

# The Effect of Cryogenic Treatment on Some Chemical, Physical, and Mechanical Properties of Thermowood® Oriental Spruce

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Effects of cryogenic treatment on the chemical, physical, and mechanical properties of oriental spruce wood, which was heat-treated with the Thermowood® method, were investigated in this work. Cryogenic treatment, which is a secondary process applied to industrially heat-treated ferrous and non-ferrous metallic materials, was applied to Thermowood® Oriental spruce wood. For this purpose, Oriental spruce wood was first heat-treated at two different temperatures (190 and 212 °C), and then both Thermowood® and control samples were cryogenically treated at -80 °C. The effects on shrinkage and swelling pressure resistance parallel to fibers, and the elemental structure were examined. The findings revealed that the improvement in shrinkage and swelling continued with heat treatment, and there was an average increase of 18 and 14.5%, respectively, in the compressive strength parallel to fibers compared with control and heat-treated samples. The FT-IR analysis showed that the wood compound structure was mostly cellulosic. The difference between the carbon-oxygen ratio in the cryogenically-treated wood decreased compared to the percentage change in the three basic elements, and the amount of hydrogen increased proportionally.

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## INTRODUCTION

To date, the effects of cryogenic treatment on the physical, mechanical, and microstructural properties of many different types of materials have been investigated, and the strength-enhancing mechanisms of this process have been explained. Although the mechanisms causing the increase in performance are not clear, it is thought that microstructural changes are the main reason for these increases. For example, the transformation of residual austenite in the microstructure into martensite after the hardening process in iron alloys and the homogeneous distribution of the precipitate phase carbides were observed in these studies (Akincioglu *et al.* 2015). Cryogenic treatment significantly increased properties such as tensile strength, yield strength, modulus of elasticity, hardness, wear, corrosion, and surface roughness in different types of steels, aluminum and magnesium alloys and super alloys. The main factors affecting this enhancement are cryogenic processing time, processing temperature, and the material.

Many businesses provide industrial cryogenic treatment services and guarantee an increase in product life. Cryogenic treatment is generally applied to metallic-based materials as a secondary heat treatment after heat treatment, hardening, and tempering processes. In practice, the cryogenic process is divided into two categories according to the

temperature: shallow (-50 to -100 °C) and deep (-100 to -196 °C). Generally, nitrogen gas is used as the cooling medium for the subzero process. Industrial laboratory deep freezers can be used for shallow cryogenic processing. In the cryogenic process, the temperature is aimed to reach the core part first, and then the samples are brought to room temperature and tested after they are kept in the environment for a designated period of time. (Akincioglu *et al.* 2015, 2016; Arslan *et al.* 2015; Uygur *et al.* 2015; Ateş *et al.* 2017; Demir and Uygur 2019).

Wood is used extensively in many industrial and engineering processes due to its advantages such as aesthetic appearance, specific strength, specific weight, easy supply, low cost, and recyclability. The usage performance of wood material mostly depends on ambient conditions, and its structural properties also affect this performance (Tascioglu *et al.* 2012; 2013). It is possible to increase the performance of wood material by using various tools and techniques. One of these tools and techniques is the application of heat treatment. In heat-treated wood material, the composition and physical properties of the cell wall have been modified through exposure to a temperature greater than 160 °C (240 to 250 °C) and to conditions with reduced oxygen availability (TS CEN/TS 15679/2010.) ThermoWood®, Plato Wood, Oil Heat Treatment, Rectification and Perdure Bois heat treatment methods, are physical modification process that causes permanent changes in the chemical structure of wood cell wall polymer. Heat treatment improves the dimensional stability of wood without completely destroying its structure of the material (Kacikova *et al.* 2020; Bytner *et al.* 2021), its ability to increase resistance to biological degradation (Shukla 2019), and allowing homogeneity and darkening in color (Johansson 2005; Torniaainen *et al.* 2021). Heat treatment, which significantly affects the physical and mechanical properties of wood (Aytin *et al.* 2015; Korkut and Aytin 2015), causes a decrease in shrinkage and swelling values and an increase in pressure and hardness resistance values parallel to fibers (Aytin *et al.* 2022). However, it causes a significant decrease in some mechanical resistance values, especially in bending and dynamic bending resistances (Özçiftçi *et al.* 2018). This is due to the increase in the proportion of carbon in the elemental structure of the wood material after heat treatment, as well as the decrease in the proportion of oxygen, leading to a change in the cell wall main component ratios and in the performance of the physico-mechanical properties (Aytin *et al.* 2022). Thus, the losses that occur in some of the mechanical resistance properties of wood material with heat treatment and the changes in the behavioral characteristics of the material under load restrict the use of the heat-treated wood if it is intended to be used for structural purposes, since adequate safety requirements may not be met (Anon. 20003; Korkut and Kocafe 2009).

It is important to tolerate (recover) the losses in mechanical resistance values that occur as a result of the effect of heat treatment in wood material and/or increase these values, as is the improvement achieved in metals using cryogenic treatment. Aytin *et al.* (2016) subjected the ThermoWood® *Populus tremula* samples to deep cryogenic treatment at -145 °C for 24 h, and then measured the compressive strength parallel to the fibers. The heat-treated samples had a 24% to 54% increase in resistance values compared with the control samples. In another study Aytin (2019) applied shallow cryogenic treatment to ThermoWood® Maple Leaf Rowan (*Sorbus torminalis*) samples at -80 °C for three different periods of time (6, 18, and 54 h) and found an increase of up to 43% in the compressive strength parallel to the fibers compared to the control samples. As in the compressive strength parallel to the fibers, the strength increases that may occur in the other resistance properties of the wood material after research and examination are

considered important in terms of allowing it to be used under higher load effects.

Although cryogenic treatment applications of metal-based materials are widespread and still attracting attention, cryogenic treatment applications of wood materials are almost non-existent. In this respect, it is still unclear what kind of changes the cryogenic process causes in the microstructural, physical, mechanical, and chemical properties of wood materials. In one of the first studies of cryogenic treatment of wood, an increase of up to 26% was observed in some mechanical resistance values of wood samples kept at  $-190\text{ }^{\circ}\text{C}$  for 24 h (Kolman 1940). In addition, the cryogenic treatment improved the permeability and drying properties of wood materials, and liquid nitrogen facilitated the transport in cell walls, enabling the impregnation materials to be transmitted more easily. Another study reported that the cryogenic process can provide high strength and long service life in wood materials (Yorur and Kayahan 2018). Ganesan and Kaliyamoorthy (2020) applied cryogenic treatment to wood-based fiber-reinforced polyester composite materials at  $-196\text{ }^{\circ}\text{C}$ , measured the residual compressive stress on the material surfaces, and found that the fiber and matrix material formed a better interface. The same study revealed that shear strength and shear modulus values increased with cryogenic treatment.

Oriental spruce is found in the coastal areas of Northeast Anatolia and the Caucasus, forming pure and mixed stands on the slopes of the mountains facing the sea and reaching 40 to 50 (m) sometimes 60 (m) heights and 1.5 to 2 (m) diameter. It is a first class forest tree with a full and smooth trunk and a pointed top. The sapwood and heartwood are indistinguishable in color, and there is mature wood with the same color as the sapwood in the inner part of the trunk, but with less water content. The summer wood in the annual ring is reddish yellow and very narrow, forming parallel stripes in the radial section. The summer wood participation rate ranges between 6 and 50%, and the most common value is 22%. Narrow and sparsely dispersed longitudinal resin channels are usually seen as light colored dots in the summer wood. The dry oriental spruce wood has an average specific gravity of  $0.416\text{ g/cm}^3$  and an air-dry specific gravity of  $0.451\text{ g/cm}^3$ . The amount of cellulose in Oriental spruce wood is 56.39%, the amount of lignin is 27.5%, the amount of holocellulose is 71.18%, the amount of ash is 0.38%, and the amount of extractive substance dissolved in alcohol-benzene is 1.72%. The compressive strength parallel to the fibers is on average  $644\text{ kg/cm}^2$ ; the bending strength is  $870\text{ kg/cm}^2$ ; the shear strength is  $150\text{ kg/cm}^2$ ; and the cleavage resistance is  $8.6\text{ kg/cm}^2$  (Çayirova 2011).

In this study, Oriental spruce wood, one of the coniferous tree species commonly used in many industrial applications, were subjected to shallow cryogenic treatment at  $-80\text{ }^{\circ}\text{C}$  for three different periods of 36, 72, and 144 h after heat treatment with the ThermoWood<sup>®</sup> method. The physical, mechanical and chemical properties such as shrinkage, swelling, full and air-dry density, pressure resistance parallel to the fibers, FTIR, and elemental structure were examined, and the effect of shallow cryogenic treatment on heat-treated wood material was evaluated.

## EXPERIMENTAL

### Materials

Oriental spruce (*Picea orientalis*) tree, which grows naturally in Turkey, was used in the study. The selection of the working trees was based on TS 4176/1984, and the trunks taken from the forest were cut into 60 mm thick planks (TS 2470/1976). Then, the planks were dried to an average of 12% result humidity with the classical drying method, and

20x100x500 (mm x mm x mm) wood samples were prepared from the planks.

### Heat Treatment (HT), Shallow Cryogenic Treatment (SCT), and the Development of the Working Pattern

Wood samples prepared from working trees were subjected to HT together with air-dried wood materials in the factory of Nova Forest Products Inc. in Gerede/Bolu, and ThermoWood® Oriental spruce was produced. The heat treatment of the samples was carried out at 190 and 212 °C and 1 h, which is the most preferred in commercial enterprises. After, samples with nominal dimensions of 20 x 20 x 300 (mm x mm x mm) were prepared from ThermoWood® templates, and SCT was applied together with the control sample (CD). Shallow cryogenics was applied to the samples in a specially manufactured deep freezer.

Core DF 490 type deep freezer with 611 L capacity and 1°C temperature sensitivity without icing was used in the shallow cryogenic process. N-SmArt™ control system, which can store temperature data numerically and graphically for ten years with one-hour recording intervals, is used in the Core DF 490 type deep freezer (Anon. 2022) and the device can be cooled down to -86 °C. After all the samples were placed in separate compartments, a 12-hour pre-waiting was performed to allow the ambient temperature to reach -80 °C. The samples to cooled over the entire section, and then SCT was started. At this stage, the samples were kept at -80 °C for 36, 72, and 144 h. The study samples and the trial design are given in Table 1.

**Table 1.** Classification of Working Samples and Abbreviations

Control and HT* Variations	Abbreviation	Number of groups	Number of samples	Shallow Cryogenic Treatment (SCT)	
				Time (hour)	Abbreviation
Natural	CD	6	5	36	SCT <sub>1</sub>
190 °C, 1 hour	TW <sub>1</sub>	6	5	72	SCT <sub>2</sub>
212 °C, 1 hour	TW <sub>2</sub>	6	5	144	SCT <sub>3</sub>

\* One group of control and heat treatment variants were used for control purposes without undergoing shallow cryogenic treatment and were expressed as control samples (CD) within the study.

### Determining Shrinkage ( $\beta$ ) and Swelling ( $\alpha$ ) Values

The standards TS 4083 (1984), TS 4085 (1983), TS 4084 (1984), and TS 4086 (1983) were used to determine the amount of shrinkage and swelling. The number of samples used for each variation in the study was determined according to TS CEN/TS standard 15679/2010 (Aytin *et al.* 2019).

### Determining Compressive Strength Parallel to Fibers (CS)

The CS was determined according to the principles of TS standard 2595 (1977). A total of 45 test samples were prepared, 15 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  $\pm 0.01$  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 CS was calculated using Eq. 1,

$$\sigma_w \text{ (N/mm}^2\text{)} = F_{\max} / A \quad (1)$$

where  $\sigma_w$  is the compressive strength (N/mm<sup>2</sup>),  $F_{\max}$  is the maximum force at break (N), and  $A$  is the cross-sectional area of the sample (mm<sup>2</sup>).

### Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Fourier transform infrared (FTIR) spectroscopy was recorded with an ATR 189 Attached Shimadzu IR Prestige 21 spectrometer. The spectrum analysis was performed between 400 nm and 4000 nm, with 64 scans. The ATR Attached Shimadzu IR Prestige 21 spectrometer is shown in Fig. 2 (Aytin *et al.* 2022).

### 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 200 CHNS and oxygen in any sample (Aytin *et al.* 2022)

### Statistical Evaluation

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



Fig. 1. The ATR Attached Shimadzu IR Prestige 21 spectrometer

## RESULTS AND DISCUSSION

### Shrinkage and Swelling

The results for the multiple analysis of variance (MAV) of the shrinkage and swelling values determined after SCT are presented in Table 2.

**Table 2.** MAV Results for Shrinkage and Swelling Values Determined after SCT

Factor (F)	$\beta$ - $\alpha$	Fiber Dimension	Sum of Squares	df	Mean of Squares	F value	Significant	Partial Eta Squared
SCT	$\beta$	t	32.451	11	2.950	3.291	0.002	0.430
		r	38.626	11	3.511	4.189	0.000	0.490
		V	211.928	11	19.266	12.183	0.000	0.736
	$\alpha$	t	35.763	11	3.251	2.090	0.039	0.324
		r	76.979	11	6.998	6.110	0.000	0.583
		V	192.163	11	17.469	8.496	0.000	0.661

The MAV results between the volumetric  $\beta$  and  $\alpha$  values determined as % after SCT revealed that there were significant differences at  $p \leq 0.05$  significance level. In order to better understand the differences, the mean values of the volumetric  $\beta$  and  $\alpha$  values determined according to the SCT variations after SCT (in %) and the Duncan test results are given in Table 3.

SCT had an effect on dimensional stability. According to the cryogenic processing times, the smallest  $\beta_v$  and  $\alpha_v$  mean values (6.258 and 8.200, respectively) were obtained in TW<sub>2</sub>, SCT<sub>2</sub>, and SCT<sub>3</sub> variations. These values show that there was a decrease of 26.8% and 18.4% in  $\beta$  and  $\alpha$ , respectively, in the shallow cryogenically untreated TW<sub>2</sub> value. It is understood that after SCT, the amounts of both SCT- $\beta_v$  and SCT- $\alpha_v$  decreased in different amounts depending on the SCT times compared to CD (excluding CD shrinkage).

**Table 3.** Volumetric  $\beta$  (SCT- $\beta_v$ ) and  $\alpha$  (SCT- $\alpha_v$ ) Mean Values after SCT (in %) and Duncan Test Results

SCT- $\beta_v$			SCT- $\alpha_v$		
F	M	HG	F	M	HG
TW <sub>2</sub> SCT <sub>2</sub>	6.258	a	TW <sub>2</sub> SCT <sub>3</sub>	8.200	a
TW <sub>2</sub> SCT <sub>3</sub>	8.514	b	TW <sub>2</sub> SCT <sub>2</sub>	9.176	ab
TW <sub>2</sub>	8.552	b	TW <sub>2</sub> SCT <sub>1</sub>	9.302	ab
TW <sub>1</sub> SCT <sub>2</sub>	8.836	b	TW <sub>1</sub> SCT <sub>1</sub>	9.345	ab
TW <sub>1</sub> SCT <sub>1</sub>	9.217	b	TW <sub>1</sub> SCT <sub>2</sub>	9.352	ab
TW <sub>2</sub> SCT <sub>1</sub>	9.261	b	TW <sub>1</sub> SCT <sub>3</sub>	9.435	ab
TW <sub>1</sub> SCT <sub>3</sub>	9.397	b	TW <sub>2</sub>	10.054	ab
TW <sub>1</sub>	10.118	bc	TW <sub>1</sub>	10.608	b
CD SCT <sub>2</sub>	11.580	cd	CD SCT <sub>2</sub>	11.156	b
CD SCT <sub>3</sub>	11.786	cd	CD SCT <sub>3</sub>	13.136	bc
CD	12.609	d	CD SCT <sub>1</sub>	13.292	bc
CD SCT <sub>1</sub>	12.961	d	CD	13.793	bc

The results revealed that the improvement in dimensional stability with HT was maintained with SCT, and even the improvement in dimensional stability continues with SCT. There are almost no scientific studies in the literature investigating the effect of cryogenic treatment on dimensional change in wood material, and there is no study on dimensional stability change after cryogenic treatment in heat-treated wood materials.

Therefore, in order to understand the importance of the results of the study, it is necessary to consider the results of the study on dimensional change in heat-treated tree species.

In the study of Çaliova (2011),  $\beta_v$  amounts in oriental spruce are given as 10.00% in control samples, 7.97% in 190°C Thermowood® samples, and 5.19% in 212°C Thermowood® samples. Bozkurt *et al.* (1993) found the  $\beta_v$  amounts of spruce species to be 10.2% in *Picea orientalis* (planting-Turkey), 11.5% in *Picea orientalis* (natural-Turkey), 11.8% in *Picea abies* (planting-Norway), and 11.8% in *Picea abies* (natural-Norway). In both studies on various spruce trees, we see that the dimensional stability values were higher than the values obtained in the present study.

### Compressive Strength Parallel to Fibers

The mean values for CS determined after SCT and the results of the simple analysis of variance (SAV) are given in Table 4.

**Table 4.** Mean Values for CS to Fibers after SCT and SAV Results

Factor	Relationship	Sum of squares	df	Mean of squares	F	Sig.
SCT	Intergroup	539.031	11	49.003	1.403	0.203
	Intragroup	1676.737	48	34.932		
	Total	2215.768	59			

The SAV results following SCT showed that there were significant differences between the CS at  $p \leq 0.05$  significance level. To clarify the differences, the mean values for CS calculated according to the SCT variations after SCT and the Duncan test results are given in Table 5. The highest CS was obtained in TW<sub>2</sub> SCT<sub>2</sub> as 59.8 N/mm<sup>2</sup>, and the lowest was obtained in CS as 50.3 N/mm<sup>2</sup>.

**Table 5.** The Mean CS Values for CD and HT Determined after SCT (N/mm<sup>2</sup>) and Duncan Test Results

F	HG	
	a	b
CD	50.306	
TW <sub>2</sub>	52.174	52.174
TW <sub>1</sub>	52.862	52.862
TW <sub>1</sub> SCT <sub>1</sub>	55.908	55.908
CD SCT <sub>1</sub>	56.449	56.449
TW <sub>1</sub> SCT <sub>3</sub>	56.896	56.896
TW <sub>2</sub> SCT <sub>3</sub>	57.059	57.059
CD SCT <sub>2</sub>	58.816	58.816
CD SCT <sub>3</sub>	58.842	58.842
TW <sub>2</sub> SCT <sub>1</sub>	58.929	58.929
TW <sub>1</sub> SCT <sub>2</sub>		59.474
TW <sub>2</sub> SCT <sub>2</sub>		59.829
Sig.	0.056	0.092

The results also show that the values for CS obtained in all SCT-treated variations are higher than the values determined in both natural and heat-treated (TW<sub>1</sub> and TW<sub>2</sub>) but not cryogenically treated samples. Çaliova (2011) reported the amount of CS in Oriental spruce as 37.0% in control samples, as 42.9% in 190 °C Thermowood® samples, and as 44.7% in 212 °C Thermowood® samples. These values are approximately 24% lower than the values we obtained after SCT. Bozkurt *et al.* (1993) found the CS value as 28.2 N/mm<sup>2</sup>.

## Fourier Transform Infrared (FTIR) Spectroscopy Analysis

### FT-IR results after SCT<sub>1</sub>

The FT-IR results of control samples and HT samples after SCT<sub>1</sub> are given in Fig. 2. According to the FT-IR results for the SCT<sub>1</sub> variation samples after SCT, the change in the state of carbohydrates and lignins from the characteristic structure peaks of the tree at 1670 and 590 cm<sup>-1</sup> is shown in Fig. 2. The cellulose structure started to change in heat-treated oriental spruce wood samples because there was a change in the formation of the peaks at 810, 1029, and 1157 cm<sup>-1</sup>, which are the primary lignin peaks. In addition, it is seen that the intensity of the peaks observed at 1032 and 2920 cm<sup>-1</sup> wavelengths belonging to hemicellulose decreased, and the alpha cellulose structure showed a low level of transmittance.

To better understand the change in carbohydrate and lignin structure, elemental analysis was performed and chemical bond structure was examined after SCT, and the bond and element structure of the SCT<sub>1</sub> variation is given in Table 6.

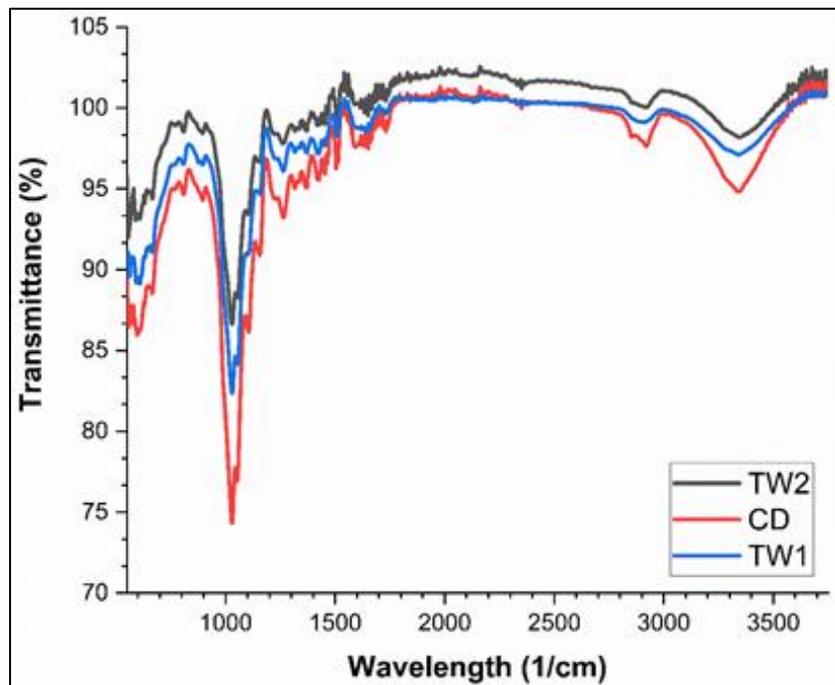


Fig. 2. FT-IR results of control and HT samples after SCT<sub>1</sub>

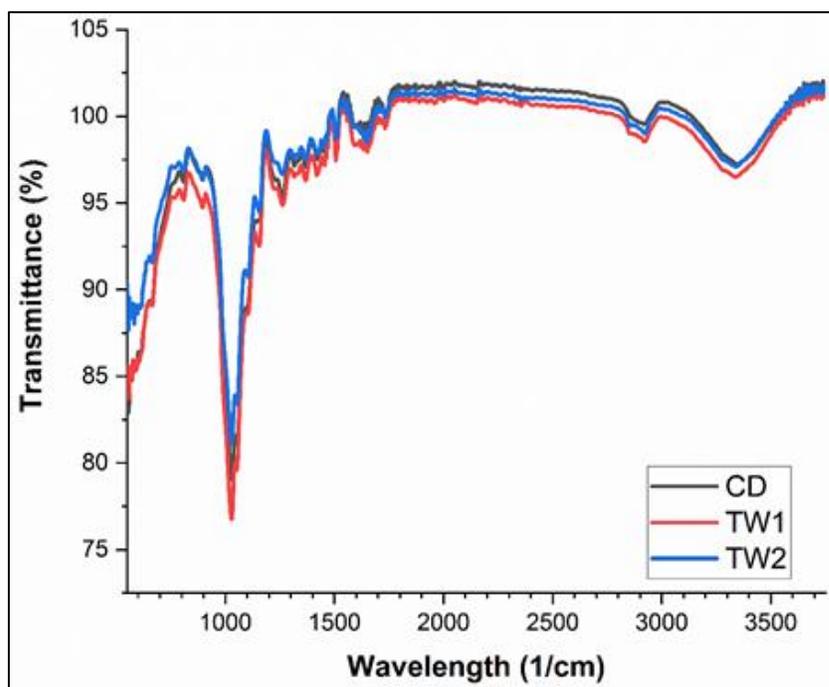
**Table 6.** Change in Bond and Element Structure after SCT<sub>1</sub>

Frequency (cm <sup>-1</sup> )	Functional Group	Elemental Analysis (%)*				
			N	C	H	O
810	β-glycosidic bonds, C-H cellulose deformation					
1029	Aromatic C-H deformation, C-O deformation	CD	0.08	45.32	6.09	48.51
1157	Vibration in C-O-C Cellulose and Hemicellulose	TW <sub>1</sub>	0.20	47.86	6.42	45.52
1269	C= resistance and syringyl ring in lignin and xylan	TW <sub>2</sub>	0.10	48.66	6.15	45.09
1367	C-O vibration in syringyl derivatives and C-H vibration					
1429	Aromatic ring vibration combined with CH in	**CD	0,03	46,11	6,00	47,87
1456	CH- deformation, asymmetric in CH <sub>2</sub> and CH <sub>3</sub>	TW <sub>1</sub>	0,04	47,06	5,99	46,91
1506	Aromatic ring vibration, plus C=O tension	TW <sub>2</sub>	0,65	49,50	6,21	43,63
1670	C=O tension in unconjugated ketone, carbonyl, and					

Note: \*N: nitrogen; C: carbon; H: hydrogen; and O: oxygen, \*\* Elemental analysis values of oriental spruce control and heat-treated samples (Aytin *et al.* 2022)

*FT-IR results after SCT<sub>2</sub>*

The FT-IR results of control samples and HT samples after SCT<sub>1</sub> are given in Fig. 3. When the spectrum of characteristic peaks of SCT<sub>2</sub> variation samples after SCT is examined, it is apparent that the formation of peaks increased at 1159 cm<sup>-1</sup>, 1029cm<sup>-1</sup>, and 888 cm<sup>-1</sup>, which are the main peaks of lignin.

**Fig. 3.** FT-IR results of control and HT samples after SCT<sub>2</sub>

According to the spectrum, as the heat treatment temperature increases, it is the cellulose bonds begin to break compared to normal wood. In addition, it is observable that the peaks at 1026 cm<sup>-1</sup> and 2926 cm<sup>-1</sup> are representative of hemicellulose, the intensity of

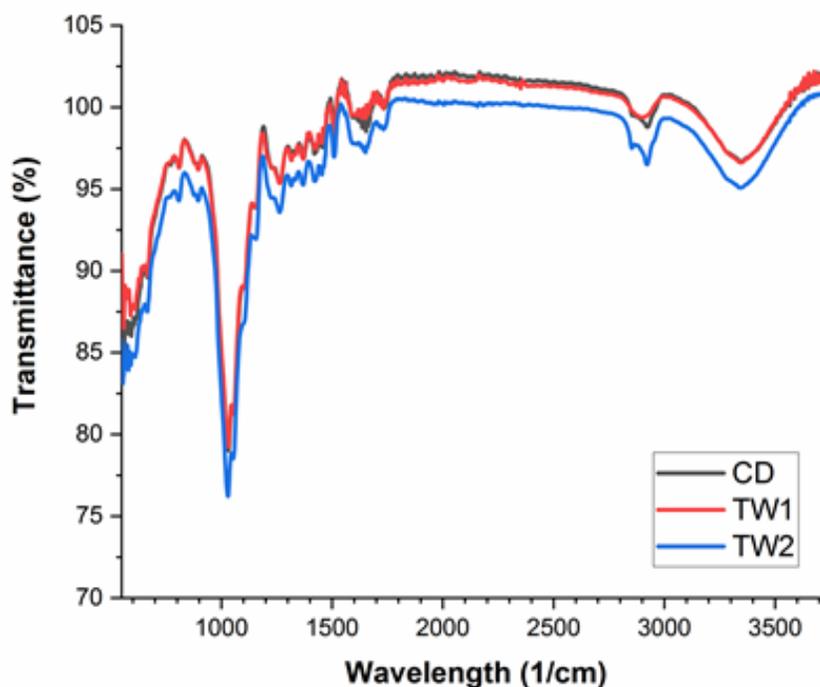
the peaks at TW<sub>2</sub> decreased compared to TW<sub>1</sub>, while the intensity of the peaks and alpha cellulose amount of the structure increased with heat treatment (starting from 190 °C). The bond and element structure of the SCT<sub>2</sub> variation is given in Table 7.

**Table 7.** Change in Bond and Element Structure after SCT<sub>2</sub>

Frequency (cm <sup>-1</sup> )	Functional Group	Elemental Analysis (%)				
		N	C	H	O	
888	β-glycosidic bonds, C-H cellulose deformation					
1026	Aromatic C-H deformation, C-O deformation	CD	0.05	44.99	6.15	48.81
1159	Vibration in C-O-C Cellulose and Hemicellulose	TW <sub>1</sub>	0.18	47.75	6.72	45.35
1273	C= resistance and syringyl ring in lignin and xylan	TW <sub>2</sub>	0.12	48.21	6.36	45.31
1367	C-O vibration in syringyl derivatives and C-H vibration					
1415	Aromatic ring vibration combined with CH in					
1456	CH- deformation, asymmetric in CH <sub>2</sub> and CH <sub>3</sub>					
1506	Aromatic ring vibration, plus C=O tension					
1635	C=O tension in unconjugated ketone, carbonyl, and					

#### FT-IR results after SCT<sub>3</sub>

The FT-IR results of control samples and HT samples after SCT<sub>3</sub> are given in Fig. 4. The FT-IR results for the SCT<sub>3</sub> variation samples after SCT revealed that based on the spectrum of the wood structure, TW<sub>1</sub> and TW<sub>2</sub> cellulose structures of the samples exhibited degradation at the lignin peaks of 1128, 1029, and 894 cm<sup>-1</sup>. However, the peaks at 1029 and 2912 cm<sup>-1</sup> are characteristic peaks showing hemicellulose.



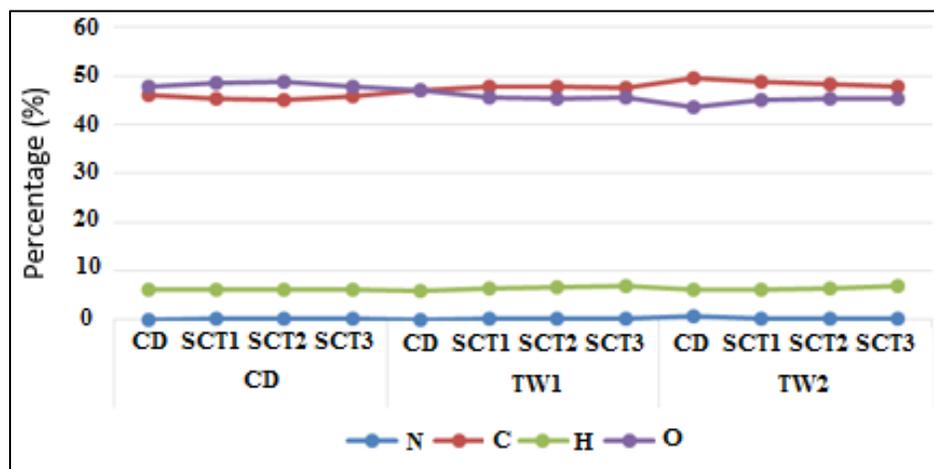
**Fig. 4.** FT-IR results of control samples and HT samples after SCT<sub>3</sub>

Based on the spectrum, the intensity of the peaks decreased in TW<sub>1</sub> and TW<sub>2</sub>, and the structure tried to transform into a cellulose structure. The bond and element structure of the SCT<sub>3</sub> variation is presented in Table 8.

**Table 8.** Change in Bond and Element Structure after SCT<sub>3</sub>

Frequency (cm <sup>-1</sup> )	Functional Group	Elemental Analysis (%)				
		N	C	H	O	
894	β-glycosidic bonds, C-H cellulose deformation					
1033	Aromatic C-H deformation, C-O deformation	CD	0.09	45.82	6.23	47.86
1128	Vibration in C-O-C Cellulose and Hemicellulose	TW <sub>1</sub>	0.09	47.62	6.86	45.43
1251	C= resistance and syringyl ring in lignin and xylan	TW <sub>2</sub>	0.11	47.81	6.86	45.22
1365	C-O vibration in syringyl derivatives and C-H vibration in					
1423	Aromatic ring vibration combined with CH in deformation					
1454	CH- deformation, asymmetric in CH <sub>2</sub> and CH <sub>3</sub>					
1514	Aromatic ring vibration, plus C=O tension					
1654	C=O tension in unconjugated ketone, carbonyl, and					

There are many studies on the effects of heat treatment on tree material and on the changes in the chemical structure of wood (Výbohová *et al.* 2018; Kučerová *et al.* 2019; Nge *et al.* 2020). However, the application of cryogenic processing in tree material is a recent application. For this reason, it is not possible to have a well-informed debate and evaluation on the chemical structure changes in natural wood materials, wood materials to which heat treatment was applied, and wood materials to which cryogenical treatment was applied after heat treatment. However, findings on the element structure of the samples that have been applied cryogenic treatment and findings on the element structure of another group of the same samples are important in terms of giving an idea to the readers, albeit limited. The element structure for oriental spruce after natural, heat treatment and cryogenic treatment processes is given in Fig. 5.



**Fig. 5.** The change in the element structure of oriental spruce in percentage with thermal processing and cryogenic process

## CONCLUSIONS

1. Following SCT, Thermowood® oriental spruce shrinkage and swelling values were generally lower than those of the control samples, and SCT was found to have a positive effect on dimensional stability.
2. Considering the values for compressive strength parallel to fibers, it can be stated that an increase up to 14% has been recorded in all groups that were subjected to SCT compared to those that were not subjected to SCT. Changes are observed in the chemical bond structure of the samples after SCT, and the amount of cellulose in the structure increases in % and the structure is transformed into a cellulose structure. It can be stated that the increase in cellulose has a positive effect on the increase in compressive strength parallel to fibers.
3. The chemical structure of the wood is generally transformed into a cellulose structure after heat treatment. The increase in cellulose structure with both thermal and subsequent SCT is scientifically, technically, and industrially important.
4. Significant changes occur in the element structure of oriental spruce wood which is heat treated after SCT. It is seen that the amount of oxygen and hydrogen increases in the structure, whereas the amount of carbon decreases.

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