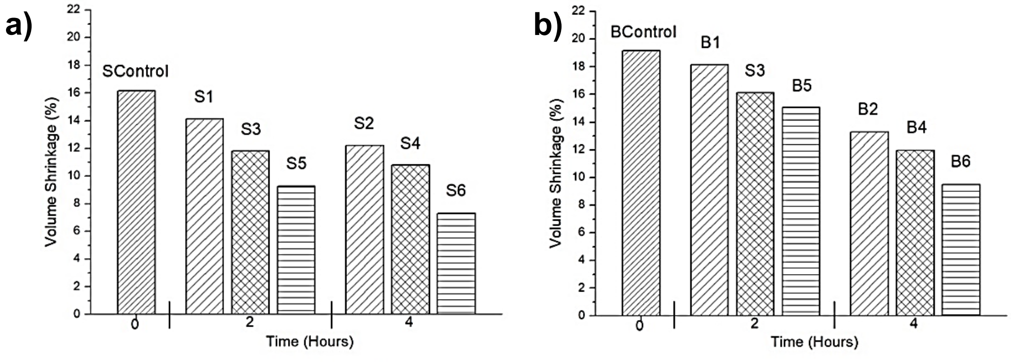
Table 2. Physical Properties of Scots Pine and Beech Wood (D_0 and D_{12}, g/cm^3; others, %)

Groups	D_0	D_{12}	β_r	β_t	β_l	β_v	α_r	α_t	α_l	α_v
SControl	0.54 (0.06)*	0.54 (0.03)	6.52 (0.16)	8.94 (0.37)	0.72 (0.13)	16.18 (1.32)	6.97 (1.13)	9.81 (1.23)	0.73 (0.21)	17.52 (2.01)
S1	0.52 (0.02)	0.52 (0.04)	6.06 (0.13)	7.39 (0.42)	0.66 (0.15)	14.12 (1.17)	6.45 (0.97)	7.98 (1.04)	0.66 (0.12)	15.10 (1.68)
S2	0.52 (0.02)	0.52 (0.07)	5.53 (0.09)	6.11 (0.32)	0.57 (0.09)	12.21 (1.43)	5.85 (0.36)	6.51 (1.21)	0.57 (0.23)	12.93 (1.73)
S3	0.49 (0.05)	0.49 (0.04)	4.92 (0.15)	6.36 (0.28)	0.54 (0.11)	11.82 (1.03)	5.17 (0.73)	6.80 (1.39)	0.54 (0.09)	12.51 (1.38)
S4	0.48 (0.05)	0.48 (0.06)	4.65 (0.11)	5.72 (0.13)	0.44 (0.05)	10.81 (1.13)	4.87 (0.48)	6.07 (1.18)	0.44 (0.07)	11.38 (0.23)
S5	0.47 (0.04)	0.47 (0.06)	3.29 (0.07)	5.54 (0.25)	0.42 (0.03)	9.26 (0.94)	3.41 (0.16)	5.87 (0.58)	0.42 (0.12)	9.70 (1.38)
S6	0.46 (0.06)	0.46 (0.07)	3.22 (0.09)	3.86 (0.17)	0.24 (0.06)	7.32 (0.79)	3.33 (0.36)	4.02 (0.23)	0.24 (0.08)	7.58 (1.61)
BControl	0.65 (0.04)	0.65 (0.04)	8.61 (0.23)	9.77 (0.54)	0.78 (0.14)	19.16 (1.47)	9.42 (1.35)	10.82 (1.67)	0.79 (0.14)	21.04 (2.79)
B1	0.63 (0.04)	0.63 (0.04)	8.47 (0.31)	8.95 (0.43)	0.72 (0.09)	18.15 (1.64)	9.26 (1.21)	9.83 (1.28)	0.73 (0.12)	19.82 (2.92)
B2	0.62 (0.03)	0.62 (0.05)	7.25 (0.17)	8.17 (0.39)	0.69 (0.13)	16.11 (0.36)	7.82 (0.99)	8.89 (1.41)	0.70 (0.09)	17.41 (1.94)
B3	0.62 (0.03)	0.62 (0.03)	6.91 (0.24)	7.49 (0.29)	0.67 (0.05)	15.07 (1.25)	7.43 (0.74)	8.09 (1.22)	0.68 (0.11)	16.20 (1.49)
B4	0.61 (0.04)	0.61 (0.03)	5.95 (0.15)	6.80 (0.21)	0.56 (0.07)	13.31 (1.33)	6.32 (0.48)	7.30 (1.29)	0.56 (0.04)	14.18 (2.04)
B5	0.60 (0.03)	0.60 (0.04)	5.61 (0.31)	5.97 (0.32)	0.40 (0.07)	11.97 (0.47)	5.94 (0.24)	6.35 (0.53)	0.40 (0.12)	12.69 (1.65)
B6	0.59 (0.05)	0.59 (0.03)	3.33 (0.19)	5.78 (0.17)	0.37 (0.04)	9.48 (1.16)	3.44 (0.34)	6.13 (1.21)	0.37 (0.07)	9.95 (1.35)

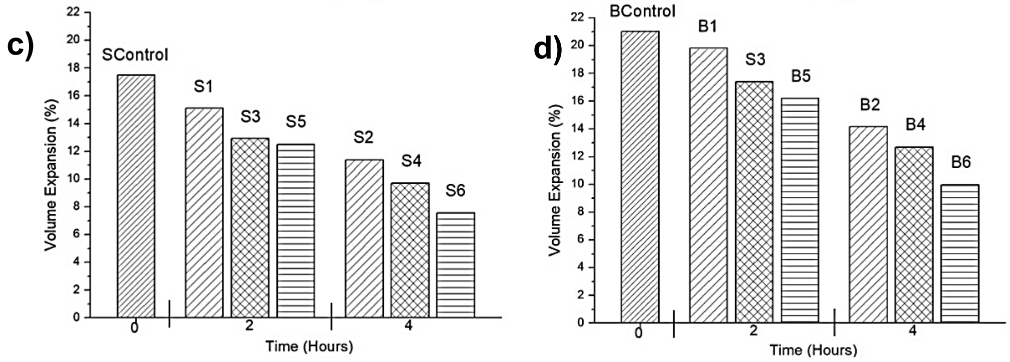
*Values in parentheses are the standard deviations
D_0, oven dry density; D_{12}, air dry density; β_r, radial shrinking; β_t, tangential shrinking; β_l, longitudinal shrinking; β_v, volume shrinking; α_r, radial swelling; α_t, tangential swelling; α_l, longitudinal swelling; α_v, volume swelling.

The percentages of the radial (α_r), tangential (α_t), longitudinal (α_l), and volume swelling (α_v) percentages of the Scots pine and beech samples are shown in Table 2. When the volume swelling percentages were examined, it was determined that the least volume swelling percentage was in the S6 and B6 groups, and the highest volume swelling percentage was in the SControl and BControl groups. When the effect of heat treatment temperature and duration on the volume swelling was examined, the percentage of volume swelling decreased in all the groups as the temperature and time increased (Fig. 1). The dimensional stability of the wood samples increased in direct proportion with the increase of heat treatment, temperature, and time parameters.

Heat treatment reduces the moisture adsorption in wood. The presence of free hydroxyl groups in wood plays an important role in moisture adsorption and desorption. As a result of the heat treatment, the number of free hydroxyl groups in the wood decreased. This was due to the depolymerisation of carbohydrates, which decreased the total amount of free hydroxyl groups. In addition, the increase in the relative ratio of crystalline cellulose, where hydroxyl groups cannot easily reach water molecules, and the cross-linking of lignin, which prevents the accessibility of free hydroxyl groups to water, is very effective in reducing hygroscopicity in wood (Hill 2006).



Scots Pine - β_v Beech- β_v



Scots Pine - α_v Beech- α_v

Fig. 1. The volume shrinkage test for the a) Scots pine and b) beech wood; the volume expansion test for the c) Scots pine and d) volume expansion

The heat treatment imparted the Scots pine wood with more dimensional stability than the beech wood. Comparing the S6 and B6 groups with the least swelling and shrinking percentage to the control groups provided insight to which tree species gain more dimensional stability with heat treatment. The less the difference between the divisor and the dividend in ratio expressions (*a*/*b*) in mathematics, the closer the result is to 1. If this ratio approaches 1, the dimensional stability decreases. When the shrinking ratio was compared (β6/βcontrol), the shrinking ratio of beech wood (0.4948) was higher than the shrinking ratio of Scots pine (0.4524). When the swelling ratios (α6 / αcontrol) were compared, the swelling ratio of beech wood (0.4729) was higher than the Scots pine swelling ratio (0.4327). According to the results, it can be said that the heat treatment of Scots pine and beech wood at 210 °C for 4 h enables the Scots pine wood to gain more dimensional stability than the beech wood. On the other hand, it was understood that the dimensional stability increased in all groups with the increase of heat treatment time at a constant temperature. The obtained results were compatible with the studies in the literature. In a study conducted by Tjeerdsma *et al.* (1998) Scots pine and beech wood were subjected to gradual heat treatment, and it was determined that the efficiency of heat treatment on the dimensional stability was 40% in the Scots pine and 22% in the beech wood. Burmester (1975) concluded that heat treatment leads to a high reduction in the hemicellulose content in wood, which increases the dimensional stability of the wood.

Mechanical Properties

The compressive strength, bending strength, MOE, and hardness properties of the heat-treated Scots pine and beech wood samples are shown in Table 3.

Table 3. The Mechanical Properties of Scots Pine and Beech Wood

Groups	Compressive Strength (N/mm^2)	Bending Strength (N/mm^2)	MOE (N/mm^2)	Hardness (Shore D)	
				Radial	Tangential
SControl	51.34 (0.18)*	89.08 (2.10)	10,255.53 (424.03)	1.44 (0.11)	1.45 (0.11)
S1	60.43 (0.80)	82.87 (1.30)	9,552.46 (239.76)	1.41 (0.03)	1.42 (0.03)
S2	59.25 (1.41)	78.09 (1.24)	8,954.22 (498.07)	1.21 (0.05)	1.26 (0.06)
S3	62.04 (1.29)	92.66 (2.70)	9,894.23 (423.09)	1.40 (0.04)	1.44 (0.04)
S4	61.13 (1.67)	85.98 (3.24)	9,058.73 (304.49)	1.19 (0.08)	1.20 (0.11)
S5	59.17 (0.91)	62.47 (3.18)	8,813.76 (427.49)	1.22 (0.03)	1.29 (0.05)
S6	53.29 (1.78)	40.34 (1.44)	7,509.79 (105.78)	1.19 (0.07)	1.22 (0.09)
BControl	67.38 (0.56)	124.53 (1.77)	11,780.20 (488.88)	1.64 (0.03)	1.64 (0.04)
B1	71.37 (1.38)	118.98 (1.70)	11,050.46 (558.94)	1.60 (0.05)	1.57 (0.05)
B2	70.80 (2.34)	113.07 (3.11)	10,615.46 (254.90)	1.42 (0.03)	1.45 (0.06)
B3	73.16 (0.72)	125.75 (2.27)	11,412.93 (336.44)	1.62 (0.06)	1.60 (0.06)
B4	72.88 (0.65)	106.68 (2.22)	10,787.43 (222.28)	1.46 (0.12)	1.52 (0.05)
B5	69.80 (0.95)	78.87 (1.72)	10,327.45 (113.35)	1.43 (0.14)	1.41 (0.12)
B6	68.17 (1.36)	64.41 (2.41)	9,417.07 (459.04)	1.22 (0.06)	1.29 (0.13)

* Values in parentheses are the standard deviations.

With the heat treatment, the compressive strength values of the Scots pine and beech wood increased in all the sample groups compared to the control group. As the heat treatment time increased at a constant temperature, there was very little loss in the compressive strength. When the time was kept constant, the compressive strength increased up to 180 °C with the increase in the heat treatment temperature, while it tended to decrease at 210 °C. Compared to the control group, the highest rate of increase in compressive strength was seen in the S3 (20.85%) and B3 (8.58%) groups (180 °C, 2 h), while the lowest rate was seen in the S6 (3.80%) and B6 (1.17%) groups (210 °C, 4 h). According to these results, it can be said that with the heat treatment, the compressive strength properties of the Scots pine wood improved more than the beech wood. The amount of highly regular crystalline cellulose increased due to the degradation and/or crystallization of amorphous cellulose as a result of the heat treatment. Since crystalline cellulose exhibits anisotropic structure, its solid and rigid structure provides a slight increase in the longitudinal compressive strength (Bhuiyan and Hirai 2005; Korkut and Kocaefe 2009; Beroual *et al.* 2020; Wang *et al.* 2020; Wu *et al.* 2021; Cao *et al*. 2022).

Boonstra *et al.* (2007b), stated that the loss of some mechanical strength with heat treatment is mainly due to the degradation of hemicellulose. In addition, it has been stated that crystallization of amorphous cellulose plays an important role in the loss of mechanical strength. Polycondensation reactions of lignin resulting in cross-linking basically have a positive effect on the wood material in the longitudinal direction. The decrease in the amount of equilibrium moisture can positively affect the strength properties of the heat-treated wood material. However, this effect is eliminated by the degradation of cell wall components (Esteves and Pereira 2009).

One of the mechanical properties most affected by heat treatment is the bending strength. This reduction varies depending on the heat treatment conditions and the wood species. The bending strength of Scots pine and beech wood with heat treatment decreased up to 150 °C compared to the control samples, and then increased up to 180 °C. When the heat treatment temperature increased to 210°C, the bending strength decreased sharply. As the heat treatment time increased at the same temperatures, the bending strength decreased in all the groups. Compared to the control Scots pine and beech wood samples, the highest decrease was in the S6 (54.7%) group, and the highest increase was in the S3 (4.02%) group when the rate of change in the bending strength with heat treatment was compared. The degradation of hemicellulose was primarily responsible for the diminished bending strength, rather than the degradation of lignin and cellulose during the heat treatment. The decreased bending strength values continued with the heat treatment time and temperature. Of the cell wall components, hemicellulose is the most sensitive to heat. LeVan *et al.* (1990) stated that as a result of the breaking of the side chains of hemicellulose in the lignin-hemicellulose matrix, the load-sharing capacity is impaired and therefore it can be held responsible for strength losses. Another reason is that the degree of polymerization of hemicellulose is reduced due to the disruption of the backbone of hemicellulose (Winandy and Lebow 2001; Esteves *et al*. 2008; Korkut and Kocaefe 2009).

The MOE values of Scots pine and beech wood decreased with the heat treatment. This decrease was not the same when the temperature and time parameters were considered. Compared to the control group, the S6 and B6 groups had the highest decrease in MOE values (26.8% and 20.8%, respectively), while the S3 and B3 groups had the lowest decrease in MOE values (3.52% and 4.01%, respectively). In the heat treatments where the time was fixed and temperatures were variable, the maximum loss in temperature and MOE was experienced at 210 °C, while the least loss was experienced at 180 °C. In all the groups, it was observed that the MOE values decreased as the heat treatment time increased. The MOE increases as the cellulose crystallinity increases and the wood moisture decreases. The effect of crystallinity is valid at the beginning of the heat treatment process, but decomposition with temperature is more dominant in the advanced stages of the heat treatment. This causes the MOE to decrease (Esteves and Pereira 2009).

As seen by the hardness values in Table 3, there was no change in the hardness values with the increase of the heat treatment temperature and time up to 180 °C in the Scots pine and beech wood. It is understood that the hardness decreases at temperatures of 210 °C. The biggest reason for this is thought to be that lignin starts to degrade at 210 °C (Korkut *et al.* 2008). With the degradation of hemicellulose, the thickness of the crystallites, and the increase in the cellulose crystallization degree, some of the strength and hardness properties of the wood decrease (Korkut and Kocaefe 2009).

When the results were examined, it was seen that the physical and mechanical properties of beech and Scots pine woods were affected differently with the heat treatment applied in the same parameters. Differences in strength properties between wood species may be due to the inherent strength of each wood species and the different effect of heat treatment on each wood species. The ratio and composition of hemicelluloses in wood differ in softwood and hardwood. Softwoods contain predominantly galactoglucomannan and arabinoglucuronoxylan, while hardwoods contain glucuronoxylan and small amounts of glucomannan. Because softwoods and hardwoods have rather different densities, their differing thermodegradation characteristics are most likely caused by differences in their chemical components. With heat treatment, softwoods can decompose in a shorter time than hardwoods. In addition, it is stated in the literature that the hemicelluloses of softwoods and hardwoods are different and the amount of acetic acid formed in hardwoods with heat treatment is higher (Boonstra *et al.* 2007a; Chaouch *et al.* 2010, 2013; Yildiz *et al.* 2013; Barlovic *et al.* 2022).

The FTIR Analysis

Within the scope of the study, FTIR analyses of all groups were carried out to show the presence of chemical changes in wood with the heat treatment. The FTIR spectra of the Scots pine and beech wood in the wavelength range of 800 to 1800 cm^{-1} are shown in Fig. 2.

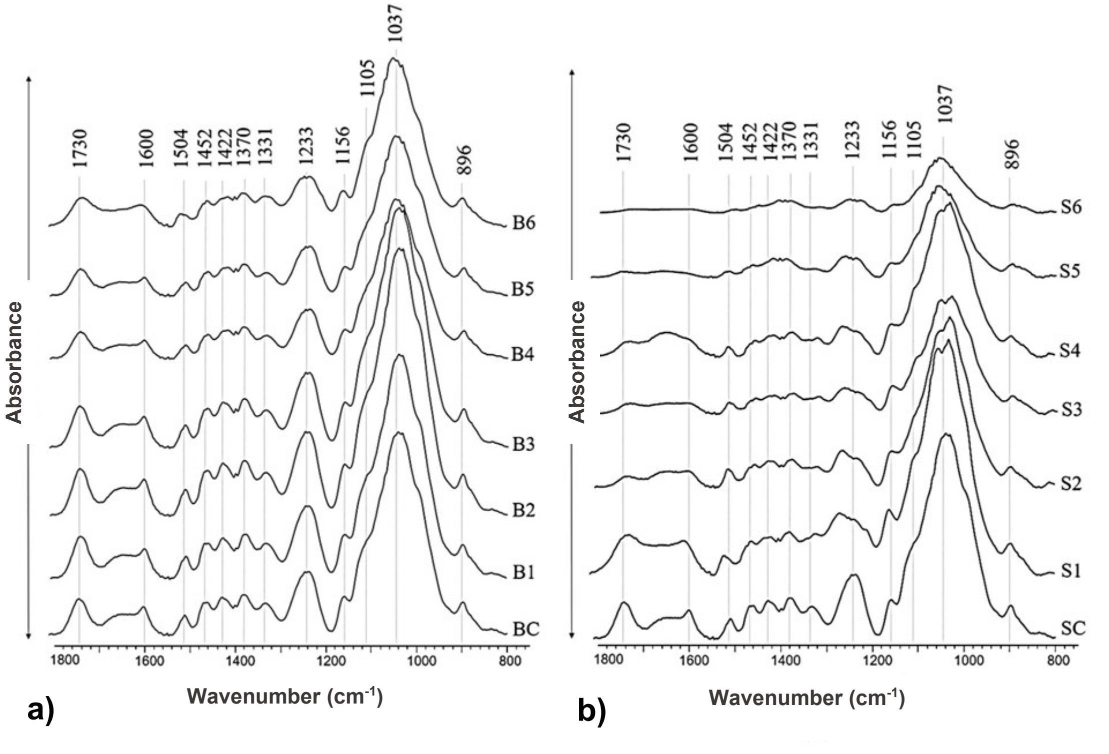


Fig. 2. The FTIR spectra of the a) beech wood and b) Scots pine samples

Table 4 shows the assignment of important absorption bands in the wood samples between 800 cm^{-1} and 1800 cm^{-1}. When the FTIR graphics of the beech wood and Scots pine woods in Fig. 2 were examined, it was seen that the peak at 896 cm^{-1} decreased. This decrease was probably due to the vibration of organic acids in the C–H bond, which occurs when the hemicellulose and cellulose chains are hydrolyzed by heat treatment (Nuopponen *et al.* 2003; Kocaefe *et al.* 2008; Özgenç *et al*. 2017).

Table 4. The FTIR Peaks Varying in the Wavelength Range of 800 to 1800 cm^{-1} by the Heat Treatment of Wood

Wavenumber (cm^{-1})	Remarks
896	C_1-carbon in hemicelluloses and in cellulose (pyranose ring) (Kotilainen *et al.* 2000)
1037	C-O deformation in aliphatic alcohols and ethers, symmetric C-O-C stretching of dialkyl ethers, aromatic C-H deformation in plane (Kotilainen *et al.* 2000)
1105	OH association (cellulose) (Vix-Guterl *et al.* 2004; Özgenç *et al.* 2017)
1156	C-O-C symmetric stretching (Kotilainen *et al.* 2000; Özgenç *et al.* 2017)
1233	Alkyl-aryl-ether bonds, lactones (Kotilainen *et al.* 2000)
1331	Phenol group (Kotilainen *et al.* 2000)
1370	C-H bending, $-CH_3$ (lignin), $-CH_2$ (carbohydrates), lignin-carbohydrate complexes bonds (Nuopponen 2005; Özgenç *et al.* 2017)
1422	aromatic skeletal vibrations (lignin) and C-H deformation in plane (cellulose) (Kotilainen *et al.* 2000)
1452	C=C and C-H bond, extractives, O-H in plane deformation, CH_3 asymmetric bending in (lignin) (Nuopponen 2005; Ishimaru *et al.* 2007)
1504	C=C stretching of the aromatic skeletal vibrations (lignin) (Nuopponen *et al.* 2004; Nuopponen 2005).
1600	aromatic skeletal vibrations, affected by aromatic C-O stretching mode and by conjugation with α-carbonyl groups (Kotilainen *et al.* 2000; Özgenç *et al.* 2017).
1730	carboxyl- and ester groups, nonconjugated aldehyde (Kotilainen *et al.* 2000; Özgenç *et al.* 2017).

The peaks at 1105 and 1156 cm^{-1} were related to the crystal and amorphous cellulose content. These peaks generally increased in both the beech wood and Scots pine species. This increase may have been attributed to the effect of increasing heat treatment on amorphous cellulose (Kotilainen *et al.* 2000; Nuopponen *et al.* 2004; Özgenç *et al.* 2017).

The peak at 1331 cm^{-1} indicates the presence of syringyl rings, guayasil rings, and phenol groups. Both wood species decreased in these peaks with heat treatment (Bates 1976; Hakkou *et al.* 2005).

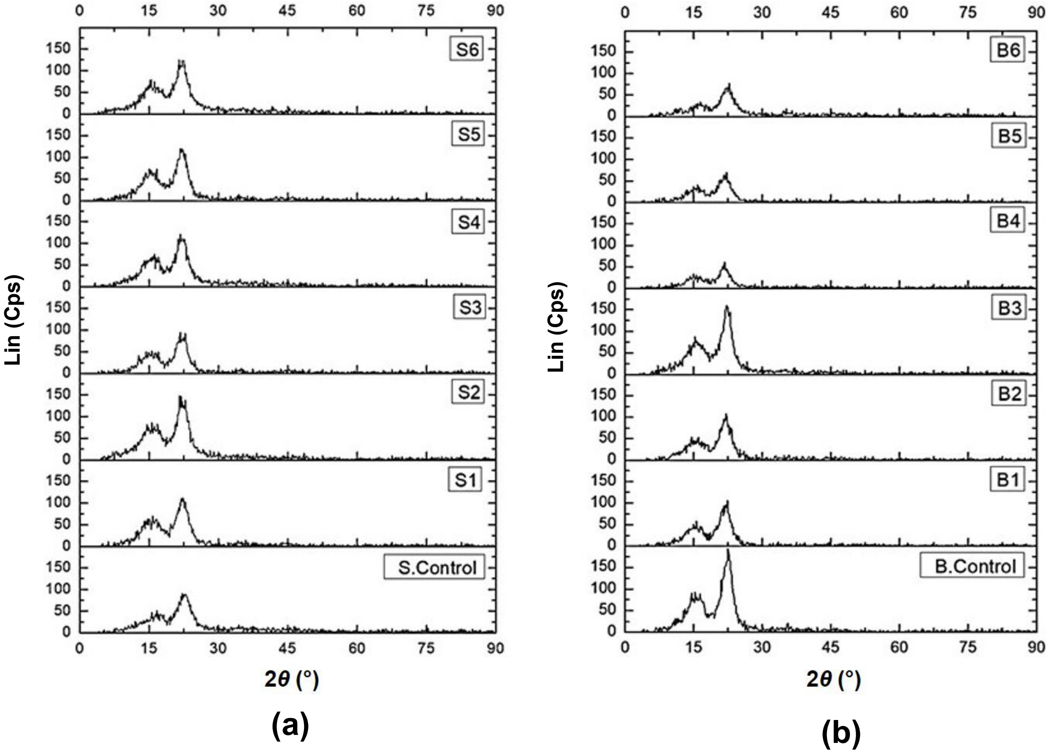
The peak at 370 cm^{-1} was caused by the lignin and carbohydrate complexes. When the FTIR graphs of both wood species were examined, there was a decrease in this peak. This decrease is thought to be due to the condensation of lignin and the depolymerization of carbohydrates (Akgül *et al*. 2007; Gérardin *et al.* 2007; Fengel and Wegener 2011).

The peaks at 1422, 1452, and 1504 cm^{-1} express the changes in the lignin with the heat treatment. These peaks decreased with the heat treatment in both wood species. This reduction is thought to be due to the cleavage of aliphatic side chains in lignin and the condensation of lignin with temperature (Tjeerdsma and Militz 2005; Mburu *et al.* 2008; Emmanuel *et al.* 2015; Özgenç *et al.* 2017).

The peaks at 1600 and 1730 cm^{-1} generally decreased for both wood species. This reduction may have been due to the degradation of hemicellulose with the heat treatment (Tjeerdsma and Militz 2005; Akgül *et al.* 2007; Gérardin *et al.* 2007; Özgenç *et al.* 2017).

Crystallinity Properties

The XRD patterns of the Scots pine and beech wood samples can be seen in Fig. 3. As the heat treatment time and temperature increased in the Scots pine samples, the XRD peaks partially increased before they tended to decrease. The crystallinity index values were calculated from the XRD graphs (Fig. 4).



(a)

(b)

Fig. 3. The XRD graphs of the a) Scots pine and b) beech wood samples

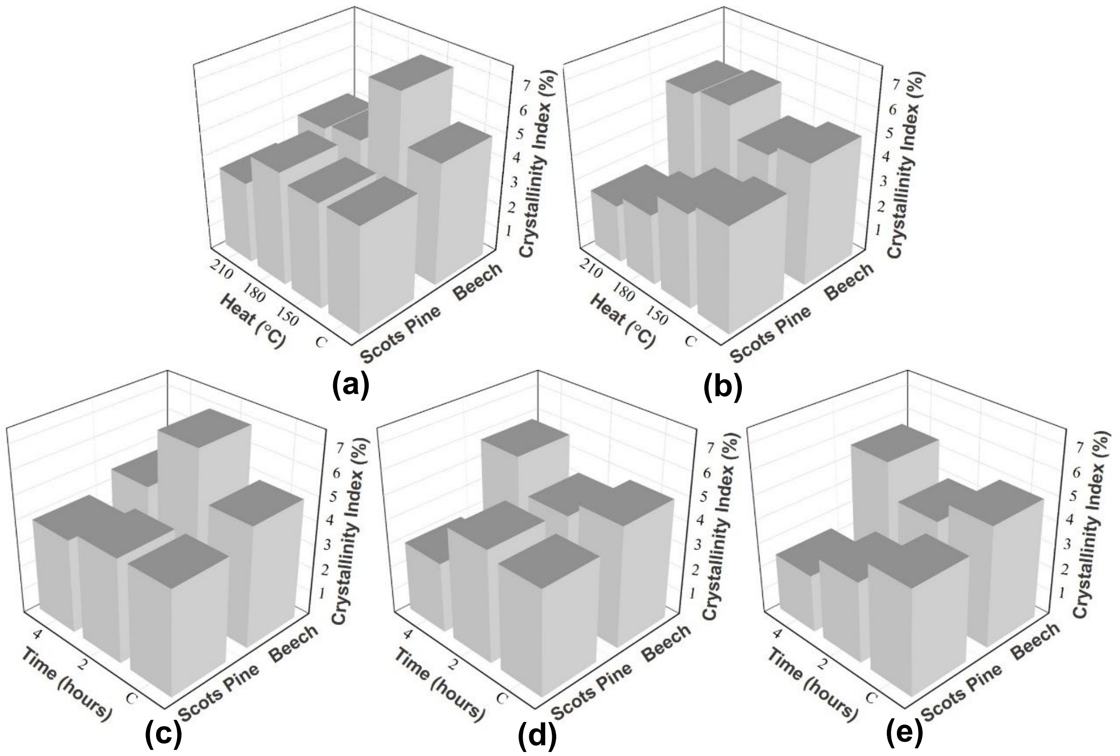


Fig. 4. The crystallinity index graphs of the samples heated for a) 2 h, b) 4 h and heated to c) 150 °C, d) 180 °C, and e) 210 °C

When Fig. 4 was examined, it was determined that the crystallinity index first increased a little before it gradually decreased with the increase of temperature in the Scots pine and beech wood samples, which were heat-treated for 2 h and 4 h. In general, the crystallinity index increased a little and then decreased with the increase of heat treatment time in the Scots pine and beech wood samples that were heat-treated at 150, 180, and 210 °C. It is thought that the initial increase in crystallinity is mainly due to the decomposition of hemicellulose, and the subsequent decrease is due to damage to the cellulose (Durmaz *et al.* 2019; García-Iruela *et al.* 2021; Lin *et al.* 2022; Wang *et al.* 2022).

CONCLUSIONS

1. According to the results of the physical tests, it was determined that the volume shrinking percentage of the Scots pine and beech wood samples decreased as the heat treatment temperature increased. As the heat treatment time increased, the volume shrinking percentage decreased in all groups. It was determined that the dimensional stability of the Scots pine and beech wood samples increased in direct proportion with the increase of the heat treatment, temperature, and time parameters.

2. The compressive strength increased in the Scots pine and beech wood samples with heat treatment. The bending strength decreased up to 180 °C. When the heat treatment temperature increased to 210 °C, the bending strength decreased sharply. With the increase in heat treatment time at the same temperatures, the bending strength decreased in all the groups. The MOE values in the Scots pine and beech wood decreased with the heat treatment. This decrease was not the same when the temperature and time parameters were considered.
3. There was no change in the hardness values as the heat treatment temperature and time increased up to 180 °C and 4 h, respectively, in both wood species. It was understood that the hardness decreases at temperatures of 210 °C. The FTIR analysis results supported the changes in the physical and mechanical properties of wood by heat treatment.
4. As the heat treatment temperature and duration increased, the crystallinity index values firstly increased partially and then decreased.
5. This study, which examined the relationship between heat treatment and the change in the crystallinity of the wood, and the change in the physical and mechanical properties of the wood, will contribute to the literature. It is recommended to carry out new studies by testing different heat treatment parameters, especially the heat treatment environment.

REFERENCES CITED

Akgül, M., Gümüşkaya, E., and Korkut, S. (2007). “Crystalline structure of heat-treated Scots pine [*Pinus sylvestris* L.] and Uludağ fir [*Abies nordmanniana* (Stev.) subsp. *bornmulleriana* (Mattf.)],” *Wood Science and Technology* 41, 281-289. DOI: 10.1007/s00226-006-0110-9

Alexander, L. (1971). “X-ray diffraction methods in polymer science,” *Journal of Materials Science* 6(1), 93-93. DOI: 10.1007/BF00550300

Andersson, S., Serimaa, R., Paakkari, T., Saranpää, P., and Pesonen, E. (2003). “Crystallinity of wood and the size of cellulose crystallites in Norway spruce (*Picea abies*),” *Journal of Wood Science* 49(6), 531-537. DOI: 10.1007/s10086-003-0518-x

Balta-Calleja, F. J., and Vonk, C. G. (1989). *X-ray Scattering of Synthetic Polymers*, Elsevier Science, Amsterdam, Netherlands.

Barlovic, N., Cavlovic, A. O., Pervan, S., Klaric, M., Prekrat, S., and Spanic, N. (2022). “Chemical changes and environmental issues of heat treatment of wood,” *Drvna Industrija* 73(2), 245-251. DOI: 10.5552/drvind.2022.000

Bates, J. B. (1976). “Fourier transform infrared spectroscopy: The basic principles and current applications of a rapidly expanding technique are reviewed,” *Science* 191, 31-37. DOI: 10.1126/science.1246596

Beroual, M., Trache, D., Mehelli, O., Boumaza, L., Tarchoun, A. F., Derradji, M., and Khimeche, K. (2020). “Effect of the delignification process on the physicochemical properties and thermal stability of microcrystalline cellulose extracted from date palm fronds,” *Waste Biomass Valor* 12, 2779-2793. DOI: 10.1007/s12649-020-01198-9

Bhuiyan, T. R., Hirai, N., and Sobue, N. (2002). “Changes of crystallinity in wood cellulose by heat treatment under dried and moist conditions,” *Journal of Wood*

Science 46(6), 431-436. DOI: 10.1007/BF00765800

Bhuiyan, T. R., and Hirai, N. (2005). "Study of crystalline behavior of heat-treated wood cellulose during treatments in water," *Wood Science and Technology* 51, 42-47. DOI: 10.1007/s10086-003-0615-x

Boonstra, M. J., Acker, J. V. and Kegel, E. (2007a). "Effect of a two-stage heat treatment process on the mechanical properties of full construction timber," *Wood Material Science and Engineering* 3(4), 138-146. DOI: 10.1080/17480270801945439

Boonstra, M. J., Acker, J. V., Tjeerdsma, B. F., and Kegel, E. V. (2007b). "Strength properties of thermally modified softwoods and its relation to polymeric structural wood constituents," *Annals of Forest Science* 64(7), 679-690. DOI: 10.1051/forest:2007048

Bourgois, J., and Guyonnet, R. (1988). "Characterisation and analysis of torrefied wood," *Wood Science and Technology* 22, 143-155. DOI: 10.1007/BF00355850

Burmester, A. (1975). "Zur Dimensionsstabilisierung von Holz (The dimensional stability of wood)," *Holz als Roh- und Werkstoff* (*European Journal of Wood and Wood Products)* 33(9), 333-335. DOI: 10.1007/bf02612789

Cao, S., Cheng, S., and Cai, J. (2022). "Research progress and prospects of wood high-temperature heat treatment technology," *BioResources* 17(2), 1-16. DOI: 10.15376/biores.17.2.Cao

Chaouch, M., Petrissans, M., Petrissans, A., and Gerardin, P. (2010). "Use of wood elemental composition to predict heat treatment intensity and decay resistance of different softwood and hardwood species," *Polymer Degradation and Stability* 95(12), 2255-2259. DOI: 10.1016/j.polymdegradstab.2010.09.010

Chaouch, M., Dumarçay, S., Petrissans, A., Petrissans, M., and Gerardin, P. (2013). "Effect of heat treatment intensity on some conferred properties of different European softwood and hardwood species," *Wood Science and Technology* 47, 663-673. DOI: 10.1007/s00226-013-0533-z

Emmanuel, V., Odile, B., and Céline, R. (2015). "FTIR spectroscopy of woods: A new approach to study the weathering of the carving face of a sculpture," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 136, 1255-1259. DOI: 10.1016/j.saa.2014.10.011

Esteves, B. M., Domingos, I. J., and Pereira, H. M. (2008). "Pine wood modification by heat treatment in air," *BioResources* 3(1), 142-154. DOI: 10.15376/biores.3.1.142-154

Esteves, B. M., and Pereira, H. M. (2009). "Wood modification by heat treatment: A review," *BioResources* 4(1), 370-404. DOI: 10.15376/biores.4.1.370-404

Fengel, D., and Wegener, G. (2011). *Wood: Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin, Germany

García-Iruela, A., Esteban, L. G., García Fernández, F., Palacios, P., Rodrigues-Navarro, A. B., Martin Sampedro, R., and Eugenio, M. E. (2021). "Changes in cell wall components and hygroscopic properties of *Pinus radiata* caused by heat treatment," *European Journal of Wood and Wood Products* 79, 851-861. DOI: 10.1007/s00107-021-01678-2

Gérardin, P., Petrič, M., Petrissans, M., Lambert, J., and Ehrhrardt, J. J. (2007). "Evolution of wood surface free energy after heat treatment," *Polymer Degradation and Stability* 92(4), 653-657. DOI: 10.1016/j.polymdegradstab.2007.01.016

Gosselink, R. J. A., Krosse, A. M. A., van der Putten, J. C., van der Kolk, J.C., de Klerk-Engels, B., and van Dam, J. E. G. (2004). "Wood preservation by low-temperature carbonization," *Industrial Crops and Products* 19(1), 3-12. DOI: 10.1016/S0926-6690(03)00037-2

Hakkou, M., Pétrissans, M., Zoulalian, A., and Gérardin, P. (2005). "Investigation of wood wettability changes during heat treatment on the basis of chemical analysis," *Polymer Degradation and Stability* 89(1), 1-5. DOI: 10.1016/j.polymdegradstab.2004.10.017

Hill, C. A. S. (2006). *Wood Modification: Chemical, Thermal and Other Processes*, Wiley, Hoboken, NJ.

Ishimaru, K., Hata, T., Bronsveld, P., Meier, D., and Imamura, Y. (2007). "Spectroscopic analysis of carbonization behavior of wood, cellulose and lignin," *Journal of Materials Science* 42(1), 122-129. DOI: 10.1007/s10853-006-1042-3

Kim, U.-J., Eom, S. H., and Wada, M. (2010). "Thermal decomposition of native cellulose: Influence on crystallite size," *Polymer Degradation and Stability* 95(5), 778-781. DOI: 10.1016/j.polymdegradstab.2010.02.009

Kocaefe, D., Poncsak, S., and Boluk, Y. (2008). "Effect of thermal treatment on the chemical composition and mechanical properties of birch and aspen," *BioResources* 3(2), 517-537.

Kong, L., Zhao, Z., He, Z., and Yi, S. (2017). "Effects of steaming treatment on crystallinity and glass transition temperature of *Eucalyptuses grandis* × *E. urophylla*," *Results in Physics* 7, 914-919. DOI: 10.1016/j.rinp.2017.02.017.

Korkut, S., Akgül, M., and Dündar, T. (2008). "The effects of heat treatment on some technological properties of Scots pine (*Pinus sylvestris* L.) wood," *Bioresource Technology* 99(6), 1861-1868. DOI: 10.1016/j.biortech.2007.03.038

Korkut, S., and Kocaefe, D. (2009). "Effect of heat treatment on wood properties," *Duzce University Journal of Forestry* 5(2), 11-34.

Kotilainen, R. A., Toivanen, T.-J., and Alén, R. J. (2000). "FTIR monitoring of chemical changes in softwood during heating," *Journal of Wood Chemistry and Technology* 20(3), 307-320. DOI: 10.1080/02773810009349638

Lee, C. L. (1961). "Crystallinity of wood cellulose fibers studies by Xray methods," *Forest Products Journal* 11, 108-112.

LeVan, S. L., Ross, R. J., and Winandy, J. E. (1990). "Effects of fire retardant chemicals on the bending properties of wood at elevated temperatures" (FPL-RP-498), U.S. Department of Agriculture Forest Products Laboratory, Madison, WI.

Lin, L. D., Tsai, M. J., Chang, F. C., Ko, C. H., and Yang, B. Y. (2022). "Influence of torrefaction on the heating values and energy densities of hardwood and softwood," *BioResources* 17(1), 316-328. DOI: 10.15376/biores.17.1.316-328

Mburu, F., Dumarçay, S., Bocquet, J.-F., Pétrissans, M., and Gérardin, P. (2008). "Effect of chemical modifications caused by heat treatment on mechanical properties of *Grevillea robusta* wood," *Polymer Degradation and Stability* 93(2), 401-405. DOI: /10.1016/j.polymdegradstab.2007.11.017

Nada, A.-A. M. A., Kamel, S., and El-Sakhawy, M. (2000). "Thermal behaviour and infrared spectroscopy of cellulose carbamates," *Polymer Degradation and Stability* 70(3), 347-355. DOI: 10.1016/S0141-3910(00)00119-1

Nuopponen, M., Vuorinen, T., Jämsä, S., and Viitaniemi, P. (2003). "The effects of a heat treatment on the behaviour of extractives in softwood studied by FTIR spectroscopic methods," *Wood Sci. Technol.* 37(2), 109-115. DOI: 10.1007/s00226-003-0178-4

Nuopponen, M., Wikberg, H., Vuorinen, T., Maunu, S. L., Jämsä, S., and Viitaniemi, P. (2004). "Heat-treated softwood exposed to weathering," *Journal of Applied Polymer*

Science 91(4), 2128-2134. DOI: 10.1002/app.13351

Nuopponen, M. (2005). *FT-IR and UV-Raman Spectroscopic Studies on Thermal Modification of Scots Pine Wood and Its Extractable Compounds*, Ph.D. Dissertation, Helsinki University of Technology, Espoo, Finland.

Obataya, E., and Higashihara, T. (2017). "Reversible and irreversible dimensional changes of heat-treated wood during alternate wetting and drying," *Wood Science and Technology* 51(4), 739-749. DOI: 10.1007/s00226-017-0918-5

Özgenç, Ö., Durmaz, S., Boyacı, I. H., and Eksi-Kocak, H. (2017). "Determination of chemical changes in heat-treated wood using ATR-FTIR and FT Raman spectrometry," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 171, 395-400. DOI: 10.1016/j.saa.2016.08.026

Poletto, M., Zattera, A. J., Forte, M. M. C., and Santana, R. M. C. (2012). "Thermal decomposition of wood: Influence of wood components and cellulose crystallite size," *Bioresource Technology* 109, 148-153. DOI: 10.1016/j.biortech.2011.11.122

Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the x-ray diffractometer," *Textile Res. J.* 29(10), 786-794. DOI: 10.1177/004051755902901003

Tjeerdsma, B. F., Boonstra, M., Pizzi, A., Tekely, P., and Militz, H. (1998). "Characterisation of thermally modified wood: Molecular reasons for wood performance improvement," *Journal of Wood and Wood Products* 56(3), 149-153. DOI: 10.1007/s001070050287

Tjeerdsma, B. F., and Militz, H. (2005). "Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood," *Journal of Wood and Wood Products* 63(2), 102-111. DOI: 10.1007/s00107-004-0532-8

TS 2472 (1976). "Wood—Determination of density for physical and mechanical tests (ICS 79.040)," Turkish Standards Institution, Ankara, Turkey.

TS 2474 (1976). "Wood – Determination of ultimate strength in static bending," Turkish Standards Institution, Ankara, Turkey.

TS 2478 (1976). "Wood – Determination of modulus of elasticity in static bending," Turkish Standards Institution, Ankara, Turkey.

TS 2595 (1977). "Wood-Determination of Ultimate Stress In Compression Parallel to Grain" Turkish Standards Institution, Ankara, Turkey.

TS 4083 (1983). "Wood – Determination of radial and tangential swelling," Turkish Standards Institution, Ankara, Turkey.

TS 4084 (1983). "Wood – Determination of radial and tangential swelling," Turkish Standards Institution, Ankara, Turkey.

TS 4085 (1983). "Wood – Determination of volumetric shrinkage," Turkish Standards Institution, Ankara, Turkey.

TS 4086 (1983). "Wood – Determination of volumetric shrinkage," Turkish Standards Institution, Ankara, Turkey.

TS 4176 (1984). "Wood – Sampling sample trees and long for determination of physical and mechanical properties of wood in homogeneous stands," Turkish Standard Institution, Ankara, Turkey.

Vix-Guterl, C., Couzi, M., Dentzer, J., Trinquecoste, M. and Delhaes, P. (2004). "Surface characterizations of carbon multiwall nanotubes: Comparison between surface active sites and Raman spectroscopy," *Journal of Physical Chemistry B* 108(50), 19361-19367. DOI: 10.1021/jp047237s

Wang, Q., Wu, X., Yuan, C., Lou, Z., and Li, Y. (2020). "Effect of saturated steam heat treatment on physical and chemical properties of bamboo," *Molecules (Basel, Switzerland)* 25(8), 1999. DOI: 10.3390/molecules25081999

Wang, D., Fu, F., and Lin, L. (2022). "Molecular-level characterization of changes in the mechanical properties of wood in response to thermal treatment," *Cellulose* 29, 3131-3142. DOI: 10.1007/s10570-022-04471-3

Wei, L., McDonald, A. G., and Stark, N. M. (2015a). "Grafting of bacterial polyhydroxybutyrate (PHB) onto cellulose via in situ reactive extrusion with dicumyl peroxide," *Biomacromolecules* 16(3), 1040-1049. DOI: 10.1021/acs.biomac.5b00049

Wei, L., Stark, N. M., and McDonald, A. G. (2015b). "Interfacial improvements in biocomposites based on poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) bioplastics reinforced and grafted with α-cellulose fibers," *Green Chemistry* 17(10), 4800-4814. DOI: 10.1039/C5GC01568E

Winandy, J. E., and Lebow, P. K. (2001). "Modeling strength loss in wood by chemical composition. Part I. An individual component model for southern pine," *Wood and Fiber Science: J. Society of Wood Science and Technology* 33(2), 239-254.

Wu, Z., Deng, X., Li, L., Xi, X., Tian, M., Yu, L., and Zhang, B. (2021). "Effects of heat treatment on interfacial properties of *Pinus massoniana* wood," *Coatings* 11, article no. 543. DOI: 10.3390/coatings11050543

Yun, H., Tu, D., Li, K., Huang, J., and Ou, L. (2015). "Variation and correlation of heat-treated wood's crystalline structure and impact toughness," *BioResources* 10(1), 1487-1494. DOI: 10.15376/biores.10.1.1487-1494

Yildiz, S., Tomak, E. D., Yildiz, U. C., and Ustaomer, D. (2013). "Effect of artificial weathering on the properties of heat-treated wood," *Polymer Degradation and Stability* 98(8), 1419-1427. DOI: 10.1016/j.polymdegradstab.2013.05.004

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