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EFFECTS OF HEAT TREATMENT ON SOME CHEMICAL COMPOUND AND MECHANICAL PROPERTIES OF BLACK PINE WOOD

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ABSTRACT

In this study, effects of heat treatment on bending strength, compression strength, chemical compound and solubility of Black pine wood (*Pinus nigra* J.F. var. seneriana) was examined. For this purpose, Black pine wood samples were kept in temperature of 250°C for 2 hours. Test results of heat-treated Black pine wood and control samples indicated that mechanical characteristics including compression strength and bending strength were affected negatively with heat treatment. Bending strength of heat treated and non-treated test samples were 129 and 76 $N \cdot mm^{-2}$, respectively. Compression strength of heat treated and non-treated test samples were 53 and 43 $N \cdot mm^{-2}$, resp. In addition, level of extractives, cellulose and hemicellulose decreased while lignin content increased with percentage of 40%. Significant decreases occurred in all chemical solubility values.

KEYWORDS: Bending strength, heat treatment, Anatolian black pine, compression strength, lignin, cellulose, hemicellulose.

INTRODUCTION

In the heat treatment application, temperature generally varies depending on type of wood material, dimensions, initial moisture percentage, material expectation, mechanical characteristics, dimensional stability and resistance to biotic and abiotic attacks. Temperature generally varies between 180ºC and 280ºC, while heat treatment time is applied between 15 min and 24 hours (Kamdem et al. 2002).

Today, heat treatment is applied in many countries in Europe under different commercial brands and performed with different methods. Some of these methods include the Finnish process (Heat treatment) method using steam for heating wood material, Plato method with

Dutch steam and hot air, French method using an inert gas (Rectification), and German (OHT) method using hot oil (Mayes and Oksanen 2002).

Rozsa and Fortes (1989) investigated the effect of heat treatment on pressure resistance of *Quercus suber* wood heat-treated at 100°C and 300°C. The study stated that resistance losses were higher in samples under heat treatment in a water vapor environment at 300°C than in the control samples due to thermal decomposition of wood material under heat. Viitaniemi (1997) investigated the bending strength of pine wood subjected to heat treatment under water vapor protection at 180°C to 250°C. As a result, there were losses of bending resistance at certain rates compared to control samples under the heat treatment,

It was specified that there was a decrease in elasticity modulus in bending, especially at 150°C above in both tree species in experimental investigations of pine and beech sapwood exposed to heat treatment at different temperatures and periods. However, pressure resistance is slightly affected, while shock resistance is more affected (Schneider 1971). Impacts of heat treatment on resistance characteristics of Eucalyptus (*Eucalyptus saligna*) wood were investigated (Vital and Lucia 1983). The samples were heat-treated at 105°C to 155°C for 10 to 160 hours. The experiment with increasing temperature and time reported a significant decrease in bending resistance, modulus of elasticity in bending, pressure, and shear resistance parallel to fibers. Modification and degradation of hemicellulose are primarily responsible for initial losses in bending strength, not degradation or depolymerization of lignin and cellulose during heat treatment. The bending resistance is reduced more considering heat treatment time and temperature. It was stated that the load sharing capacity of hemicellulose in the lignin-hemicellulose matrix is broken, causing loss of resistance. Another reason is a decrease in the degree of hemicellulose polymerization due to disruption of the spine of hemicellulose (LeVan et al. 1990). Degradation of hemicelluloses results in cross-linking reactions between components of the material, crystallization of microfibrils, and a reduction in the accumulation of tension in microfibrils (Dwianto et al. 1996). It was reported that bending resistance decreases between 4% and 49% depending on different wood species and heat treatment conditions (Esteves et al. 2007, Shi et al. 2007). Changes in pressure value are related to the method and application parameters of heat treatment and chemical structure that change. It has more lignin ratio and less acid number in heat-treated wood species than the normal material has, which indicates that hemicelluloses and some extractives are degraded (Nuopponen et al. 2005). Hemicellulose, which constitutes the structure of wood material, changes at 180°C, lignin at 200°C, and cellulose at 210°C leading to the start of decomposition. As seen here, the first deteriorating structure in wood material is followed by hemicellulose containing acetyl group, followed by lignin, and finally cellulose structure (Jeske et al. 2012, Ndiaye and Tidjani 2012, Tufan et al. 2015).

The aim of this study is to examine the effects of heat treatment on bending strength, compression strength, chemical compositions, and solubility of black pine (*Pinus nigra* J.F. var. seneriana) wood.

MATERIAL AND METHODS

Samples of Anatolian Black pine used in this study were obtained from Domanic Forest Management Directorate Ala Goz Forest Management Department of Kutahya, in 104 sections, in the north of Karakiran hill at 1025 m altitude. In the bending strength tests, TS 2474 (1976) rules were followed. The following equations were used to calculate bending strength (σ_e):

$$\sigma_e = \frac{3 \cdot F_{max} \cdot L}{2 \cdot b \cdot h^2} \quad (N \cdot mm^{-2}) \qquad (1)$$

where: σ_e is bending strength ($N \cdot mm^{-2}$), b is the width of sample piece (mm), h is the thickness of sample piece (mm), F_{max} is the maximum force at breaking point (N), and L is the distance between supports (mm).

Compression strength tests were carried out according to TS 2595 (1976) standards. The following equations were used to calculate compression strength parallel to grain ($\sigma_{c//}$):

$$\sigma_{c//} = \frac{F_{max}}{b \cdot h} \quad (N \cdot mm^{-2}) \qquad (2)$$

where: F_{max} is the maximum force at breaking point (N), b is the width of sample (mm), h is the thickness of the sample (mm).

Air-dried Black pine chips were ground to 60 mesh fractions using a mill and were chosen to determine chemical components in accordance with relevant TAPPI Standard methods. Humidity, lignin, ashes, and α-cellulose values were determined using the standards Tappi T 264 om-88, Tappi T 222 om-88, Tappi T 211 om-85, and Tappi T 203 os-71, respectively. Solubility in NaOH 1% and water was determined using Tappi T 207 om-88, resp. Cellulose and holocellulose contents were determined according to Kurschner Hoffer nitric acid and Wise's chlorite methods, respectively (Browning 1967, Wise and Karl 1962, Kurschner and Hoffer 1993). Based on the methods listed above, three replicates were performed for each experiment. Chemical analyzes were carried out in Forest Products Chemical and Technology Laboratory, Kahramanmaras University, Forest Industry Engineering Department. Black pine wood was used in all sample experimental studies. Black pine wood samples used in this study were kept at 250°C for 2 hours.

RESULTS AND DISCUSSION

Chemical and mechanical tests were performed on wood samples of black pine (*Pinus nigra* ssp. Pallasiana var. seneriana) before and after heat treatment. The findings are given below.

Bending strength results

The bending strength data for heat treated and non-treated pine wood were given in Tab. 1 (Akman et al. 2018). When the data in Tab. 1 are analyzed, it can be easily seen that heat treatment affected the bending strength of the wood. The percentage of the bending strength decreased approximately by 41%. In previous studies, some researchers reported that heat treatment affects the mechanical properties of the wood. For example, Esteves et al. (2014) investigated sapwood and heartwood samples of *Pinus pinaster* treated at 190 and 200ºC and reported the decreased bending strength by 50 and 30% for sapwood and heartwood, respectively. Similar results on bending strength were reported by Bekhta and Niemz (2003) related to spruce wood treated at high temperatures. Bal (2014) reported that heat treatment had lower effects on the mechanical properties such as modulus of rupture, modulus of elasticity, and IB of juvenile wood than of mature wood. Xie et al. (2020) determined similar results about reducing the bending strength of the heat-treated *Toona sinensis* wood.

Tab. 1: Bending strength results ($N \cdot mm^{-2}$).

Samples	**Bending strength results**	
	Non-treatment	**Heat treatment (**250°C, 2 hours)
1	165.22	100.28
2	142.62	71.71
3	174.70	83.40
4	107.15	69.24
5	116.88	76.45
6	98.81	65.15
7	108.33	62.11
8	69.91	82.00
9	150.86	81.09
10	163.50	72.65
Average	129.80	76.41
Standard deviation	34.48	11.01

Heat treatment negatively affected the bending strength properties of Anatolian black pine wood. The interaction between these obtained values was examined with variance analysis, and obtained results are given in Tab. 2.

Tab. 2: Variance analysis results of bending strength.

Variance source	**Df**	**Sum of squares**	**Mean squares**	**F test**	**P**
Heat treatment	1	14252.461	142461.461	21.754	0.000
Error	18	11792.958	655.164		
Corrected total	19	26045.418			

According to the results of the conducted variance analysis, the effects of heat treatment on the bending strength of black pine wood were found significant with a 5% of error.

Compression strength results

Test results of compression strength are given in Tab. 3. When the data in Tab. 3 are analyzed, it can be shown that heat treatment affect the compression strength of pine wood.

The compression strength of heat treated samples is greater than that of non-treated samples. Similar results were obtained in previous studies conducted by some researchers. For example, Yıldız et al. (2006) reported the decreases of compression strength of spruce wood treated with four different temperatures. Bal and Bektaş (2013) noted that compression strength of juvenile and mature wood of *Eucalyptus grandis* decreased in different proportions. Xie et al. (2020) determined compressive strength decreased by 33.84% at the temperature 220ºC compared to control samples. But, conversely, Some researchers reported that heat treatment increased the compression strength of the heat treated wood (Kol 2010, Perçin et al. 2016).

Tab. 3: Compression strength results ($N \cdot mm^{-2}$) (Akman et al. 2018).

Samples	**Compression strength results**	
	Non-treatment	**Heat treatment** (250°C, 2 hours)
1	52.68	36.06
2	42.14	46.57
3	56.95	47.36
4	55.85	42.20
5	56.61	47.44
6	62.92	46.02
7	56.56	38.78
8	54.17	42.26
9	58.23	41.38
10	54.24	49.21
11	57.05	37.05
12	48.64	47.70
13	57.60	34.06
14	39.63	50.68
15	55.08	48.91
Average	53.89	43.71
Standard deviation	6.12	5.30

Heat treatment negatively affected the compression strength properties of black pine wood. The interaction between these obtained values was examined with variance analysis, and the obtained results are given in Tab. 4.

Tab. 4: Variance analysis results of compression strength.

Variance source	**Df**	**Sum of squares**	**Mean squares**	**F test**	**P**
Heat treatment	1	776.938	776.938	23.734	0.000
Error	28	916.571	32.735		
Corrected total	29	1693.509			

According to the results of variance analysis conducted, effects of heat treatment on compression strength of black pine wood were found significant with 5% of error.

Chemical compositions results

Values of chemical composition results for black pine wood are given in Tab. 5. The amount of extractive agent after heat treatment decreased more than that of the holocellulose and cellulose. Since gelling occurs during heat treatment, alpha-cellulose

content could not be measured after heat treatment. After heat treatment, a decrease in ash value was also observed. The amount of lignin increased after heat treatment. Extractive, holocellulose, cellulose, and ash amount decreased after heat treatment in different proportions. Conversely, lignin content increased after heat treatment. Similar results were reported in previous studies on chemical compositions of heat-treated wood (Yıldız et al. 2006, Brito et al. 2008, Xie et al. 2020).

Tab. 5: The chemical compositions of black pine (Akyurek 2019).

Chemical compositions	**Standards**	**Non-treatment**	**Heat treatment** (250°C, 2 hours)
Extractives (%)	ASTM D1107-96	8.71 ± 0.35	0.61 ± 0.1
Holocellulose (%)	Wise et al. (1946)	64.67 ± 0.36	51.76 ± 0.23
Cellulose (%)	Kurschner and Hoffer (1993)	48.27 ± 1.61	39.35 ± 1.39
Alfa Cellulose (%)	TAPPI T203 om-93	40.10 ± 0.24	*
Lignin (%)	TAPPI T222 om-98	34.32 ± 0.82	48.21 ± 0.03
Ash (%)	TAPPI T211 om-02	0.60 ± 0.07	0.33 ± 0.06

± - standard deviation, *- alpha cellulose content could not be determined because gelling occurred during determination of alpha cellulose of heat-treated wood sample.

Chemical solubility results

The values of chemical solubility results for black pine wood are given in Tab. 6 (Akyurek 2019). After heat treatment, solubility values significantly decreased. Chemical solubility and compositions of some pine wood species are given in Tab. 7.

Tab. 6: The chemical solubility of black pine.

Chemical solubility	**Standards**	**Non-treatment**	**Heat treatment** (250°C, 2 hours)
% 1’ NaOH (%)	TAPPI T212 om-02	19.75 ± 0.55	1.66 ± 0.07
Hot water (%)	TAPPI T207 om-93	8.68 ± 0.26	2.12 ± 0.07
Cold water (%)	TAPPI T207 om-93	7.42 ± 0.24	0.94 ± 0.12

Tab. 7: Chemical solubility and of components some type of tree.

		Pinus brutia Gultekin (2014)	***Pinus sylvestris*** Gultekin (2014)	***Pinus nigra*** Kılıc et al. (2010)
Chemical components	**Holocellulose (%)**	74.7	75.4	-
	Cellulose (%)	53.7	56.0	-
	Extractives (%)	-	-	-
	Lignin (%)	25.1	26.1	-
	Ash (%)	0.39	0.27	0.19
	Alfa cellulose (%)	70.5	69.7	50.41
Solubility	**1% NaOH (%)**	15.0	10.8	12.76
	Hot water (%)	5.09	5.3	4.18
	Cold water (%)	3.39	1.97	2.11

CONCLUSIONS

After heat treatment of Black pinewood material, decreases in bending resistance and compressive strength values were observed in proportion to temperature and time. Bending

resistance decreased more than the pressure resistance. This may be due to greater and earlier degradation of cellulose than those of lignin.

After chemical analysis of cell wall components of black pine, it was found that the amount of extractive material was 8.71% without heat treatment and 0.61% with heat treatment. The amount of holocellulose was 64.67% without heat treatment and 51.76% with heat treatment. The amount of cellulose was 48.27% without heat treatment and 39.35% with heat treatment. The amount of alpha-cellulose was 40.10% without heat treatment. The amount of lignin was 34.32% without heat treatment and 48.21% with heat treatment; the amount of ash was 0.60% without heat treatment and 0.33% with heat treatment. Although alpha-cellulose was measured as 40.1% without heat treatment, the value after heat treatment could not be measured due to gelling. An increase in the amount of lignin may be due to faster and earlier degradation of other components. The reason is that lignin appears to be proportionally high due to later degradation rather than an increase.

After chemical analyses of solubility values of black pine, it was detected that 1% NaOH solubility was 19.75% without heat treatment and 1.66% with heat treatment. Hot water solubility was 8.68% without heat treatment and 2.12% heat treatment. Cold water solubility was 7.42% without heat treatment and 0.94% without heat treatment. Significant reductions occurred in all solubility values after heat treatment.

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