

## The Effects of Liquid Nitrogen and Impregnation on Physical and Mechanical Properties of Fir Wood

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### Abstract

**Aim of study:** To improve and develop the wood impregnation process. Therefore, the aim was to use liquid nitrogen application as a new method to determine its effects on impregnation and mechanical properties

**Area of study:** Fir wood (*Abies bornmülleriana* Mattf.), widely used in the forest industry, was selected for the study. Liquid nitrogen pretreatment and impregnation methods were applied.

**Material and method:** Fir wood samples prepared according to relevant standards were exposed to liquid nitrogen for 15 minutes, 90 minutes, and 6 hours. The samples were impregnated with diammonium sulfate using brushing, short-term and long-term immersion, and pressure methods. Retention levels were measured, and flexural strength and modulus of elasticity tests were conducted to evaluate the effects on mechanical properties.

**Main results:** As a result of the study, the retention rate of the samples increased with each application of liquid nitrogen. Differences in flexural strength and modulus of elasticity were detected due to the increased retention properties of liquid nitrogen application.

**Research highlights:** Increasing the retention rate with liquid nitrogen application increased the material's lifespan and durability. It can be used as an alternative method for difficult-to-impregnate materials.

**Keywords:** Wood Material, Impregnation, Retention, Liquid Nitrogen, Mechanical Strength

## Sıvı Azot ve Emprenye Uygulamasının Gökna Odununun

## Fiziksel ve Mekanik Özellikleri Üzerine Etkisi

### Öz

**Çalışmanın amacı:** Ağaç malzemede emprenye işlemini iyileştirmek ve geliştirmektir. Bu nedenle yeni bir yöntem olarak sıvı azot uygulamasından yararlanmak, sıvı azot uygulamasının, emprenye ve mekanik özelliklerine etkilerini belirlemektir.

**Çalışma alanı:** Orman endüstrisinde yaygın olarak kullanılan Gökna (*Abies bornmülleriana* Mattf.) odunu seçilmiştir. Sıvı azot ön işlemi ve emprenye yöntemleri uygulanmıştır.

**Materyal ve yöntem:** İlgili standartlara göre hazırlanan Gökna odunu numuneleri 15 dakika, 90 dakika ve 6 saat sıvı azot içerisinde bekletilmiştir. Numuneler Diamonyum Sülfat kullanılarak emprenye edilmiştir. Emprenye yöntemi olarak fırça ile sürme, kısa ve uzun süreli daldırma ve basınç yöntemleri uygulanmıştır. Emprenye yapılan numunelerin retensiyon miktarları belirlenmiştir. Yapılan uygulamaların malzemenin mekanik özelliklerine etkilerini belirlemek için numunelere eğilme direnci ve elastikiyet modülü deneyleri yapılmıştır.

**Temel sonuçlar:** Çalışma sonucunda; Sıvı azot uygulaması ile numunelerin retensiyon miktarında her uygulamada artış sağlanmıştır. Sıvı azot uygulaması ile retensiyon miktarındaki artışa bağlı olarak eğilme direnci ve elastikiyet modülü değerlerinde farklılıklar tespit edilmiştir.

**Araştırma vurguları:** Sıvı azot uygulamasının retensiyon miktarını artırması ile malzemenin kullanım ömrü ve dayanımı arttırılmıştır. Zor emprenye olan malzemelerde alternatif bir yöntem olarak kullanılabilir.

**Anahtar kelimeler:** Ağaç Malzeme, Emprenye, Retensiyon, Sıvı Azot, Mekanik Mukavemet



## Introduction

Wood material is an important construction material that has been used in internal and external decoration processes since ancient times. Its lightness and resistance to physical and mechanical effects are among its most important properties. Its low heat and sound conductivity, ease of processing, and being a natural and renewable raw material are characteristics that distinguish wood material from other construction elements. Wood has come to the fore in the forestry industry in recent years due to its superior properties. However, factors such as changes in different weather conditions and dimensions, as well as damage from insects, fungi and marine organisms, must be taken into account when using wood. (Levan and Winandy, 1990; Örs et al., 2005; Gérardin, 2016; Esteves and Pereira, 2020). To protect wood materials against these adverse effects, drying, impregnation and surface treatments are applied (Higley and King, 1990). It has also been reported that impregnation can be used to increase the fire resistance of wood materials (Kesik et al., 2015; Özcan et al., 2016; Tomak and Cavda, 2013). The resistance of impregnated wood materials to biotic and abiotic pests increases their economic and aesthetic value (Kartal, 1998; Hill and Altgen, 2019; Sumarni and Nawawi, 2022).

The use of animal, plant and mineral oils to protect wood from external influences has been attempted since ancient times. This process has undergone a major transformation with the impact of industrialization and the use of new synthetic chemicals (Mohan and Shi, 2022). In impregnation processes carried out to protect the material, the ability to perform the protective function is directly related to the impregnation liquid penetrating deeply and being permanent. (Bozkurt and Göker, 1993; Hill, 2007). The permeability, type, fibre structure, density, and anatomical structure of wood have a significant effect on its impregnability (Gérardin, 2016; Mantanis, 2017). Different impregnation methods, materials, and processes are used in impregnation treatments. In addition to the protective properties of the materials used, it is important that they do not harm the

environment, are cost-effective, and have fire-retardant properties (Huo et al., 2016).

Various studies have been conducted in recent years to improve impregnation results in wood. Li et al. (2023) investigated the impregnation of poplar wood using a silica sol/phenolic resin mixture and observed a 52% improvement in water resistance. Jo and Park (2024) used grooves before impregnation and then applied pressure impregnation, achieving a 35% increase in retention rate. Liquid nitrogen application is another alternative new method for enhancing retention.

Recent studies on liquid nitrogen application have reported that liquid nitrogen can increase the retention rate of impregnating agents by creating microcracks in the wood structure (Wang et al., 2021). At the same time, new system designs and applications related to liquid nitrogen application have begun to be tested. Kurt, S., and colleagues designed a system to increase retention in impregnated hardwood materials. In their system, they added a liquid nitrogen tank next to the impregnation tank and conducted trials of liquid nitrogen application prior to impregnation. (Kurt et al., 2014) In a different study, Scots pine and Oriental spruce wood materials were exposed to liquid nitrogen for 30 minutes before impregnated with Firetex by using pressure-vacuum method and the results indicated that liquid nitrogen application positively altered the retention rate in the wood materials. (Yörür et al., 2017)

In this study, liquid nitrogen application prior to impregnation was tested on Uludağ Fir (*Abies bornmülleriana* Mattf.), which is difficult to impregnate. Liquid nitrogen was applied to the samples for 15 minutes, 90 minutes, and 6 hours. Diammonium sulphate was chosen as the impregnation agent. This substance was selected because it is widely reported in the literature for its fire-retardant properties and because its effects in increasing biological resistance have been reported (Bekhta et al., 2016). Brushing, short and long-term immersion, and pressure methods were applied as impregnation methods. After application, the retention amounts, bending, and elasticity values of the impregnated samples were examined.

Applying liquid nitrogen to wood is a new method being tested in recent years. Liquid nitrogen application is considered a potential pretreatment method because it provides better results in difficult-to-impregnate species. This study will contribute to the industry by demonstrating the relationship between liquid nitrogen application, retention rate, and impregnation efficiency.

## Material and Methods

### Wood Material

In this study, Fir wood (*Abies bornmülleriana* Mattf.), which is widely used in the wood construction and furniture industry, was used as the wood material. The materials were dried until they reached air-dry condition. Samples were then prepared to represent the control group and other groups according to the experiments to be conducted

### Impregnation Material and Methods

Diammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  was used as the impregnation agent due to its fire-retardant properties and its ability to enhance biological resistance (Bekhta et al., 2016). Impregnation was performed using four different methods: brushing, short-term immersion, long-term immersion, and pressure impregnation.

### Liquid Nitrogen

Nitrogen, which constitutes 78% of the atmosphere, is a gas that is used extensively in many industries with two basic properties. Nitrogen is quite cold in liquid form. It is a freezing liquid and causes sudden freezing in contact with living tissue. If properly isolated from ambient temperature, it creates a nitrogen gas source that does not require pressurization. The ability to remain at temperatures far below the freezing point of water makes it possible to use liquid nitrogen in many different areas. Physical properties of liquid nitrogen are given in Table 1 (URL-1, 2014).

Table 1. Physical properties

| State of the matter     | Gas                         |
|-------------------------|-----------------------------|
| Density                 | 0.001251 g/cm <sup>3</sup>  |
| Density in liquid state | 0.808 g/cm <sup>3</sup>     |
| Melting point           | -210.00 °C                  |
| Boiling point           | -195.79 °C                  |
| Melting temperature     | 0.720 kJ/mol                |
| Heat of vaporisation    | 5.57 kJ/mol                 |
| Heat capacity           | 29.124 (25 °C)<br>J/(mol-K) |

### Preparation of Test Samples

For the preparation of test samples, specimens selected from Fir trees were prepared in accordance with TS 1476 standards. They were selected from the resin-free, growth defect-free, sound, straight-grained, live wood portion of the tree, without knots or branches, and cut tangentially to dimensions of 2x2x32 cm. The prepared samples were first treated with liquid nitrogen. Subsequently, all samples, which were conditioned in a climate chamber, underwent an impregnation process.

### Air Dry Density

The moisture content and specific gravity of the samples were determined in accordance with TS 2471 and TS 2472 respectively. Accordingly, the test samples were kept in a cabinet at  $20 \pm 2^\circ\text{C}$  temperature and  $65 \pm 3\%$  relative humidity until they reached constant weight. Then they were weighed on an analytical balance with a sensitivity of 0.001g.

### Liquid Nitrogen Operations

The 2x2x32 cm sized samples, which were acclimatized in the air conditioning cabinet, were divided into 4 groups as control group, 15 minutes, 90 minutes and 6 hours. Here, the control group was kept separately and the other samples were treated with liquid nitrogen at the specified times. The samples kept in liquid nitrogen for the specified periods were weighed again on an analytical balance with a sensitivity of 0.001g and made ready for impregnation.

The samples treated in liquid nitrogen were impregnated by four different methods using Diammonium Sulphate impregnating agent. With the brush application method, the liquids were thoroughly absorbed into the test specimens and left to dry. The test specimens,

which were kept in the liquid for 15 minutes with the short-term immersion method and 90 minutes with the long-term immersion method, were removed from the liquid and taken to the waiting room for drying. Pressurized impregnation was carried out according to the Full Cell (Bethell) Method. The impregnation of the test specimens was carried out at 10-12 bar pressure according to ASTM D 1413- 07.

#### *The Determination of Moisture Content*

The moisture contents of the wood used in the preparation of the test samples were measured before and after the treatment in accordance with TS 2471 using Equation (1):

$$r = \frac{Mr - Mo}{Mo} \times 100 \quad (1)$$

Where: Moisture content (r), Mr is the moist weight and Mo is the oven dry weight (g).

#### *Determination of Density*

The densities of the wood used in the preparation of the test samples were evaluated before and after the process in accordance with TS 2472. Density ( $\delta$ , g/cm<sup>3</sup>) was calculated according to Equation (2):

$$\delta = \frac{M}{V} \quad (2)$$

Where M is the weight (g) and V is the volume (cm<sup>3</sup>) of wood

#### *Retention Amount and Retention Rate*

The retention amount (R, kg/m<sup>3</sup>) and retention percentage (R, %) of the water-soluble salt-based impregnants were calculated using Equations (3) and (4), respectively.

$$R = \frac{G \times C}{V} \times 10 \text{ (kg/m}^3\text{)} \quad (3)$$

$$R\% = \frac{Moes - Moeö}{Moeö} \times 100 \quad (4)$$

Where G: Amount of impregnant solution absorbed by the sample (g), V: Sample volume (cm<sup>3</sup>), C: Concentration of

impregnant solution (%), Moes= Complete dry weight of the test sample after impregnation (g), Moeö= Complete dry weight (g) of the test sample before impregnation.

#### *Mechanical Features*

After the impregnation process, the control and liquid nitrogen treated test specimens of Uludağ Fir wood material with dimensions of 2x2x32 cm were kept in an air conditioning cabinet at 20 ± 2°C and 65 ± 3% relative humidity until they reached constant weight and 12% moisture content. The specimens were placed in a universal testing machine with a fulcrum span of 30 cm and load was applied tangentially to the annual rings and from the centre of the fulcrum span until breakage occurred.

The following formula was used to calculate the bending resistance, as given in Equation (5):

$$\sigma_e = \frac{3.F.Ls}{2b.h^2} \text{ (N/mm}^2\text{)} \quad (5)$$

Where  $\sigma_e$ : Bending resistance (N/mm<sup>2</sup>), F: Maximum force measured at fracture (N), Ls Clearance between abutments (mm), b: Sample width (mm), h: Sample height (mm)

#### *Modulus of Elasticity in Bending*

The modulus of elasticity in bending was determined in accordance with TS 2478 standard. The bending force was applied perpendicularly to the test specimen at a constant rate of increase, and the modulus of elasticity (E) values were calculated according to Equation (6):

$$E = \frac{F.Ls^3}{4.b.h^3} \text{ (N/mm}^2\text{)} \quad (6)$$

Where E: Modulus of elasticity (N/mm<sup>2</sup>), F: Applied force difference (N), Ls: Distance between support points (mm), b: Width of the test specimen (mm), h: Height of the test specimen (mm), Mechanical tests were carried out in the universal test machine in accordance with the relevant standards as shown in the Figure 1 below.

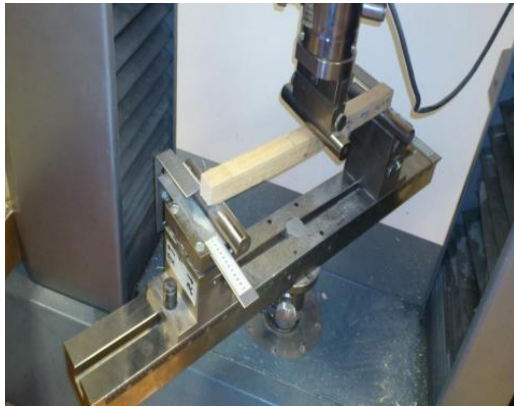


Figure 1. Mechanical test rig

## Results

The following findings were obtained because of experiments conducted on Uludağ Fir samples. Statistical information regarding the air-dry densities of spruce wood impregnated with Diammonium Sulphate and control groups, which were kept in liquid nitrogen for 15 minutes, 90 minutes and 6 hours and treated using brush application, short and long immersion and pressure methods, is given in Table 2.

Table 2. Statistical results for air dry densities of fir wood ( $\text{g/cm}^3$ )

| Imp. Agent    | Imp. Method | Hold Time |       |         |
|---------------|-------------|-----------|-------|---------|
|               |             | 15min     | 90min | 6 hours |
| Dia. Sulphate | Brush       | 0.451     | 0.448 | 0.425   |
|               | Short term  | 0.442     | 0.425 | 0.448   |
|               | Long-term   | 0.447     | 0.442 | 0.437   |
|               | Pressure    | 0.44      | 0.432 | 0.419   |
| Control       |             | 0.448     |       |         |

The highest density value in spruce wood was found in samples impregnated using the brush impregnation method after being soaked in liquid nitrogen for 15 minutes, at  $0.451 \text{ g/cm}^3$ . The lowest density value in spruce wood,  $0.419 \text{ g/cm}^3$  was found in samples treated with the pressure impregnation method after being soaked in liquid nitrogen for 6 hours. Table 3 shows the average retention values for spruce wood soaked in liquid nitrogen.

Table 3. Average values of retention values of fir woods kept in liquid nitrogen ( $\text{kg/m}^3$ )

| Imp. Agent     | Imp. Method | Control          | 15 min.          | 90 min.          | 6 hours          |
|----------------|-------------|------------------|------------------|------------------|------------------|
| Dia. Sulphate. | Brush       | 1.139<br>(0.053) | 3.920<br>(0.890) | 4.447<br>(0.226) | 4.104<br>(0.663) |
|                | Short term  | 1.605<br>(0.321) | 4.957<br>(0.152) | 4.653<br>(0.411) | 3.684<br>(0.516) |
|                | Long-term   | 2.292<br>(0.394) | 4.570<br>(0.106) | 5.252<br>(0.125) | 3.967<br>(0.665) |
|                | Pressure    | 1.925<br>(0.624) | 5.192<br>(0.911) | 7.411<br>(1.633) | 8.351<br>(0.378) |

Values in brackets indicate standard deviation

The highest retention value of  $8.351 \text{ kg/m}^3$  with diammonium sulphate impregnation agent was observed in samples impregnated by the pressure method after being exposed to liquid nitrogen for 6 hours prior to impregnation. The results of the multiple variance analysis regarding retention values are given in Table 4.

Table 4. Multiple analysis of variance results for fir wood retention values

| Variance Sources       | Sum of Squares | Degrees of Freedom | Mean Squares | F Account | Importance Level |
|------------------------|----------------|--------------------|--------------|-----------|------------------|
| Adjusted Model         | 1484.870a      | 15                 | 23.569       | 52.022    | 0.000            |
| Fixed Term             | 5531.451       | 1                  | 5531.451     | 1.22E+04  | 0.000            |
| A: Hold Time           | 793.007        | 3                  | 264.336      | 583.441   | 0.000            |
| B: Impregnation Method | 242.767        | 3                  | 80.922       | 178.612   | 0.000            |
| Interaction A*B        | 71.974         | 9                  | 7.997        | 17.651    | 0.000            |
| Error                  | 115.984        | 144                | 0.453        |           |                  |
| Total                  | 7132.305       | 160                |              |           |                  |
| Adjusted Total         | 1600.854       | 159                |              |           |                  |

R<sup>2</sup>= 0.928

According to the results of multiple analysis of variance, soaking times in liquid nitrogen and impregnation methods were found to be significant separately and simultaneously on the retention amount of fir wood. The results of Duncan's test to determine in which treatments the difference was significant are given in Table 5.

Table 5. Duncan's test results of fir wood retention values at 95 % confidence interval

| Soaking Time | Average | Impregnation Method | Average |
|--------------|---------|---------------------|---------|
| Control      | 1.595 A | Brush               | 3.270 A |
| 15 minutes   | 4.450 B | Short term          | 3.862 B |
| 6 hours      | 4.708 C | Long-term           | 3.894 B |
| 90 minutes   | 5.877 D | Pressure            | 5.603 C |

The table separately examines the effects of liquid nitrogen application, impregnation methods, and impregnation durations on spruce wood retention values. According to Duncan test results, all liquid nitrogen soaking durations were found to be significant (A, B, C, D). The highest average value was obtained in samples soaked in liquid nitrogen for 90 minutes. When the impregnation method values were examined,

short and long immersion methods were found to be insignificant among themselves (B, B) and significant with other methods (A, B, C). The average values for bending strength are given in Table 6.

Table 6. Mean values for bending resistance values of fir wood (N/mm<sup>2</sup>)

| Imp. Agent     | Imp. Method | Control           | 15 min.           | 90 min.           | 6 hours           |
|----------------|-------------|-------------------|-------------------|-------------------|-------------------|
| Dia. Sulphate. | Brush       | 84.576<br>(1.309) | 74.098<br>(8.398) | 69.264<br>(13.38) | 73.284<br>(5.114) |
|                | Short-term  | 66.364<br>(5.937) | 83.710<br>(4.490) | 73.522<br>(12.64) | 76.972<br>(10.34) |
|                | Long-term   | 74.402<br>(4.146) | 68.038<br>(7.613) | 80.722<br>(5.868) | 73.266<br>(14.53) |
|                | Pressure    | 61.038<br>(1.380) | 69.084<br>(8.337) | 72.826<br>(6.861) | 76.368<br>(5.315) |

Values in brackets indicate standard deviation

According to the averages of the bending strength values of spruce wood in relation to the pre- impregnation liquid nitrogen application, impregnation methods and impregnation materials, the highest bending strength value, 84.57 N/mm<sup>2</sup>, was observed in the control samples. The results of the multiple variance analysis in relation to the bending strength values are given in Table 7.

Table 7. Multiple analysis of variance results for bending resistance values of fir wood

| Variance Sources       | Sum of Squares | Degrees of Freedom | Mean Squares | F Account | Importance Level |
|------------------------|----------------|--------------------|--------------|-----------|------------------|
| Adjusted Model         | 14410.509a     | 15                 | 228.738      | 3.214     | 0.0000           |
| Fixed Term             | 1561890.76     | 1                  | 1561891      | 21950     | 0.0000           |
| A: Hold Time           | 1752.525       | 3                  | 584.175      | 8.208     | 0.0000           |
| B: Impregnation Method | 231.421        | 3                  | 77.14        | 1.084     | 0.3560           |
| Interaction A*B        | 1889.352       | 9                  | 209.928      | 2.95      | 0.0020           |
| Error                  | 18218.92       | 144                | 71.168       |           |                  |
| Total                  | 1594520.19     | 160                |              |           |                  |
| Adjusted Total         | 32629.429      | 159                |              |           |                  |

R<sup>2</sup>= 0.442

According to the results of multiple analysis of variance, soaking time in liquid nitrogen was found to be significant on bending resistance, soaking time in liquid nitrogen and impregnation method were found to be significant on bending resistance of fir wood at the same time. The results of Duncan's test to determine in which treatments the difference was significant are given in Table 8.

Table 8. Duncan test results for bending resistance values of fir wood

| Soaking Time | Average  | Impregnation Method | Average  |
|--------------|----------|---------------------|----------|
| Control      | 65.859 A | Short term          | 68.559 A |
| 15 minutes   | 70.605 B | Pressure            | 69.677 A |
| 90 minutes   | 71.456 B | Long-term           | 70.458 A |
| 6 hours      | 71.533 B | Brush               | 70.759 A |

According to the results of Duncan's test, it was observed that there was no difference in the bending resistance values of fir wood in liquid nitrogen retention time, but the difference was significant compared to the control samples. The difference between

impregnation methods was found to be statistically insignificant. The average values of the elasticity modulus in bending are given in Table 9.

Table 9. Average values of modulus of elasticity values of fir wood in bending (N/mm<sup>2</sup>)

| Empr. Type  | Empr. Method | Control            | 15 min.            | 90 min.            | 6 hours            |
|-------------|--------------|--------------------|--------------------|--------------------|--------------------|
| Dia. Sulph. | Brush        | 7046.4<br>(2254.6) | 8334.2<br>(1213.6) | 8158.2<br>(1613.7) | 9273.8<br>(516.5)  |
|             | Short term   | 8612.6<br>(336.3)  | 10030.0<br>(705.7) | 8754.4<br>(1399.0) | 9836.4<br>(691.9)  |
|             | Long-term    | 9344.8<br>(1088.8) | 8593.2<br>(1014.7) | 9719.0<br>(830.4)  | 8222.4<br>(1527.7) |
|             | Pressure     | 7434.2<br>(201.0)  | 9233.8<br>(575.9)  | 9674.4<br>(1202.1) | 9356.8<br>(633.2)  |

Values in brackets indicate standard deviation

The highest value of fir wood impregnated with diammonium sulphate was found to be 10030 N/mm<sup>2</sup>. This was in the samples exposed to liquid nitrogen for 15 minutes and short-term dipping method. The results of the multiple variance analysis for elasticity values are given in Table 10.

Table 10. Multiple variance analysis results for fir wood elasticity values

| Variance Sources       | Sum of Squares | Degrees of Freedom | Mean Squares | F Account | Importance Level |
|------------------------|----------------|--------------------|--------------|-----------|------------------|
| Adjusted Model         | 2.845E8a       | 15                 | 4516349      | 3.773     | 0                |
| Fixed Term             | 2.33E10        | 1                  | 2.33E10      | 19440     | 0                |
| A: Hold Time           | 3.29E07        | 3                  | 1.10E07      | 9.155     | 0                |
| B: Impregnation Method | 1.47E07        | 3                  | 4913585      | 4.105     | 0.007            |
| Interaction A*B        | 6.13E07        | 9                  | 6808081      | 5.688     | 0                |
| Error                  | 3.06E08        | 144                | 1197010      |           |                  |
| Total                  | 2.39E10        | 160                |              |           |                  |
| Adjusted Total         | 5.91E08        | 159                |              |           |                  |

R<sup>2</sup>= 0.481

According to the results of the multiple variance analysis, the impregnation method was not found to have a significant effect on the bending elasticity modulus resistance, while the other factors were found to have a significant effect on the bending elasticity modulus resistance of spruce wood, both individually and simultaneously. The results of the Duncan test conducted to determine in which applications the difference was significant are given in Table 11.

Table 11. Duncan test results for fir wood elasticity values

| Soaking Time | Average  | Impregnation Method | Average   |
|--------------|----------|---------------------|-----------|
| Control      | 8009.4 A | Short term          | 8261.6 A  |
| 15 min.      | 8518.4 B | Brush               | 8384.4 AB |
| 6 hours      | 8754.9 B | Long-term           | 8666.4 BC |
| 90 min.      | 8828.7 B | Pressure            | 8799.1 C  |

According to the Duncan test results, it was observed that the elasticity values of spruce wood did not differ significantly among themselves (B, B, B) in terms of the soaking time in liquid nitrogen, but the difference was significant compared to the control samples. The impregnation methods were found to be significant among themselves.

## Conclusions

The penetration depth of the impregnation agent into the wood material is important for the use of wood material in outdoor environments, as the impregnation agent remaining on the surface will wash away over time, leaving the wood material unprotected against biotic factors. Therefore, treating the wood material with liquid nitrogen (-196°C) prior to the impregnation process will cause physical changes in the anatomical structure of the wood material (in the cell walls and especially in the passages) due to the increase in the volume of frozen liquids, and the penetration of the impregnation agent into the wood material will be facilitated and increased.

After the liquid nitrogen application, an increase in density values was observed in the samples impregnated with diammonium sulphate. The highest value was reached at 0.467 g/cm<sup>3</sup>. after 15 minutes of liquid nitrogen application in the spruce sample treated with the long-term impregnation method. This result represents a 4.23% increase compared to the control sample.

All attempts to increase the retention amount with liquid nitrogen application were successful. In the brush application method, a 292% increase was observed in the 90 minute liquid nitrogen application compared to the control group samples. In the short-term immersion method, the highest increase was calculated as 208% in 15 minutes. In the long-term immersion method, the highest increase was observed as 129% in 90 minutes. In the pressure method, the highest increase was obtained as 334% in samples treated with liquid nitrogen for 6 hours. The increase in retention amount can be explained by microcracks and passage openings formed in the wood cell structure due to the freezing-expansion effect of liquid nitrogen (Hao et al., 2018). This increase is consistent with previous studies (Kurt et al., 2014; Yörür et al., 2017).

This study demonstrated that liquid nitrogen could be an effective pre-treatment for enhancing impregnation performance in spruce wood. The findings are consistent with the results reported by Yörür et al. (2017) and Altun et al. (2020). However, decreases in some mechanical properties are noteworthy. This may be related to sudden temperature changes causing brittleness in the cell walls.

In the brush application method, the maximum decrease in bending strength values was observed to be 18.1% in 90 minutes. The greatest increase was found to be 25.1% in the 6-hour liquid nitrogen application and the pressure impregnation method. This is consistent with findings reported in the literature that impregnation agents can negatively affect the mechanical properties of wood (Zhang et al., 2020).

The largest decrease in elastic modulus values was found in the long-term immersion method, with a 12.2% decrease over 6 hours. The largest increase, 30.1%, was observed in the 90-minute pressure impregnation method. Significant increases in elastic modulus values were observed in the pressure method and in the 90-minute liquid nitrogen application. This finding indicates that liquid nitrogen increases the permeability of the wood, resulting in a more homogeneous distribution of the impregnation agent (Liu et al., 2021).

Liquid nitrogen led to significant increases in retention values in all applications. The effects of increased retention on flexural strength and flexural modulus of elasticity were investigated. Increases and decreases in flexural strength and modules of elasticity were observed over different time periods and with different application methods.

Liquid nitrogen application appears to increase material adhesion and therefore service life. However, the limited use of liquid nitrogen in industry and the lack of necessary systems have limited its use. Future studies should examine the duration of liquid nitrogen application and post-impregnation aging tests together. Additionally, environmental impact and industrial-scale applicability analyses should be conducted.

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## Ethics Committee Approval

N/A

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## Author Contributions

Conceptualization Ş.K., S.Ö.; Investigation: Ş.K., Z.T.Y., S.Ö.; Material and Methodology: Ş.K., Z.T.Y.; Visualization: Z.T.Y., S.Ö.; Writing - Original Draft: Z.T.Y., S.Ö.; Writing - Review & Editing: Ş.K., Z.T.Y., S.Ö. Author has read and agreed to the published version of manuscript.

## Conflict of Interest

The authors declare that they have no conflict of interest.

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