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Changes in hardness values of Scotch Pine (*Pinus sylvestris* L.) heat treated with tannin modification under different climatic conditions

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Abstract
It is known that wood undergoes dimensional changes due to its hygroscopic properties. At the same time, various methods such as impregnation and heat treatment modification are applied to protect wood against biological pests. These methods also have strengths and weaknesses compared to each other. It is known that the mechanical properties of wood materials subjected to thermal modification generally decrease. The most important factors causing this decrease in mechanical properties are; wood type, exposure temperature and duration. As the heat treatment temperature and exposure time increases, the mechanical properties of wood decrease. In this study, in order to reduce the degrading effect of heat treatment and increase mechanical resistance, Scots pine samples were impregnated with 10% acorn tannin solution and then subjected to heat treatment at 150°C for 2 hours. After the samples were conditioned in the climatic conditions of 20°C and 65% relative humidity, 40°C and 35% relative humidity and 10°C and 50% relative humidity, density, equilibrium moisture and Brinell hardness values were determined. There was a 20% increase in the hardness values of the tannin-modified samples conditioned at 40°C and 35% relative humidity.

Keywords: *Heat treatment, acorn tannin, Brinell hardness, climate, Scotch pine.*

Tanen modifiyesi ile ısıl işlem uygulanmış Sarıçam'ın (*Pinus sylvestris* L.) farklı iklim şartlarında sertlik değerlerindeki değişimler

Özet
Ahşabın higroskopik özelliği nedeni ile boyutsal değişikliğe uğradığı bilinmektedir. Aynı zamanda ahşabı biyolojik zararlılara karşı korumak için emprenye ve ısıl işlem modifikasyonu gibi çeşitli yöntemler uygulanmaktadır. Bu yöntemlerin birbirlerine göre güçlü ve zayıf özellikleri de bulunmaktadır. Termal modifikasyon uygulanan ahşap malzemede mekanik özelliklerin genel olarak düşüş gösterdiği bilinmektedir. Mekanik özelliklerdeki bu düşüşe neden olan en önemli etkenler; ağaç türü, maruz kalma sıcaklığı ve süresidir. Isıl işlem sıcaklığı ve maruz kalma süresi arttıkça ahşabın mekanik özellikleri azalmaktadır. Bu çalışmada, ısıl işlemin bozundurucu etkisini azaltmak ve mekanik direnci artırmak için Sarıçam örnekler %10'luk meşe palamudu taneni çözeltisi ile emprenye edikten sonra 150°C'de 2 saat ısıl işleme tabi tutulmuştur. Örnekler 20°C ve %65 bağıl nem, 40°C ve %35 bağıl nem ve 10°C ve %50 bağıl nem iklim şartlarında kondüsyonlandıktan sonra yoğunluk, denge rutubeti ve Brinell sertlik değerleri belirlenmiştir. Tanen modifiyeli ve 40°C sıcaklık ve %35 bağıl nemde iklimlendirilen örneklerin sertlik değerlerinde %20 artış gerçekleşmiştir.

Anahtar Kelimeler*: Isıl işlem, meşe palamudu taneni, Brinell sertlik, iklim, Sarıçam.*

1. Introduction

Wooden materials have been utilized in various forms throughout history to meet human needs. Today, with technological advancements, wood, now an industrial product, has found numerous applications. The increase in human population and the expansion of new application areas for wood have escalated its demand, leading to a surge in the need for quality wood. Consequently, this necessitates the more efficient use of existing resources, modification of less durable tree species for industry use, and the production of different materials [1].

Wood boasts many commendable features in terms of its mechanical and physical properties, aesthetics, and its environmental and health benefits. In many countries, wood is a widely used construction material, and in some regions, it is the primary material for construction and decoration. Impregnation of wood with chemicals is absolutely essential in many applications to protect the wood insects, fungi, and other such agents [3].

Applying high-temperature thermal treatment to solid wood materials, which are used as engineering materials, has been observed to alter certain physical and mechanical properties. While these alterations have negatively affected mechanical features, they've positively impacted physical features [3,4]. Inevitably, wood also presents certain adverse and undesirable properties. These include its susceptibility to deformations caused by fungi, insects, and microorganisms that consume it as food, its anisotropic structure which results in differential behavior in longitudinal, radial, and tangential directions, its hygroscopic nature which causes it to absorb and release moisture, resulting in dimensional changes, and its heterogeneous structure which results in color variations.

Previous studies have indicated that thermal modification (thermal modification) increases the resistance of solid wood material against microorganisms [5], reduces its swelling and shrinkage properties [6], decreases the percentage of moisture absorption and release [7], and leads to a significant darkening of the natural wood color [8]. When comparing data obtained from previous thermal modification studies, it has been pointed out that the physical and mechanical properties of the wood change according to the applied thermal treatment method, the tree species, its density, the applied temperature, and the exposure duration [9]. A higher density in wood is generally associated with better mechanical properties. Some studies have reported a direct positive correlation between hardness and wood density. It has been understood that wood species with a higher density show higher resistance values in terms of hardness compared to those with a lower density [10].

As previously indicated in other studies, thermal modification has both positive and negative effects on wood. From a negative perspective, the mechanical property most affected is the shock resistance [11]. The modulus of elasticity, bending strength, and tensile strength have also been reported to decrease in wood treated at high temperatures, based on exposure time [12]. Although hardness values decrease with increasing temperature and waiting times [13], some studies have found that tannin-modified wood has increased mechanical resistances [14] and a slight increase in hardness values [15]. Overall, the literature indicates that thermal treatment generally causes a decrease in mechanical properties but brings about positive improvements in physical properties. This study examines the changes in the physical properties (density and equilibrium moisture content) and hardness values of Scotch pine wood impregnated with tannin, under low temperature and short thermal treatment durations in external conditions.

2. Materials and Experimental Method

2.1. Wood material

The timber of this effective Scotch Pine (*Pinus sylvestris* L.) tree, which grows widely in Turkey, was preferred. Timber was obtained from the Siteler region of Ankara province by random selection method with a moisture content of approximately 12±2%. Test samples don't include, knots, fiber curls, cracks, etc. To obtain spreading and splintering pieces from Scotch Pine wood, rough-sized pieces were cut and made ready before tannin impregnation (Figure 1).

Figure 1. Scotch Pine pieces

2.2. Tannin solution

For the solution, 90 liters of distilled water and 1000 g of acorn tannin(T) were mixed in an impregnation container and 100 lt of the solution was heated to 80°C with an electric heater (Figure 2). All of the samples remained in the solution and were immersed in the container for 24 hours, without touching the bottom.

Figure 2. Acorn Tannin solution

2.3. Heat treatment

Thermal modification was applied to the test samples with the HT furnace located in the Woodworking Industrial Engineering laboratory of Gazi University Faculty of Technology. In the first stage of the heat treatment (HT), the sample pieces were pre-dried so that the oven temperature reached 100°C in 6 hours, then the oven temperature was increased to 130°C in 12 hours for high temperature drying, and then the oven temperature was increased to 150°C in 6 hours. After the drying process of the samples was completed, they were subjected to HT at 150°C for 3 hours. In the final stage of the HT, the temperature was reduced to 50°C within 10 hours to cool the samples. During the process, 3 atm of hot steam was sprayed into the oven for 10 seconds every 1 minute to prevent the risk of fire and cracks that may occur in the wooden material. The temperature and time graph of HT parameters are shown in Figure 3.

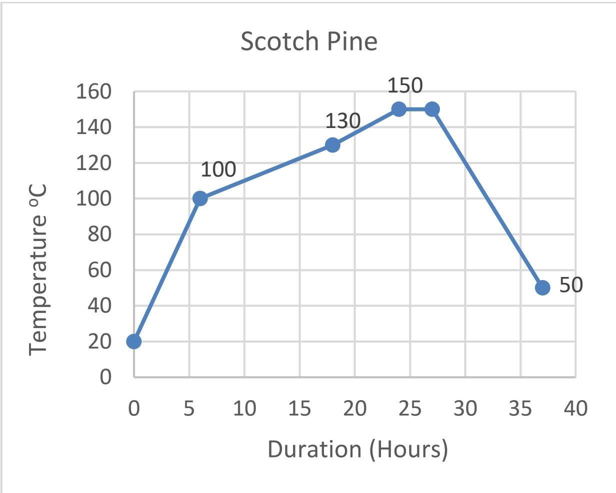

Figure 3. Heat treatment temperature time graph

2.4. Air conditioning

Test samples prepared in dimensions of 50x50x20 mm according to TS ISO 13061-12:2017 [17] were positioned in the air-conditioning cabinet after HT and conditioned under different climatic conditions (CC). The samples were first kept at 20°C and 65% relative humidity until they reached a constant weight. The samples that reached a constant weight were taken one by one from the CC cabin, and then the hardness test was applied by positioning them on the machine in the test device in such a way that the force was applied to the midpoints of the cross-sections in perpendicular and tangential directions to the annual rings. These tests were applied in the same way to samples that reached constant weight under the CC of 40°C temperature, 35% relative humidity and 10°C temperature, 50% relative humidity.

2.5. Brinell hardness test

A steel sphere with a diameter of 10 mm was used in the experiments, and the force to be applied was applied as in Figure 4, with a force of 50 kg, which is recommended for medium-hard trees such as Scotch pine. The experimental speed was adjusted to reach the maximum force within 15 seconds, and this force was continued for 30 seconds and then reduced to zero within 15 seconds.

Brinell hardness tests were carried out in accordance with ASTM D 4366:2021 [18] principles and the hardness resistance of the samples was calculated with the formula below.

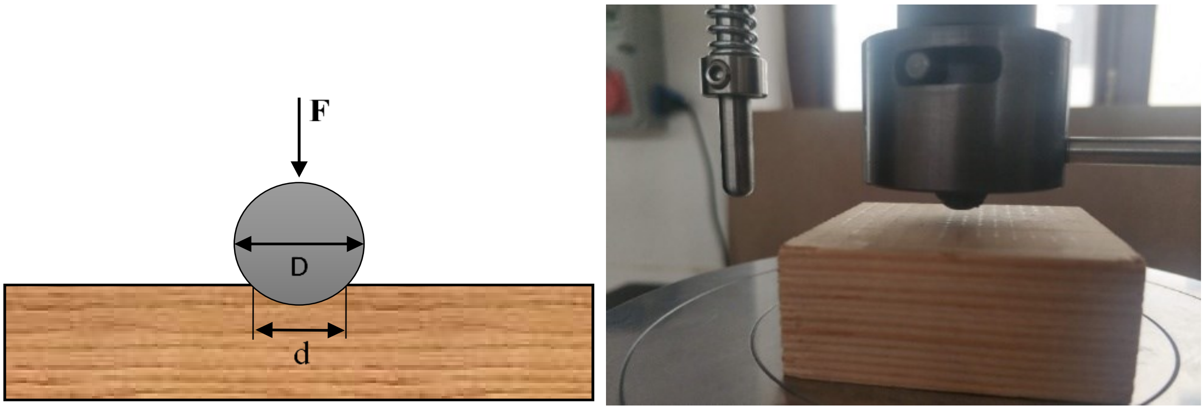

Figure 4. Brinell Hardness test and its application method

$$BSD = \frac{2F}{\pi D\left(D-\sqrt{D^2-d^2}\right)} \tag{1}$$

Tests were carried out by positioning the iron ball in the middle of the test sample. An example with a hardness test is shown in Figure 5. The test was applied to the parts close to the edge of the sample and the average values were measured.

Figure 5. Test applied sample

3. Results

In Scotch pine wood control samples, the air-dry density was determined as 0.485 g/cm³, and the density values decreased in parallel with the material loss and decreased to 0.464 g/cm³ after the HT. In the samples where tannin impregnation was applied before the heat treatment, the density increased and reached 0.513 g/cm³ due to the amount of T substance penetrating into the wood. Table 1 shows the statistical findings of the air-dry density values of Scotch pine wood samples, and Figure 6 shows the corresponding min, max and average values graph.

Table 1. Air dry density statistics

	Air dry density (g/cm^3)			
	X_{min}	X_{max}	X_{avr}	sd
Control	0.468	0.516	0.485	0.015
HT	0.454	0.474	0.464	0.009
T+HT	0.494	0.533	0.513	0.012

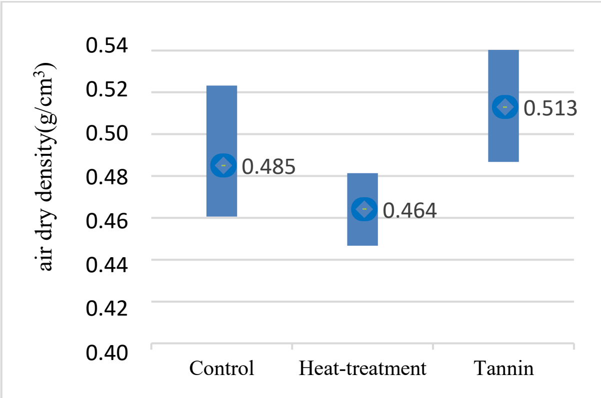

Figure 6. Air dry density values

The highest equilibrium humidity averages are shown in Table 2 and are respectively in 20/65 CC; control (12.4%) was obtained in HT and T impregnated HT samples. The lowest equilibrium moisture rates were obtained in tannin (3.8%), HT and control samples under 40/35 CC, respectively. Equilibrium humidity was higher in control samples than in HT samples under all CC. Among the HT samples, the equilibrium moisture rates of the samples impregnated with T were obtained lower than the HT samples in all CC. In all HT samples, it may cause decreases in the equilibrium moisture rates due to the decrease in the main wood components and material losses compared to the control samples.

Table 2. Percentages of change in equilibrium moisture

	Climate	Equilibrium moisture (%)			
		X_{min}	X_{max}	X_{avr}	sd
Control	20/65	9.3	13.3	12.4	1.06
	40/35	3.7	4.3	4.1	0.08
	10/50	9.5	10.0	9.7	0.14
HT	20/65	8.5	10.1	9.7	0.40
	40/35	3.6	4.2	4.0	0.12
	10/50	8.6	9.9	9.6	0.30
HT+T	20/65	8.47	9.71	9.04	0.34
	40/35	3.65	4.05	3.82	0.12
	10/50	8.22	9.22	8.74	0.32

Equilibrium moisture percentage change data and the process-climate interaction chart of these data are given in Figure 7.

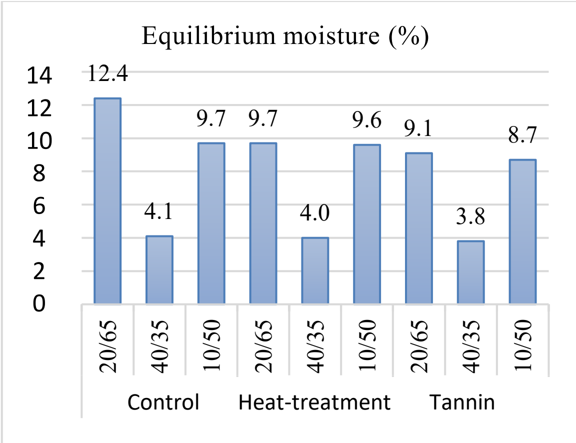

Figure 7. Balance humidity chart

Table 3. Multiple variance analysis of Brinell hardness resistance averages

Variance Source	Degrees of Freedom	Squares Total	Average squares	F-Value	p-Value
Treatment (A)	2	0.232	0.118	31.775	0.000
Climate (B)	2	0.914	0.461	125.283	0.000
AxB	4	0.065	0.016	4.152	0.003
Error	81	0.293	0.003		
Total	89				

In Table 3, a multivariance analysis of hardness resistance was performed and all factors were found to be statistically significant ($p<0.05$) and it was understood that the factor affecting hardness the most was climate. Duncan test results are shown in the tables to determine significant differences between Brinell hardness resistance groups at the factorial level. Brinell hardness resistance homogeneity groups according to process type are given in Table 4.

Table 4. Brinell hardness resistance homogeneity groups according to process type

Treatment	X (N/mm^2)	HG
Control	1.110	B
HT	1.041	C
HT+T	1.163	A
LSD: 0,0325		
X: Average, HG: Homogeneity Group		

After the HT, there were decreases in the hardness values of Scotch pine, similar to the literatüre [2,14]. However, it was determined that the hardness values in the T impregnated samples were higher than the control samples. It can be said that this is due to the increase in density as the amount of substance in T-modified wood increases. Brinell hardness resistance homogeneity groups according to CC are given in Table 5.

Table 5. Brinell hardness resistance homogeneity groups in terms of climatic conditions

Climate condition	X (N/mm^2)	HG
20/65	1.015	C
40/35	1.251	A
10/50	1.068	B
LSD: 0,032		

The highest hardness resistance value was determined as 1.251 N/mm^2 at 40°C temperature and 35% relative humidity, and the lowest was 1.015 N/mm^2 at 20°C temperature and 65% relative humidity. It is understood that one of the important factors affecting hardness resistance is the CC. Since wood is a hygroscopic material due to its structure, it works in radial, tangential and transverse directions by binding the moisture in the environment to the hydroxyl (OH^-) groups within it. As more water molecules bind to the wood material, the attractive force in the bonds between the fibers decreases, negatively affecting the mechanical properties [16]. For this reason, there was an increase in hardness resistance values at high temperature and low relative humidity.
The interaction between process type and climate conditions. Brinell hardness resistance homogeneity groups are shown in Table 6.

Table 6. Brinell hardness resistance homogeneity groups in terms of process type - climate condition interaction

Treatment	X (N/mm^2)	HG
Control 20/65	0.968	D
Control 40/35	1.264	A
Control 10/50	1.083	C
HT 20/65	0.951	D
HT 40/35	1.190	B
HT 10/50	0.973	D
HT+T 20/65	1.102	C
HT+T 40/35	1.275	A
HT+T 10/50	1.127	C
LSD: 0.056		

The highest hardness resistance was determined as 1.275 N/mm^2 in the T modified and HT samples conditioned at 40°C temperature and 35% relative humidity, and the lowest was 0.951 N/mm^2 in the HT samples conditioned at 20°C temperature and 65% relative humidity. Figure 8 shows the graph of Brinell hardness resistance data depending on the process type and CC. When the results were examined, the highest resistance values were found in samples conditioned in 40/35 CC and the lowest in samples conditioned in 20/65 CC. In addition, it was determined that the resistance values in all T modified samples were higher than in other treated samples.

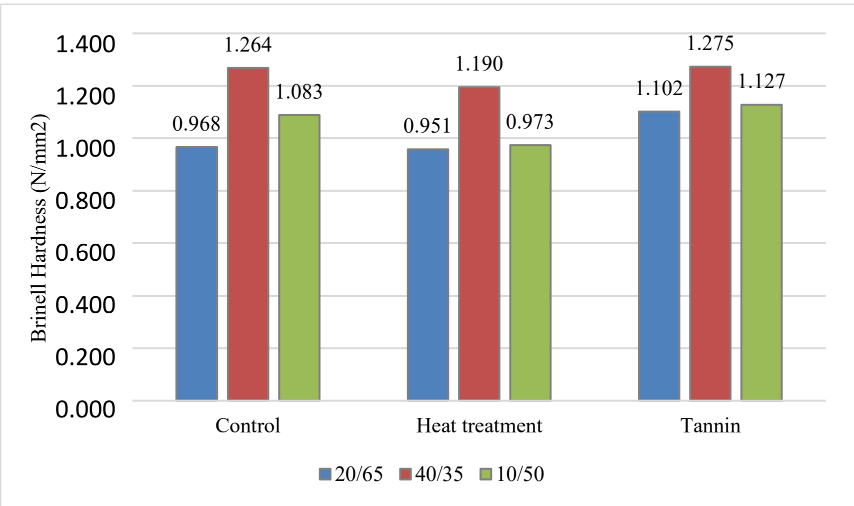

Figure 8. Interaction graph of process type and climate condition

4. Conclusion and Recommendations

In this study, the changes in the hardness values of Scotch pine wood modified with tannin and treated with low HT time and temperature were examined and some positive and negative changes occurred as stated below. Although Scotch pine wood was HT at low temperatures and times, decreases in hardness values were detected in parallel with the decrease in density values. However, there was an increase in the hardness resistance values and positive improvements in the equilibrium moisture of the samples HT with T modification. Since T modification causes an increase in density, increases in hardness values compared to control samples were observed in parallel with the increasing amount of substance. In addition, since HT causes a decrease in the OH^- groups in the wood material, HT samples have less water retention ability compared to control samples. There has been a positive decrease in the equilibrium moisture content of the wood material, whose water exchange has decreased. Positive improvements were observed in the hardness resistance and equilibrium humidity of the samples HT with T modification in different CC.

In future studies, the effects of Tannin modification at different solution rates at different processing temperatures and duration on the physical and mechanical properties of commonly used wood species can be investigated. In addition, according to these results, optimization can be done using different algorithms with artificial intelligence-supported programs to reduce the number of samples.

Declarations and Ethical Standards

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

List of Symbols

BSD	Hardness value (N/mm^2)
F	Applied force (N)
d	Diameter of the hole opened by the steel ball on the surface of the test sample (mm)
D	Diameter of steel ball (mm)

Author Contribution

Author 1 conducted the literature research by supplying the experimental materials and carrying out the experiments. Author 2 took part in the interpretation of the experimental results and the execution of the experiments.

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