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SOME PHYSICAL AND BIOLOGICAL PROPERTIES OF *PINUS SYLVESTRIS* WOOD IMPREGNATED WITH NANO-SOLUTIONS

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Abstract

In this study, Scots pine (*Pinus sylvestris*) wood samples were impregnated with nano-sized MgO, ZnO, TiO_2 and SiO_2 to determine the effects of nano particles on the some psychical and biological properties of pine sapwood. Water absorption rate (WAR) and fungal decay (*Coniophora puteana*) test were performed after the full-cell impregnation process. Impregnation was carried out with solutions prepared using only water at 1.5% concentration for nano-solutions. The WAR values at the end of test for these samples were ranged between 102.916 % and 120.823% while the 135.143 % for control (not impregnated) samples. Weight losses of wood samples impregnated with nano-solutions were ranged between 1.502% and 2.142%. The results have demonstrated that all four nanoparticles used in the experiment (MgO, ZnO, TiO_2, SiO_2) can be used as impregnation materials in compliance with studied tests. Particularly, SiO_2 has exhibited high performance in increasing the antifungal properties of pine wood.

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SOME PHYSICAL AND BIOLOGICAL PROPERTIES OF *PINUS SYLVESTRIS* WOOD IMPREGNATED WITH NANO-SOLUTIONS

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1. Introduction

From the past to the present, wood material has found various uses areas in every country and every culture (Ramirez-Coretti et al., 1998). However, when wood material is left to its natural durability, it tends to deteriorate over the years and lose its economic value. To prevent this loss and extend the lifespan of wood material, it is necessary to impregnation with some chemicals which have resistant against to biological, physical and chemical factors (Chernenko, 2017).

The process of treating wood to enhance its natural resistance, extend its service life, and protect it against various biological factors is called "impregnation." Looking at today's context, the environmental sensitivity of the impregnation materials used has become of great importance (Kjellow and Henriksen, 2009). Particularly, the banning and restriction of the use of impregnation materials containing arsenic in Europe after the United States, Canada, and Japan has made significant contributions to increasing environmental awareness. Following these bans, the impregnation industry and wood preservation companies have aimed to develop environmentally friendly, more natural, next-generation impregnation materials to both prolong the life of the wood and minimize environmental harm (Schultz et al., 2004). Natural preservatives derived from various plants such as tannins, come to mind are the first ones in this field (Pizzi, 2016). These natural products provide resistance against adverse weather conditions such as sunlight and rain, as well as harmful effects from organisms like insects and fungi, but they may not fully fixate onto the wood (Tomak and Gonultas, 2018).

With the advancement of technology, new methods and materials are being discovered in the field of wood impregnation (Kurkowiak et al., 2022; Zelinka et al., 2022). One of these methods is impregnation with nanoscale materials, which has emerged with the development of nanotechnology. Nanotechnology is a branch of science and technology that involves the manipulation of atoms and molecules in the size range of 1-100 nanometers (White et al., 2009). Nanotechnology finds applications in various fields such as chemical engineering, physics, electrical engineering, materials science, chemistry, biology, and more (Stephanopoulos and Reklaitis, 2011; Bayda et al., 2019).

In recent years, the use of nanotechnology has gained significant potential in the forestry sector (Papadopoulos and Taghiyari, 2019). Nanotechnology contributes significantly to improving the use of wood and enhancing the economic value of forest products. Nanotechnology offers various opportunities in the forest products industry, ranging from the production of raw materials to new approaches for wood-based materials and applications in composites and paper products (Chauhan and Chakrabarti, 2012; Jasmani et al., 2020). Nano-scale lignocellulosic surfaces can open new possibilities for functionalizing wood materials, enabling self-cleaning surfaces and more. The use of nano-sized building blocks can make materials lighter and reduce energy requirements. Nanotechnology can also be applied to improve moisture problems in wood-based materials, making them suitable for paper product applications to use outdoor applications (Chauhan and Chakrabarti, 2012).

In a study conducted by Taghiyari (2011), *Populus nigra* samples were impregnated at 2.5 bars inside a chamber, with water-based nano-silver solution at 45°C for 24 hours. Then wood samples were treated with heat treatment at different temperatures and durations. The test results showed a decrease in resistance values. However, it was indicated that the breakdown and pyrolysis processes were not effective and did not penetrate the inner parts of the material. Additionally, heat-treated samples exhibited increases in elastic modulus and compressive strength.

In another study, Akhtari et al. (2012) impregnated *Paulownia fortunei* wood with silver, copper, and zinc oxide nanoparticles. This study aimed to investigate the effects of impregnating *Paulownia fortunei* with silver, copper, and zinc oxide aqueous nanoparticles ranging in size from 10 to 80 nm on the mechanical properties of the wood, which has a dry density of 0.37 g/cm^3. Mechanical properties are generally considered as crucial characteristics for wooden products in structural applications. Therefore, these properties hold vital importance for the material. For the study, test samples were impregnated with a 400 ppm aqueous nano-silver, nano-copper, and nano-zinc oxide suspension under a pressure of 2.5 bars in a pressure chamber for 20 minutes. The results obtained showed a significant improvement in mechanical properties, with the highest enhancement observed in samples impregnated with nano-copper.

Additionally, it was observed that nano-copper and nano-zinc oxide-impregnated samples formed chemical bonds between the nanoparticles and the wood cell structure.

In a study by Afrouzi et al. (2013) the resistance of poplar wood (*Populus deltoides*) impregnated with nano-zinc oxide to color change was investigated. For this purpose, samples were impregnated with nano-zinc oxide at three concentrations: 0.5%, 0.75%, and 1% using the full-cell method. Subsequently, the samples were exposed to artificial weathering tests for 200, 400, and 600 hours. At the end of each stage, the color change of the samples was measured. Nano-zinc oxide was found to reduce the interaction of UV radiation, especially on the lignin wood surface, by increasing the contact surface area and improving optical properties, thus preventing the formation of free radicals. These results indicate an increase in resistance to color change in wood. Additionally, nano-zinc oxide not only enhances anti-UV properties but also reduces wood's air permeability and increases its hardness. Therefore, it can be said that nano-zinc oxide reduces erosion, graying and surface deterioration occurring in outdoor environments. As a result, it was concluded that nano-zinc oxide can be used as a color change inhibitor in the formulations of materials used for wood protection.

In a study conducted by Habibzade et al. (2016) the effects of ZnO nanoparticles on the fire retardancy, physical, and mechanical properties of polymerized poplar wood were investigated. Poplar samples were impregnated with styrene monomer containing four different nano ZnO contents (0, 0.5%, 1%, and 1.5%) based on the monomer's dry weight. As a result, the presence of zinc oxide nanoparticles significantly improved the physical and mechanical properties of poplar wood impregnated with styrene. It was observed that nano-zinc oxide enhanced some fire-retardant properties of poplar wood.

This study focuses on investigating the potential use of nanoparticles which can penetrate micro-pores and provide more effective protection with smaller quantities, on wood. In accordance with this purpose, water absorption rate and fungal decay performances were investigated of Scots pine wood samples impregnated with some nanoparticles such as MgO, ZnO, TiO_2, and SiO_2.

2. Materials and Methods

Methods of data collection and analysis employed in the research are described in this section.

2.1. Material

2.1.1. Wood Material

In this study, the sapwood of Scots pine (*Pinus sylvestris* L.) trees, naturally grown in Turkey and considered a valuable timber, species was used. The wood raw material was obtained from Yıldız Village in the Torul district of Gümüşhane province. The altitude of the location where the trees were cut is 1300 meters.

2.1.2. Impregnation Solutions

Nano-sized MgO (45 nm), ZnO (25-35 nm), TiO_2 (4-28 nm), SiO_2 (28 nm) were used as impregnation agents. These chemicals were sourced from the Nanografi company (Ankara, Turkey) and were dispersed in water for the study.

2.2. Method

2.2.1. Preparation of Wood Samples

The samples used in the experiment were selected according to TS 345 (2012) criteria, ensuring that they were free from knots, in good condition, and free from decay.

2.2.2. Preparation of Impregnation Solutions

The impregnation solutions were prepared using pure water through weight percentage calculations. To ensure homogenous mixing, the prepared impregnation solutions were stirred on a magnetic shaker at a speed of 1000 rpm for 10 minutes. A concentration of 1.5% of the impregnation agent was prepared. The nano solutions used for impregnation in the laboratory experiment are shown in Figure 1.

Figure 1: Impregnation solutions prepared for experiments

2.2.3. Impregnation Process

The impregnation process was carried out using the full-cell method. According to this method, the wood samples, which were air-dried, were placed inside the impregnation vessel. Initially, a vacuum of was applied for 15 minutes to remove the air from the cell lumens. Following this, the impregnation solution was applied at 7 bars of pressure for 60 minutes.

Retention was calculated as follows Equation 1;

$$R\ (kg/m^3) = (G \times C) / V \times 10 \quad (1)$$

R represents the retention amount in kilograms per cubic meter (kg/m^3).
$G = T_2 - T_1$;
G: The amount of impregnating substance absorbed in grams (gr).
T_1 is the weight of the test sample before impregnation in grams (gr).
T_2 is the weight of the test sample after impregnation in grams (gr).
C represents the solution concentration in percentage (%).
V is referred to as the sample volume in cubic centimeters (cm^3).

2.2.4. Water Absorption Rate

The water absorption rate (WAR) was calculated for samples with dimensions of 6.4 x 25 x 50 mm^3. The impregnated samples were dried at 103±2°C until a constant weight was reached and the weight and dimensions of the completely dry samples were determined. Subsequently, a specific amount of water was placed on them, and they were left with a weight on top. The specimens were soaked in water for 2, 4, 8, 24, 48, 72 hours, and 1 week. At the end of each period, the water on the absorbing samples was wiped off and the dimensions of the test and control samples and the amount of absorbed water were determined. The initial completely dry weight values were used to calculate the WAR (%) for each individual experimental and control sample. The water absorption ratios were calculated according to Equation 2, (Tomak, 2011).

$$WAR\ (\%) = [(W_t - W_0)/W_0] \times 100 \quad (2)$$

In the equations:
W_0: Initial completely dry weight (grams).
W_t: Weight of the sample removed from water at each interval (grams).

2.2.5. Fungal Decay Test

The fungal decay test was conducted according to the European Union Standard (EN-113, 1996) with modifications. The impregnated samples (0.5x1.5x2.5 cm) were sterilized in an autoclave at 121°C for 20 minutes.

For the fungal culture medium, a malt-agar mixture was prepared. To achieve this, 140 grams of malt extract and 20 grams of agar were mixed in 1 liter of distilled water. Each culture bottle was filled with 60 ml of the prepared mixture. The bottles were sealed and sterilized in an autoclave. Once sterilization was completed, the culture bottles were placed in a UV cabinet and left for one day. After one day, fungal mycelia were inoculated into each culture bottle, and the bottles were kept in a climate chamber under conditions of 70% ± 5 relative humidity and 22 ± 2°C until the mycelia completely colonized the culture medium.

In culture bottles where fungal colonization of *Coniophora puteana* was completed, one control and one impregnated wood sample were placed. The samples were kept in the climate chamber under conditions of 70% ± 5 relative humidity and 22 ± 2°C for 14 weeks. At the end of this period, the samples were kept in an oven at 103 ± 2°C until a constant weight was reached, and their completely dry weights were calculated. After removing fungal mycelia residues from the sample surfaces, the dry weights (Ms) were recorded, and weight loss was measured using Equation 3.

$$W_L\ (\%)=[(W_t-W_0)/W_0)]x100 \quad (3)$$

In this equation:
W_L: Weight Loss (%)
W_0: Initial weight before the experiment (grams)
W_t: Weight after the experiment (grams)

According to the standard, for the test to be considered valid, the weight loss in the control (non-impregnated) samples should be at least 20%. To deem an impregnation material successful, the weight loss in the impregnated (test) wood samples should be a maximum of 5%, or according to the new European standards, 3% (EN 113, 1996).

3. Results

Retention values of impregnated wood samples were given in Table 1.

Table 1: Retention values of impregnated wood samples

	Retention (kg/m³)	
	Average	**Standard deviation**
MgO	12.237	3.036
ZnO	13.218	1.640
TiO_2	10.261	1.068
SiO_2	10.766	2.021

The water absorption rate of impregnated wood samples is shown in Figure 2.

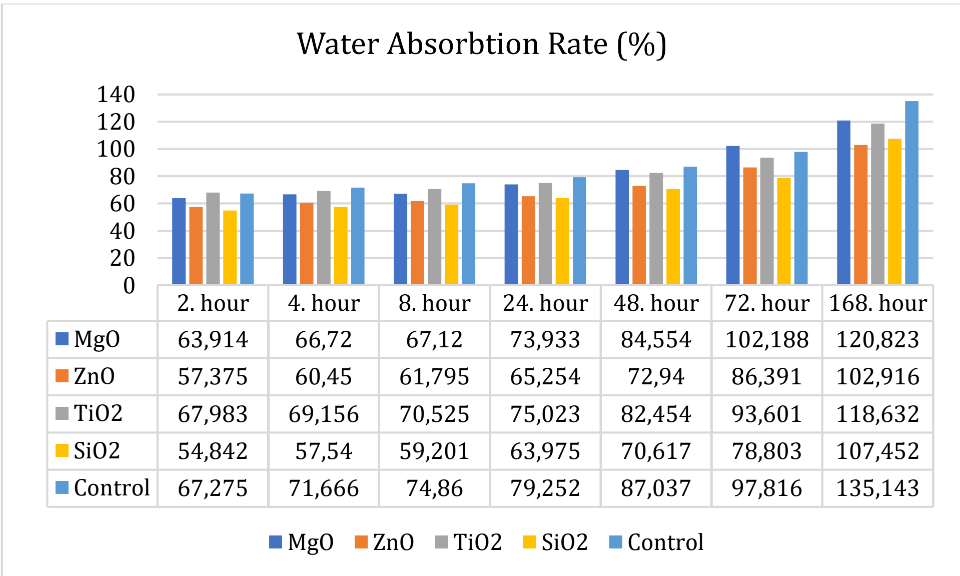

Figure 2: Water absorption rate of impregnated wood samples

Weight losses of wood samples after fungal decay test were given in Table 2.

Table 2: Weight losses of wood samples after fungal decay test

Weight losses (%)		
Impregnation solution	**Average**	**Standard deviation**
MgO	2.136	0.375
ZnO	2.142	0.456
TiO_2	1.989	0.135
SiO_2	1.502	0.103
Control	38.560	6.345

4. Discussion

The retention rate of the wood samples impregnated with nano-MgO, ZnO, TiO_2 and SiO_2 were determined 12.237±3.036, 13.218±1.640, 10.261±1.068, 10.766±2.021 kg/m^3, respectively. Muhcu (2015) impregnated Scots pine wood samples with impregnation solutions prepared at a concentration of 1.0% for nano-ZnO using ethanol as a solvent and for nano-CuO, nano-TiO_2, and nano-CeO_2 using ammonia as a solvent. They reported retention values for nano-ZnO, nano-CuO, nano-TiO_2, and nano-CeO_2 as 4.906±0.728, 5.886±0.364, 5.530±0.738, and 3.780±0.354 kg/m^3, respectively. The reason for the higher retention values compared to the results in this study can be attributed to the use of impregnation solutions at a higher concentration, despite the similar nanochemicals being used.

In the study, impregnation was carried out with solutions prepared using only water at 1.5% concentration for MgO, ZnO, TiO_2, SiO_2 and control samples. The WAR values for these samples were found to be 120.823±13.45, 102.916±12.56, 118.632±13.41, 107.452±12.59 and 135.143±14.91%, respectively. When examining the WAR values of Scots pine wood samples impregnated with the four chemicals at a concentration of 1.5% (based on 336 hours), it is observed that the highest WAR is in the control (non-impregnated) sample, while the lowest water absorption rate is in the samples impregnated with ZnO. In a previous study, Scots pine wood samples were impregnated with impregnation solutions prepared at a concentration of 1.0%, using ethanol as a solvent for nano-ZnO and ammonia for nano-CuO, nano-TiO_2, and nano-CeO_2. According to measurements taken at 24 hours, the WAR for the control sample and nano-ZnO, nano-CuO, nano-TiO_2, and nano-CeO_2 impregnated samples were reported as 71.35±4.10, 61.78±5.70, 66.72±7.16, 67.26±2.67, and 62.54±4.36%, respectively (Muhcu,2015). It can be said that the difference between the results of the mentioned study and this study is due to the difference in the solvents of the impregnation solutions. In both studies, the samples impregnated with ZnO and the control samples were the ones that absorbed the least and most water, respectively.

In another study, conducted by Kızılırmak and Aydemir (2019), the effects of impregnating thermally treated Beech (*Fagus orientalis*) and Oak (*Quercus robur*) wood with nano-sized titanium dioxide and boron nitride on wood properties were investigated. According to the results obtained from the applied method and experiments, impregnating wood with nanoparticles and the thermal treatment of wood generally reduced the wood-water relationships. It was determined that thermal treatment is a significant factor in reducing wood's water absorption and dimensional stability. It was observed that the impregnation of wood with TiO_2 nanoparticles reduced water absorption more than the impregnation with nanoboron nitride.

The fungal decay test has been successful. This is because the weight loss in the control samples was observed to be 38.560% because of the experiment. Considering the obtained results, it can be said that all four nanoparticles used in the experiment, MgO, ZnO, TiO2, and SiO2, can be used as impregnation materials in compliance with European standards. Specifically, in the MgO-impregnated sample, a weight loss of 2.136% was observed; in the ZnO-impregnated sample, a weight loss of 2.142% was observed; in the TiO2-impregnated sample, a weight loss of 1.989% was observed, and in the SiO_2-impregnated sample, a weight loss of 1.502% was observed.

In a previous study, Scots pine wood samples were impregnated with impregnation solutions prepared at a concentration of 1.0%. Ethanol was used as the solvent for nano-ZnO, and ammonia was used for nano-CuO, nano-TiO_2, and nano-CeO_2. In the decay test results against *Tramates versicolor* fungus, the weight loss for the control sample and the samples impregnated with nano-ZnO, nano-CuO, nano-TiO2, and nano-CeO_2 solutions was reported as 20.62±4.14, 8.78±4.24, 1.69±0.62, 1.60±0.53, and 7.13±4.28%, respectively (Muhcu,2015).

De Filpo et al. (2013) conducted antibacterial and antifungal tests on eight different types of wood commonly used in cultural heritage sites to measure the performance of nano-TiO_2 particles. The research results revealed that nano-TiO2 particles inhibited the growth of both *Hypocrea lixii* (white rot) and *Mucor circinelloides* (brown rot) fungi, regardless of the wood type.

Akhtari and Arefkhani and Arefkhani (2013) investigated the resistance of *Paulownia fortunei* wood treated with silver, copper, and zinc oxide nanoparticles to white rot fungus. The tree samples were pressure-impregnated with a 400 ppm aqueous suspension. The samples were inoculated with the fungus and incubated in nano-zinc oxide for sixteen weeks following the EN113 (1996) standard. According to Scanning Electron Microscopy (SEM) examinations, the average weight loss of Paulownia wood treated with nano-silver, nano-copper, and nano-zinc oxide particles was 2, 2, and 2% respectively after 16 weeks. It was found that the mass loss due to decay was higher in the control Paulownia wood (28.13%). Additionally, the formation of intercellular voids between cellulose microfibrils was observed. No noticeable differences were observed in SEM images between decayed wood treated with nanoparticles and undecayed wood.

Clausen et al. (2010) investigated the effects of zinc oxide (ZnO) nanoparticles with a diameter of 30-70 nm on the termite resistance and retention properties of pine wood. According to the obtained results, the ZnO treatment did not cause a significant change in termite resistance and peeling. It was found that only a 5% ZnO treatment reduced wood material degradation by 4%.

5. Conclusion

In the study, it was proved that all four nanoparticles (MgO, ZnO, TiO_2, SiO_2) can be used as impregnation materials. Especially, SiO_2 (Silicon dioxide) has been observed to provide high efficiency in increasing the antifungal properties of pine wood. As known, SiO_2 is naturally found on Earth in water, plants, animals and especially rocks and nanotechnology exists that allows the production of this product at the particle level. For this reason, it is estimated that SiO_2 nanoparticle will be used more widely as an effective and economical impregnation agent in the wood protection industry soon. In addition, leaching test should be performed before the fungal decay test to obtain information about its usability in the outdoor. Finally, it is also recommended to investigate the effects of nano-solutions used in this study on mechanical properties.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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