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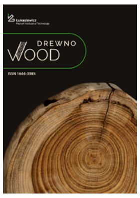

Evaluation of Pine Wood Performance Following Multifunctional Compound Treatments

Ayşenur Gürgen[a *]
Sibel Yildiz[b]

[a] Osmaniye Korkut Ata University, Osmaniye, Turkey
[b] Karadeniz Technical University, Turkey, Trabzon, Turkey

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In this study, the usability of artificial antioxidants, nano-oxides, and generally regarded as safe (GRAS) compounds in the wood preservation industry was investigated. For this purpose, some physical, biological, and mechanical properties and surface chemistry analysis of Scots pine wood impregnated with 14 different compounds selected from these three different groups was performed. The physical changes in the impregnated samples were evaluated based on water absorption rate and water repellency. In addition, combustion behavior and color changes were examined to assess fire and surface optical/color properties, respectively. To investigate the biological properties of the impregnated wood samples, a fungal decay resistance test was applied using Coniophera puteana fungus. To reveal the changes in the mechanical properties of wood compression strength parallel to grain test was applied. The limit oxygen index (LOI) test was conducted to investigate the combustion properties of the impregnated wood samples. To interpret the interaction of the impregnated samples with wood, surface chemistry analysis was carried out, and a Fourier Transform Infrared Spectroscopy (FTIR) test was performed. Scanning electron microscopy (SEM) analyses were performed to observe the distribution of impregnated samples in the wood. After all these tests, it can be concluded that the tested artificial antioxidants, nano-oxides, and GRAS compounds can be used as impregnation materials. Especially, nano-oxides exhibited good performance in many aspects. Therefore, it is recommended to examine nano-oxides more closely with other experimental variations. As a result, such multifunctional compounds could be promising protection alternatives with environmentally friendly characteristics to highly toxic biocides.

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Introduction

Wooden material, which has been used in tool making and construction timber from ancient times to the present day, continues to appear in almost every aspect of life with its many different derivatives (Järvinen et al., 2022). Due to its widespread availability, being a renewable natural resource, its pleasing aesthetic appeal, mechanical strength, relatively low cost, and ease of processing, wood is a preferred material for various applications (Iejavs & Spulle, 2016). In addition to energy production, it also serves as a raw material source in the manufacturing of paper and paper products (Haile et al., 2021). Wood is also used as a filler for plastic composites (Delviawan et al., 2019; Kim et al., 2011) and as a source of feedstock for biofuel production (Lin & Lu, 2021; Sedjo & Sohngen, 2013).

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[*] Corresponding author: aysenurgurgen@osmaniye.edu.tr

Wood is undoubtedly an excellent engineering material with high performance. However, it also has some disadvantages that cannot be ignored. Some of these disadvantages include the problem of dimensional stabilization (working) in humid environments, adverse effects of ultraviolet (UV) radiation, especially in high altitudes, flammability, and low resistance to biological degradation caused by insects, fungi, and other organisms (Goodell et al., 2020; Pánek et al., 2021; Marais et al., 2022). For this reason, it is very important that wood is treated with a few protective pre-treatments to extend its service life at the end-use location (Popescu & Pfriem, 2020).

It has been known that in the late 1990s, concerns were raised about the use of heavy metals in wood preservatives and potential emissions during their disposal at the end of their service life (Freeman et al., 2003). As a result, the use of CCA for wood preservation has been significantly reduced in most European and Asian countries, and CCA-treated wood is restricted to industrial applications in the USA (Lebow et al., 2004).

Traditionally, natural extracts have been used for wood preservation throughout history. Natural plant extracts have been a potential approach to develop chemical-free wood preservatives against wood-destroying fungi and insects (Broda, 2020; Akkuş et al., 2022). Since some natural extracts contain tannins or have toxic effects against biotic agents, they are preferred for protection against organisms that destroy wood or wood-based materials (Schultz & Nicholas, 2000). However, oils, tars, and plant extracts are difficult to obtain and, therefore, less sustainable, can be economically unfavorable, and have many disadvantages, such as being washed from wood (González-Laredo et al., 2015).

It is a fact that the use of chemicals in wood protection will continue until the disadvantages of natural extracts are overcome for a sustainable market. In this case, the search for cheaper, more environmentally friendly chemicals that only show activity against the target organism and do not show toxic effects on non-target organisms (for example, some preservative chemicals used in food, agriculture, or the textile industry) will continue. In this sense, investigating the possibilities of using preservative compounds used in food in the field of wood protection can be considered as one of the alternative solutions to meet the expectations listed. The aim of this study was to investigate the usability of a total of 14 different chemicals selected from three different multifunctional chemical groups (artificial antioxidants, generally regarded as safe additives (GRAS) compounds in the wood preservation industry. For this purpose, some physical, mechanical, biological, and combustion properties, surface chemistry, and surface morphology of yellow pine wood impregnated with these chemicals were investigated.

Material and method

1. Material

The Scots pine (*Pinus sylvestris* L.) trees felled from Yıldız village in Torul district of Gümüşhane province, Turkey. The altitude, where the trees were cut, is 1300 m, and the coordinates are 40°29’40” N, 39°10’39” E. For sectioning the samples, a “Reichert” sliding microtome equipped with a wedge-shaped blade No. II was used. From each sample, cross (transversal), longitudinal radial, and longitudinal tangential sections with a thickness of 15–20 microns were prepared. After performing the standard preparation procedures, the sections were mounted as permanent slides using glycerin-gelatin. The prepared slides were examined using an Olympus BX50 light microscope. The obtained images were transferred to the Digimizer software, and the measurements were performed using this program (Ives, 2001).

In the present study, synthetic antioxidants, including erythorbic acid, ethoxyquin, potassium disulfide, sodium ascorbate, sodium erythorbate, and tert-butylhydroquinone (TBHQ), were procured from Sigma-Aldrich (St. Louis, MO, USA). Generally Recognized as Safe (GRAS) compounds, namely dehydroacetic acid, sorbic acid, and sodium benzoate, were obtained from Merck (Darmstadt, Germany). All chemicals used throughout the experimental procedures were supplied by these manufacturers. Additionally, magnesium oxide (MgO), cerium(IV) oxide (CeO_2), zinc oxide (ZnO), silicon dioxide (SiO_2), and titanium dioxide (TiO_2) nano-oxides, pre-dispersed and activated in aqueous media, were provided by Nanografi A.Ş. (Ankara, Türkiye).

2. Impregnation Solutions

The impregnation solutions were prepared at 1.0% concentration with the appropriate solvent using percent weight by mass calculation. The prepared impregnation solutions were mixed for 10 minutes at 1000 rpm using a magnetic shaker to provide homogeneity. Synthetic antioxidants such as erythorbic acid, potassium disulfide, and sodium ascorbate were prepared in water, whereas ethoxyquin, TBHQ, dehydroacetic acid, and sorbic acid were dissolved in ethanol. Sodium benzoate and sodium erythorbate were also used in aqueous solutions. The nano-oxides (MgO, CeO_2, ZnO, TiO_2, and SiO_2) were dispersed in water.

3. Impregnation

The wood samples were prepared in accordance with the specifications outlined in the relevant testing standards. The impregnation procedure was carried out using the full-cell method. In this method, an initial vacuum of -60 mmHg was applied for 15 minutes, followed by the application of a pressure of 6000 mmHg for 45 minutes. Upon completion of the impregnation process, any excess solution on the sample surfaces was carefully removed using a dry cloth. Subsequently, the samples were weighed with a precision of ±0.01 g, and the retention values were calculated using Equation 1.

$$R\ (kg/m^3) = \frac{G\,x\,C}{V}\,x\ 10 \tag{1}$$

In this formula, the variables are defined as follows: R represents the retention amount (kg/m^3), G is the quantity of impregnation solution absorbed by the sample, calculated as the difference between the post- and pre-impregnation weights ($G = T_2 - T_1$), where T_1 is the initial weight of the test sample before impregnation (g), T_2 is the weight of the test sample after impregnation (g), C denotes the concentration of the impregnation solution (%), and V is the volume of the wood sample (cm^3).

4. Physical properties after impregnation

The physical changes in the impregnated samples were investigated by determining the water absorption rate and water repellent efficiency values, and color changes measurements.

5. Water absorption rate and water repellent efficiency values

Samples sized 15x30x30 mm were used for the calculation of water absorption ratio (WAR) and water repellent efficiency (WRE) values. For this experiment, 10 samples were used. The impregnated samples were dried at 103±2 °C until they reached constant weight, and the weight and dimensions were determined in the completely dry state. They were then placed in a certain amount of water by placing a weight on top of them. The amount of water absorbed by the experimental and control samples during 2, 4, 8, 24, 48, 72 hours, 1, and 2 weeks was determined by weighing. For this purpose, at the end of each period, the excess water on the samples taken from the water was wiped off and weighed with a sensitivity of 0.01. Using the initial full dry weight values, the WAR (%) was calculated for each experimental and control sample separately. Water repellent efficiency (WRE) values, which can be expressed as the reduction in water uptake rates of impregnated test samples compared to control samples, were determined for each test sample. WAR and WRE were calculated according to Equations 2 and 3, respectively (Kartal et al., 2007).

$$\text{WAR}\ (\%) = \left(\frac{(\text{M}_2 - \text{M}_0)}{\text{M}_0}\right)x100 \tag{2}$$

$$\text{WRE}\ (\%) = \left(\frac{(\text{WARc} - \text{WARt})}{\text{WARc}}\right)x100 \tag{3}$$

In the equations, M_0: Initial complete dry weight (g), M_2: Weight of the sample removed from the water after each period (g), WARt: Water uptake rate of test samples (%), WARc: Water uptake rate (%) of control samples.

6. Color measurement analysis

Color alterations in the wood samples following the impregnation process were assessed using a Konica Minolta CM-2600d color measurement device, in accordance with the ISO 7724 standard (ISO-7724, 2003). Measurements were conducted at four distinct points on each sample, and the mean values were calculated. A total of 10 samples were utilized for the color measurement analysis.

The color parameters were determined using the CIELAB color space (Commission Internationale de l'Éclairage), which includes three parameters: L*, a*, and b*. In this system, L* represents lightness, with higher values indicating lighter colors, while a* and b* are the chromatic coordinates. Specifically, +a* indicates redness, -a* represents greenness, +b* corresponds to yellowness, and -b* signifies blueness.

The L*, a*, and b* values were measured in samples subjected to outdoor exposure for various durations. The color changes were then calculated using the following equations (Equations 4–7).

$$\Delta L^* = L_f^* - L_i^* \tag{4}$$

$$\Delta a^* = a_f^* - a_i^* \tag{5}$$

$$\Delta b^* = b_f^* - b_i^* \tag{6}$$

$$\Delta E^* = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \tag{7}$$

7. Biological test methods

In order to investigate the biological properties of the impregnated wood samples fungal decay test was applied.

8. Fungal decay test

The fungal decay test was conducted following the EN-113 (2006) standard, using *Coniophora puteana* BAM Ebw. 15., a brown rot fungus, as specified by the standard. For this experiment, a total of 10 samples were utilized. Each test group consisted of one control (unimpregnated) sample and one impregnated sample, both of which were placed in petri dishes and kept in an acclimatization cabinet for a duration of 16 weeks.

At the conclusion of the exposure period, the samples were removed from the culture bottles and dried in an oven at 103±2 °C until they reached a constant weight. The exact dry weights of the samples were then recorded. After the removal of any dried mycelial particles from the wood, a second weight (M_2) was taken using a precision balance. The weight loss values were subsequently calculated using Equation 8.

$$\text{Weight loss (\%)} = \left(\frac{(M_2 - M_0)}{M_0}\right) x100 \qquad (8)$$

M_0: Initial complete dry weight (g), M_2: Dry weight of the sample after fungal decay test (g)

9. Mechanical properties

In order to investigate the mechanical properties of the impregnated wood samples, a compression strength parallel to grain test was applied.

10. Compression strength parallel to grain

The test was carried out in accordance with (TS-2595, 1977) standard using a universal testing machine. For this purpose, the samples prepared in the dimensions of 20×20×30 mm were impregnated and acclimatized at 20 °C and 65% relative humidity. The width and thickness of the samples, which were acclimatized and brought to air-dry humidity, were measured with the help of a micrometer with a sensitivity of ±0.01 mm before the experiment. The experiments were carried out under static load with a loading rate of 2 mm/min. The load application continued until the sample fractured, and the maximum load value read from the dial at the moment of fracture was recorded. For this experiment, 10 samples were used.

The force at the moment of fracture () was measured and the compressive resistance parallel to the fibres (was calculated using Equation 9;

$$\sigma_{B//} = \frac{F_{max}}{a * b}\left(\frac{N}{mm^2}\right) \qquad (9)$$

Here it is: a: Sample cross-section edge length (mm), b: Represents the sample cross-section edge length (mm).

11. Combustion properties

The limit oxygen index (LOI) test was performed to determine the resistance of the impregnated samples against combustion.

12. Limiting oxygen index (LOI) test

The limiting oxygen index (LOI) test for the samples was conducted using a Dynisco brand oxygen index device, following the guidelines of the D2863-10 (2000) standard. The LOI test measures the minimum concentration of oxygen in an oxygen-nitrogen mixture required to sustain the flaming combustion of a material. This standardized test method determines the minimum oxygen concentration necessary to maintain a sustained flame under the specified experimental conditions.

13. Surface chemistry analysis

To analyze the interaction between the impregnated samples and the wood, surface chemistry analysis was conducted using Fourier-transform infrared spectroscopy (FTIR). This test provides detailed information on the chemical structure and functional groups present on the wood surface, helping to assess any changes or interactions resulting from the impregnation process.

14. Fourier-transform infrared spectroscopy (FTIR)

This analysis was performed using a Shimadzu Fourier-transform infrared spectroscopy (FTIR) device. FTIR analysis was performed on impregnated and unimpregnated (control) samples by scanning in the 1800-700 cm^{-1} wave range.

15. Surface morphology analysis

Scanning electron microscopy (SEM) analyses were performed to see the distribution of impregnated samples in the wood.

16. Scanning Electron Microscopy (SEM) analysis

For scanning electron microscope (SEM) analysis, 5x5x5 mm-sized samples were used. The direction of the samples to be examined was corrected using a microtome before impregnation, and possible shape errors due to saw cutting were prevented from appearing. After the impregnated samples were dried, the surface to be examined was coated with gold, and images were taken.

17. Statistical analysis

All analyses conducted in this study were performed using the “SPSS 21.0 for Windows” software. To assess differences between the groups in the tests, simple variance analysis (ANOVA) was applied. Following ANOVA, the Duncan test was utilized at a confidence level of (α = 0.05) to identify specific differences between the groups.

Results and discussion

1. Pine wood

Based on the measurements, the tangential widths of the earlywood tracheids and latewood tracheids were calculated as 26.884 ± 5.007 µm and 11.224 ± 2.843 µm, respectively. In the radial direction, the same wood elements were measured as 29.659 ± 4.674 µm and 5.156 ± 1.814 µm, respectively. The ray width and ray length were calculated as 15.720 ± 7.857 µm and 163.037 ± 15.923 µm, respectively. The latewood cell wall thickness was found to be 7.914 ± 2.091 µm, while the earlywood cell wall thickness was measured as 3.432 ± 0.773 µm.

2. Retention

Retention values of impregnated samples are presented in Table 1.

As can be seen from Table 1, the lowest amount of retention was obtained from dehydroacetic acid solution with a value of 4,505 kg/m^{3,} and the highest value was obtained from wood samples impregnated with sodium ascorbate solution with a value of 6,563 kg/m^3. As a result of the statistical analysis, no statistically significant difference was found between the retention values calculated after impregnation with 14 chemicals ($p>0.05$). Therefore, although the retention values do not appear to be the same for each chemical, it is possible to say that they penetrate the wood at approximately the same rate, as they are very close to each other. This may be because the solutions used in this part of the study were impregnated at the same concentration (1.0%).

3. Water absorption rate and water repellent efficiency values

The water absorption rates of the impregnated wood were presented in Figure 1.

The highest water absorption rate was observed in the control (unimpregnated) sample, with a value of 177.17±6.87%. In contrast, the lowest water absorption rate was recorded for the samples impregnated with ZnO, which showed a rate of 102.49±4.62%, based on the 336-hour measurement period.

When the 3 groups were compared among themselves, it was seen that the lowest water uptake rates were in the wood impregnated with nano-oxides. This was followed by wood impregnated with artificial antioxidants and samples impregnated with GRAS compounds, in order of increasing water uptake rates. Impregnation with nanomaterials reduces the pore size and the available space within the cell wall that is typically used for the absorption of water molecules (Fufa and Hovde, 2010). This reduction in pore size limits the wood's ability to absorb water, thereby enhancing its resistance to moisture uptake.

Table 1. Retention values of impregnated samples

Group	Chemical	Solvent	Retention (kg/m^3)
Artificial antioxidants	Erythorbic acid	Water	6,124±0,556^a
	Ethoxyquin	Ethanol	5,245±0,825^a
	Potassium disulfide	Water	6,055±0,758^a
	Sodium ascorbate	Water	5,840±0,723^a
	Sodium erythorbate	Water	5,197±0,547^a
	TBHQ	Ethanol	5,358±0,261^a
GRAS	Dehydroacetic acid	Ethanol	4,505±0,834^a
	Sorbic acid	Ethanol	5,197±0,762^a
	Sodium benzoate	Water	6,051±0,856^a
Nano-oxide	MgO	Water	6,054±0,731^a
	CeO_2	Water	6,512±0,891^a
	ZnO	Water	6,127±0,492^a
	TiO_2	Water	6,536±0,863^a
	SiO_2	Water	5,974±0,625^a

* Means followed by different letter(s) differ significantly at $p<0.05$ (Duncan's multiple range test)

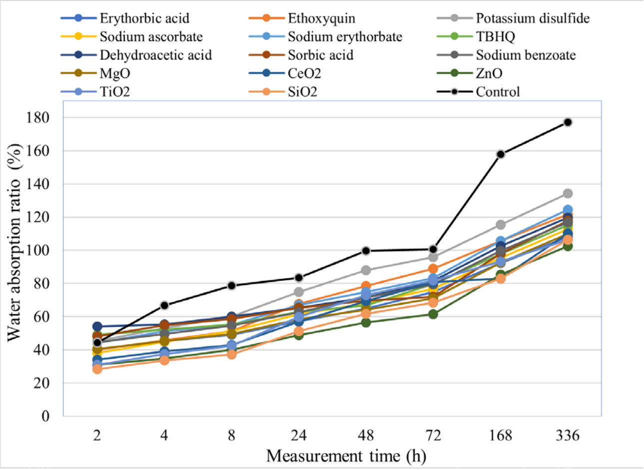

Fig. 1. Water absorption rate of impregnated wood

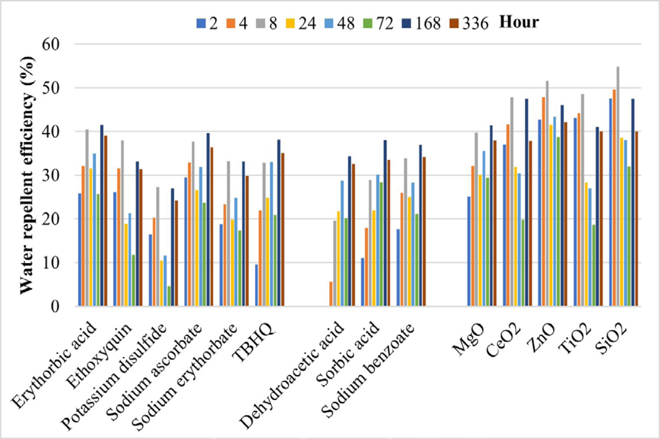

Fig. 2. Water repellent efficiency

Clausen et al. (2010) used nano-ZnO at concentrations of 1%, 2.5% and 5% in the wash resistance and wettability tests. The wood samples impregnated with nano-ZnO showed resistance to washing. The distribution of the nano-ZnO metal particles was correlated with Van der Waals forces.

Water repellent efficiency of wood samples was shown in Figure 2. The water repellent efficiency value is calculated by dividing the water uptake rate of the impregnated wood samples by the water uptake rate of the control (non-impregnated) samples. Therefore, the lower the water uptake rate of an impregnated wood sample, the higher its water repellent efficiency value. This indicates a greater resistance to water absorption, reflecting the effectiveness of the impregnation process in enhancing the wood's water-repellent properties. Therefore, since the lowest water uptake rates were observed in the samples impregnated with nano-oxides in this study, the highest water repellent efficiency values were also observed in these wood samples. When the samples impregnated with artificial antioxidants and GRAS compounds were compared among themselves, the samples impregnated with GRAS compounds were found to have the lowest water repellent efficiency. Yu et al. (2017) reported that both wax and nano-SiO2 can be useful in maintaining the dimensional stability of wood.

4. Color changes

Color changes of impregnated wood were shown in Figure 3.

Based on the ΔL* value, it can be said that all 13 chemicals except sodium erythorbate darkened the color of the wood. The highest darkening was observed in wood impregnated with ethoxyquin and TBHQ.

The ΔE* value expresses the total color change and categorizes the total color change ranges. If this value is above 12, the change is described as a completely different color (Barcík et al., 2015). Based on this classification, it can be concluded that among the artificial antioxidants studied, ethoxyquin, with a value of 27.32±3.27, and TBHQ, with a value of 29.82±4.73, completely changed the color of the wood. None of

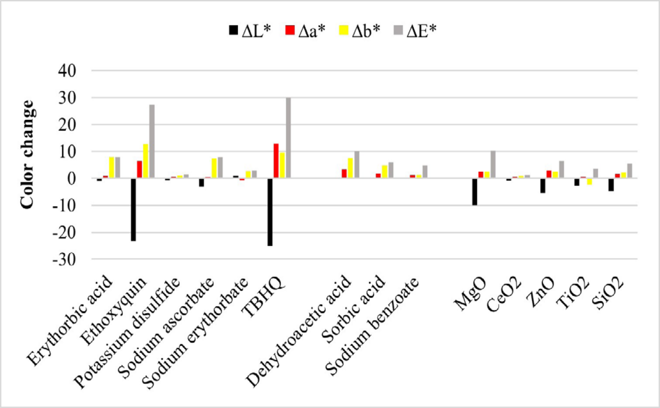

Fig. 3. Color changes of impregnated wood

the samples impregnated with GRAS compounds and nano-oxides completely changed the color of the wood.

In one study, after impregnation with nano zinc oxide, the samples showed almost no discoloration at three concentrations (0.5%, 1.0% and 1.5%). However, common preservatives such as creosote and water-soluble preservatives such as CCA have caused significant discoloration of wood (Afrouzi et al., 2013).

5. Fungal decay test

The weight losses of impregnated samples after the fungal decay test are shown in Figure 4.

The weight loss of wood samples impregnated with solutions prepared with artificial antioxidants after the fungal rot test varied between 11.21% and 8.75%. The weight loss of wood samples impregnated with solutions prepared with GRAS compounds ranged between 10.01% and 11.45%. This value is between 5,38% and 7,75% for the weight loss value of wood samples impregnated with solutions prepared with nano-oxides. The weight loss in the control samples was 39%. The best performance among these three groups was observed in nano-oxides.

Palanti & Feci (2013) in their study investigating the use of wood preservative formed by dissolving silica nanoparticles in boric acid as an impregnating agent in pine sapwood, reported that there was a 59.16% weight loss in pine control samples exposed to *Coniophora puteana* fungus damage, while the weight loss in the impregnated test sample was around 6.87%.

Mantanis et al. (2014) impregnated larch wood samples with nano-ZnO, nano-Zn-borate, and nano-CuO particles under vacuum and investigated the resistance properties of these chemicals against rot, mold fungi, and subterranean termites. They reported that nano-Zn-Borate, one of the nanoparticles used, provided some improvement in the resistance properties of wood samples against mold fungi. While the weight loss caused by the brown rot *fungus Tyromyces palustris* could not be prevented, the weight loss caused by the white rot fungus *Tramates versicolor* was reported to be significantly prevented.

In a previous study by Nair et al. (2017), the fungal decay and moisture adsorption of rubber tree (*Hevea brasiliensis* Muell. Arg) samples impregnated with nano-ZnO and nano-CuO dispersions in propylene glycol (PG) were evaluated. The dispersion of ZnO

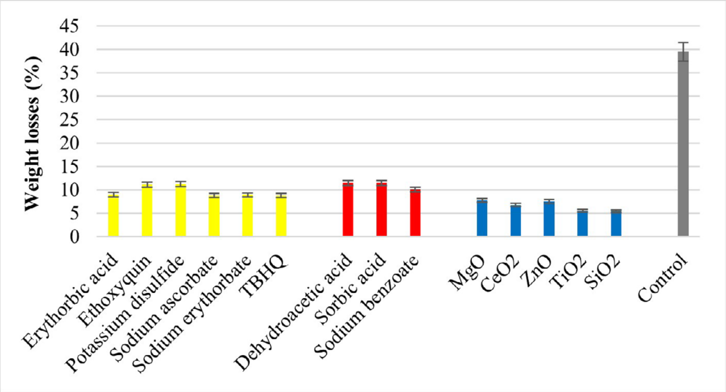

Fig. 4. The weight losses of impregnated samples after the fungal decay test

and CuO nanoparticles in PG was found to be effective in inhibiting the growth of white rot fungus (*Trametes hirsuta*) and brown rot fungus (*Polyporus meliae*). This study demonstrated the potential of nano-metal oxide impregnations in enhancing the resistance of wood to fungal decay and moisture absorption.

6. Compression strength parallel to grain

The compression strength parallel to grain values of impregnated wood samples are shown in Figure 5.

In the study, there was an increase in the compression strength parallel to grain values of the wood samples impregnated with 12 chemicals, except for those treated with impregnation solutions containing erythorbic acid and potassium disulfide. The slight decrease in the pressure values of the samples impregnated with erythorbic acid and potassium disulfide compared to the control sample was attributed to the acidic character of the solutions. It was stated that acidic solutions hydrolyze the bonds of cellulose molecules, which are the source of mechanical resistance, and have the potential to affect the mechanical resistance of wood materials (Kartal & Clausen, 2001).

The mechanical properties of wood are influenced by its isotropic characteristics, the type of treatment applied to enhance its properties, and environmental factors. Impregnating wood with nanoparticles can increase its hardness by filling the pore spaces within the wood structure (Fufa & Hovde, 2010). This enhancement in hardness occurs as the nanoparticles occupy voids in the wood, providing greater resistance to physical wear and improving overall mechanical strength.

7. Limiting oxygen index (LOI) test

Limiting oxygen index (LOI) values of impregnated samples are presented in Figure 6.

According to the LOI test, materials with high combustion properties have a low oxygen index, and materials with low combustion properties have a high oxygen index (Dönmez Çavdar et al., 2011). In other words, it is possible to say that flammability and LOI value are directly correlated. While the LOI value

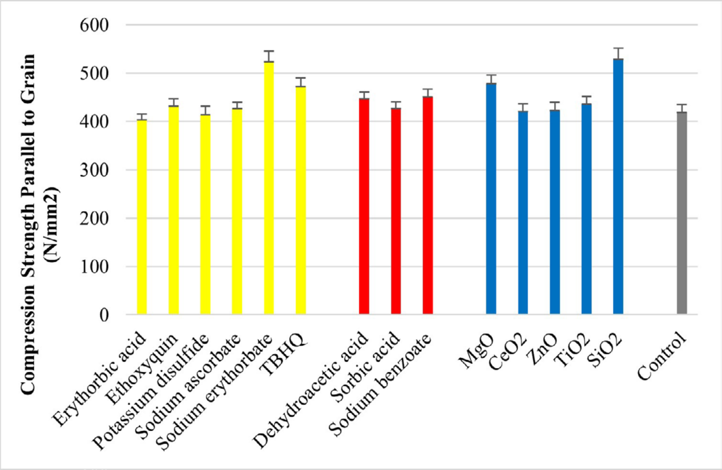

Fig. 5. Compression strength parallel to grain values of impregnated wood samples

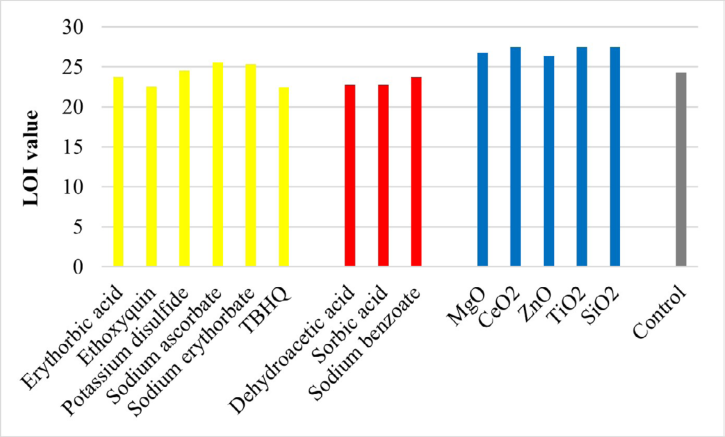

Fig. 6. Limit Oxygen Index (LOI) values of impregnated samples

of the control sample was 24.3, it is seen that each chemical has a different effect on the combustion property of wood (Figure 6). Especially, the LOI values of the samples impregnated with impregnation solutions prepared using ethanol decreased between 1.55 and 1.90 compared to the control. However, among the impregnated test samples using water as solvent, only the LOI values of erythorbic acid and sodium benzoate chemicals showed a small decrease of 0.6. The LOI values of the samples impregnated with the other chemicals increased. Therefore, it can be concluded that the solvent selected during the preparation of the impregnation solution also affects the combustion properties of the wood samples.

In this study, the increase in the LOI values of the impregnated test samples, especially those impregnated with nano-oxides, was higher compared to the impregnated samples with the other two chemical groups. Therefore, it can be said that impregnation with nano-oxides improves the combustion properties of wood more among the 3 chemical groups.

Bueno et al. (2014) reported that impregnation with a colloidal SiO_2 (3 wt%) solution was more effective in improving the combustion behavior of pine coatings compared to treatments with 3 wt% TiO_2 and ZrO_2 solutions. Similarly, Habibzade et al. (2016) investigated the combustion performance, physical, and mechanical properties of polymerized poplar wood samples treated with ZnO nanoparticles. In their study, poplar samples were impregnated with styrene monomer containing varying amounts of nano-ZnO (0%, 0.5%, 1.0%, and 1.5% by dry weight of the monomer). It was found that impregnation with a composition containing 1.5% nano-ZnO significantly increased the burning time of the samples, extending it from 15.4 to 20 seconds. Additionally, the limiting oxygen index (LOI) values of the samples impregnated with ZnO were higher than those of the control samples, indicating an improvement in their fire resistance.

8. Surface chemistry analysis

FTIR graphs of the samples impregnated with artificial antioxidants are presented in Figure 7.

In the FTIR graph, the closer the absorbance values at the peak values of the impregnated material and the control sample are to each other, the impregnant changes the chemical structure of the wood (Jones et al., 2022). The most significant changes in chemical structure were observed in the samples impregnated with ethanol. In the chemical structure of wood samples

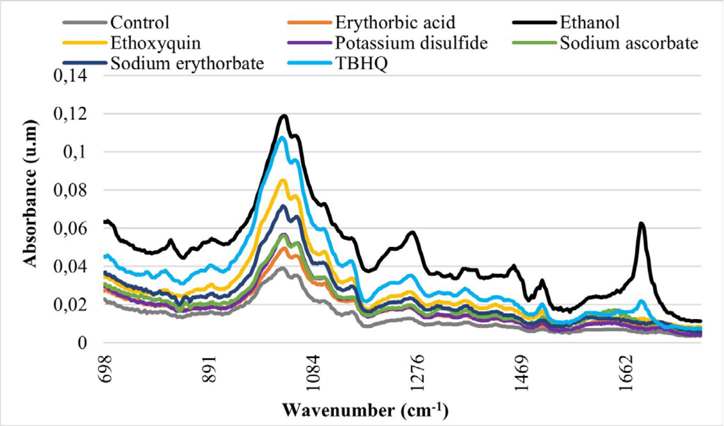

Fig. 7. FTIR graph of samples impregnated with artificial antioxidants

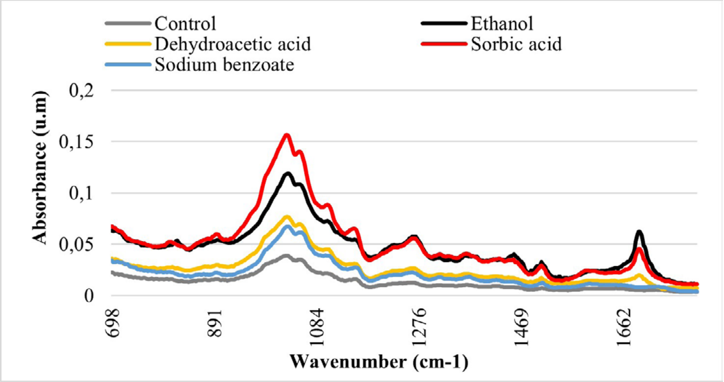

Fig. 8. FTIR graph of samples impregnated with GRAS compounds

treated with other impregnation solutions prepared using ethanol (ethoxyquin and TBHQ), it was noticed that such changes were slightly reduced. Although not for every peak value, based on the peak values between 1030-1060 cm^{-1} (C-O stretching in cellulose and hemicellulose), the effect of artificial antioxidants using water as solvent can be listed as follows: erythorbic acid>potassium disulfide>sodium ascorbate>sodium erythorbate.

The presence of free radicals and oxygen, along with the formation of oxidized species such as hydroxyl, carbonyl, carboxyl groups, and phenoxy radicals, leads to an increase in the 1740 cm^{-1} peak (Feist & Hon, 1984). In the study, regardless of the solvent type, the change in this peak was found to be more pronounced in all samples impregnated with artificial antioxidants compared to the control sample. This indicates that the impregnation with antioxidants influenced the chemical structure of the wood, particularly in terms of the formation of oxidative species that are reflected in the increased intensity of the 1740 cm^{-1} peak.

In the samples impregnated with artificial antioxidants, increases in the absorbance band intensities at 1590 and 1505 cm^{-1} were observed. These changes are attributed to the C=C stretching vibrations in the aromatic rings of lignin. The 1505 cm^{-1} peak specifically indicates cross-linking resulting from condensation reactions of lignin and the separation of aliphatic chains within the lignin structure. The formation of new cross-links in lignin can reduce the wood's water uptake, as these cross-links enhance the structural stability of the wood. As a consequence, the contraction and expansion of the wood during moisture changes can be minimized, improving its dimensional stability and resistance to moisture fluctuations. (Kocaefe et al., 2008; Tomak et al., 2018).

The 1450 cm^{-1} peak is related to CH_3 deformation in lignin and CH_2 bending in Xylan (Ximenes & Evans, 2006). Increases in the intensities of the 1590 and 1505 cm^{-1} absorption bands were observed in the samples impregnated with artificial antioxidants compared to the unimpregnated control sample.

Impregnation solutions were prepared by using ethanol as a solvent for dehydroacetic acid and sorbic acid among GRAS compounds and water for sodium benzoate. Figure 8 shows that sorbic acid made more chemical changes than ethanol, and dehydroacetic acid had fewer chemical changes than ethanol. The least change was observed in the samples impregnated with sodium benzoate. The FTIR analysis showed the following band assignments:

1. Xylan: C=O stretching at 1720-1740 cm^{-1}, CH_2 bending at 1450-1470 cm^{-1}, and C-O vibrations at 1230 ± 6 cm^{-1}.
2. Lignin: C=C stretching in aromatic rings at 1595 ± 5 cm^{-1} and 1510 ± 5 cm^{-1}, CH_3 deformation at 1450-1470 cm^{-1}, guaiacyl ring vibration at 1265 ± 5 cm^{-1}, and syringyl ring vibration at 1230 ± 6 cm^{-1}.
3. Cellulose and Hemicellulose: CH_2 sway at 1425 ± 5 cm^{-1}, CH_2 bending at 1370 ± 5 cm^{-1}, CH_2 vibrations at 1315 ± 5 cm^{-1}, C-O-C asymmetric band at 1157 ± 5 cm^{-1}, C-O stretching at 1056-1083 cm^{-1}, and C1 group vibrations at 890-899 cm^{-1}.

These band assignments are consistent with previous studies (Tshabalala et al., 2005; Ximenes & Evans, 2006). In Scots pine samples impregnated with GRAS compounds, increases were observed in all the mentioned peak values depending on the chemical used.

The FTIR graphs of the samples impregnated with nano-oxides are given in Figure 9. When Figure 9 is examined, it is seen that, as in the wood samples impregnated with artificial antioxidants and GRAS compounds, the FTIR graphs of the samples impregnated with nano-oxides show increases in all peak values given in Table 8 compared to the non-impregnated control sample. When the samples impregnated with nano-oxides are compared among themselves, the chemical change in the structure of the wood can be listed as follows from most to least: SiO_2>TiO_2>CeO_2>ZnO>MgO.

In a previous study, beech wood samples were impregnated with a nano-ZnO solution at four different

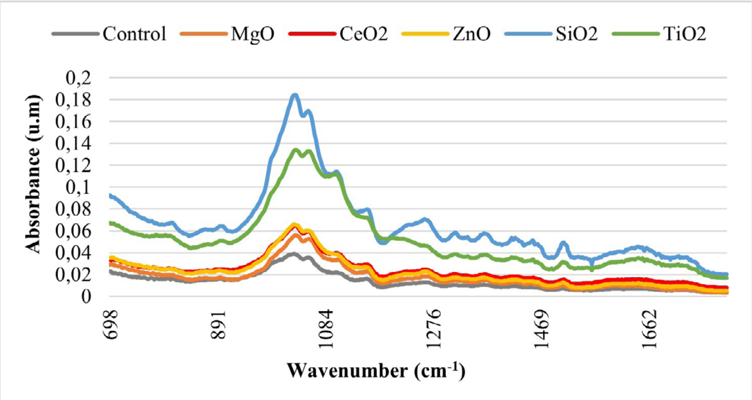

Fig. 9. FTIR graph of samples impregnated with all tested nano-oxide compounds

treatment levels (0, 10,000, 20,000, and 40,000 ppm) using a modified dipping method. Additionally, heat treatment was applied at temperatures of 60°C and 120°C. The results were analyzed using Fourier-transform infrared spectroscopy (FTIR), and it was observed that there was a strong interaction between the nano-ZnO and the chemical components of the wood. This interaction suggests that the nano-ZnO nanoparticles effectively bond with the wood's chemical structure, potentially enhancing its properties such as resistance to decay and moisture absorption (Soltani et al., 2013).

Surface morphology analysis

SEM images of wood impregnated with sodium erythorbate, sorbic acid and nano-MgO were presented at Figure 10-12, respectively.

In the samples impregnated with artificial antioxidants and GRAS compounds, it was observed that the impregnating liquid clogged the wood cells and penetrated their locations in both transverse, radial, and tangential sections. In the case of water-insoluble but water-dispersed nano-oxides, the SEM images taken from the wood samples are slightly different. Because the distribution of nano-oxides in the wood appears more clearly.

In a study conducted by Aydemir et al. (2016), it was determined with the help of electron microscopy that impregnants were present in the cell borders and passage edges in the internal structure of impregnated wood samples. In another study, some hardwoods were heat-treated at 50, 75, 100, 125, 150, and 185 °C and impregnated with 200 ppm nano-silver suspension. SEM images showed that nano-silver particles spread over the surface area of the samples. The effects of nano-silver

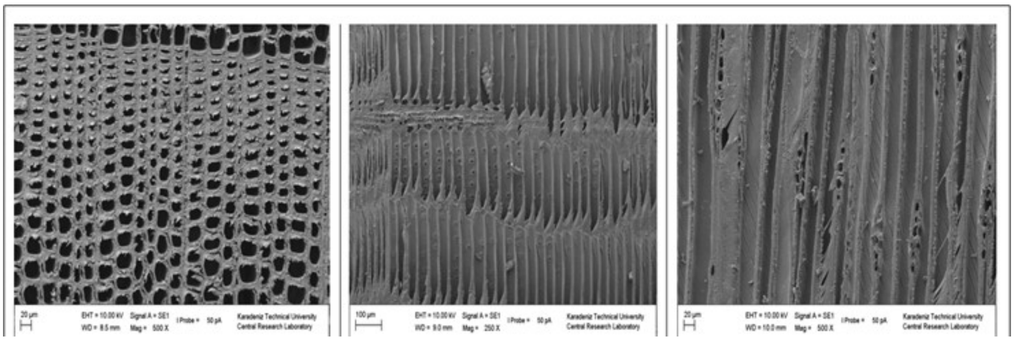

Fig. 10. SEM images of wood impregnated with sodium erythorbate

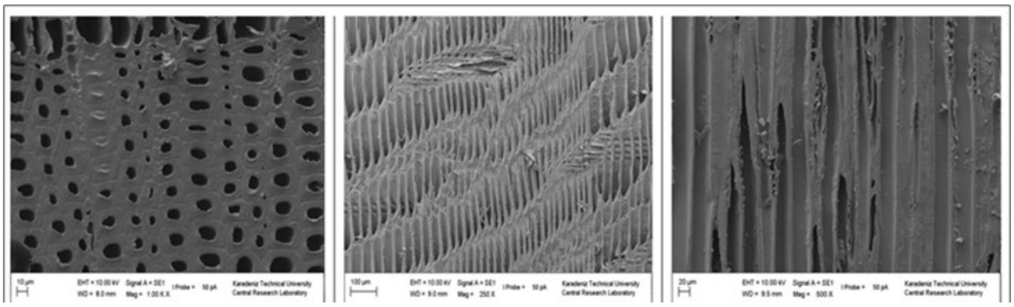

Fig. 11. SEM images of wood impregnated with sorbic acid

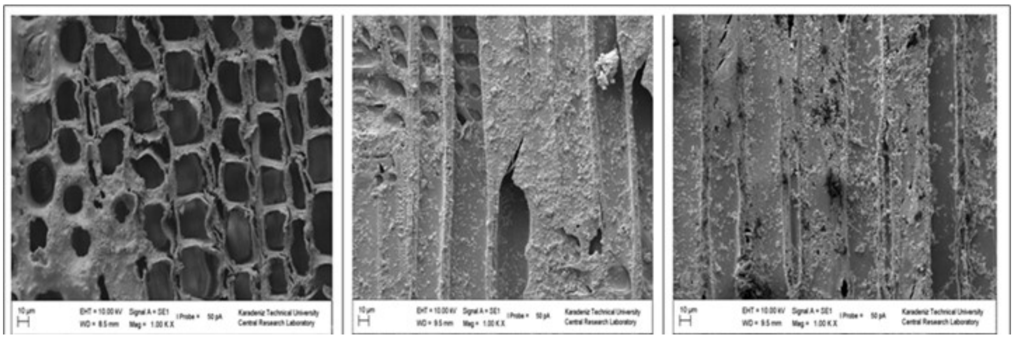

Fig. 12. SEM images of wood impregnated with nano-MgO

particles were found to be different at lower temperatures compared to higher temperatures (Taghiyari et al., 2013).

In a previous study by Bossert et al. (2020), pine and beech wood samples were subjected to pressure impregnation with nano-SiO_2 particles ranging in size from 70 to 350 nm. The particles were detected in the cell walls of both beech and pine wood samples, specifically within the water-conducting elements. The impregnation process was successful for all particle sizes in the beech wood samples, but only the 70 nm nano-oxide particles were successfully impregnated into the pine wood samples. The impregnation with 170 nm nano-oxides in pine wood was not successful.

The researchers generally found that smaller particle sizes correlate with a higher surface area, which increases the available area for oxidation. Additionally, some studies have emphasized that the viscosity of nanometal solutions is typically low, and that higher concentrations of nanometal particles, when combined with a surfactant, can improve dispersion stability by facilitating better liquid dispersion (Lykidis et al., 2013; Borges et al., 2018). This suggests that the effectiveness of impregnation and the resulting properties of treated wood may depend not only on particle size but also on the dispersion stability of the nanomaterials.

Conclusion

In the study, the possibilities of using artificial antioxidants, nano oxides, and GRAS compounds in the wood protection industry were examined. After the wood impregnation with each compound, sufficient retention amounts were reached. As a result of the statistical analysis, no statistically significant difference was found between the retention values. When the three groups are compared among themselves, it was seen that the lowest water uptake rates were in the wood impregnated with nano-oxides. The highest water repellent efficiency values were also observed in the nano-oxide samples. Ethoxyquin and reversible-butyl hydroquinone (TBHQ), which belong to the artificial antioxidants group, completely changed the color of the wood. None of the samples impregnated with GRAS compounds and nano-oxides completely changed the color of the wood. Fungal decay test results showed that the best performance was observed in nano-oxides. The weight loss values of wood samples impregnated with nano-oxides changed between 5.38% and 7.75%. Although biological test results did not meet the standard norms of European consummately, they were found to be remarkable with very low weight loss compared to the control ones. It was found that an increase in the compression strength parallel to the grain values is general. The increase in the LOI values of the impregnated test samples, especially those impregnated with nano-oxides, was higher compared to the impregnated samples with the other two chemical groups. In other words, impregnation with nano-oxides improved the combustion properties of wood much more than among the other groups. According to the FTIR graph of the samples impregnated with artificial antioxidants, it can be said that the largest changes in the chemical structure were observed only in the samples impregnated with ethanol. In the FTIR graph of the samples impregnated with GRAS compounds, it was seen that sorbic acid made more chemical changes than ethanol, and dehydroacetic acid had fewer chemical changes than ethanol. When the samples impregnated with nano-oxides were compared among themselves, the chemical change in the structure of the wood was listed as follows, from most to least $SiO_2 > TiO_2 > CeO_2 > ZnO > MgO$.

The final remark of this study underscores the necessity for further research to comprehensively elucidate and optimize the efficacy of artificial antioxidants, nano-oxides, and GRAS compounds in wood protection. While the current results demonstrate promising improvements—particularly with nano-oxide treatments—in aspects such as water repellency, biological resistance, and combustion properties, additional investigations are required to confirm the long-term performance and practical applicability of these treatments. Future studies focusing on mechanistic insights and durability assessments will be critical to advancing the implementation of these novel impregnation agents in the wood protection industry.

Conflict of interest

The author(s) declare(s) that there is no conflict of interest concerning the publication of this article.

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References

Afrouzi, Y. M., Omidvar, A., & Marzbani, P. (2013). Effect of artificial weathering on the wood impregnated with nano-zinc oxide. *World Applied Sciences Journal*, *22*(9), 1200-1203.

Akkuş, M., Akçay, Ç., & Yalçın, M. (2022). Antifungal and larvicidal effects of wood vinegar on wood-destroying fungi and insects. *Maderas. Ciencia y tecnología*, *24*.

Aydemir, D., Civi, B., Alsan, M., Can, A., Sivrikaya, H., Gunduz, G., & Wang, A. (2016). Mechanical, morphological and thermal properties of nano-boron nitride treated wood materials. *Maderas. Ciencia y tecnología*, *18*(1), 19-32.

Barcík, Š., Gašparík, M., & Razumov, E. Y. (2015). Effect of temperature on the color changes of wood during thermal modification. *Cellul. Chem. Technol*, *49*(9-10), 789-798.

Borges, C. C., Tonoli, G. H. D., Cruz, T. M., Duarte, P. J., & Junqueira, T. A. (2018). Nanoparticles-based wood preservatives: the next generation of wood protection? *Cerne*, *24*(4), 397-407.

Bossert, D., Geers, C., Placencia Peña, M. I., Volkmer, T., Rothen-Rutishauser, B., & Petri-Fink, A. (2020). Size and surface charge dependent impregnation of nanoparticles in soft-and hardwood. *Chemistry*, *2*(2), 361-373.

Broda, M. (2020). Natural compounds for wood protection against fungi—A review. *Molecules*, *25*(15), 3538.

Bueno, A. F., Bañón, M. N., De Morentín, L. M., & García, J. M. (2014). Treatment of natural wood veneers with nano-oxides to improve their fire behaviour. IOP Conference Series: Materials Science and Engineering,

D2863-10, A. (2000). Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index).

Delviawan, A., Suzuki, S., Kojima, Y., & Kobori, H. (2019). The influence of filler characteristics on the physical and mechanical properties of wood plastic composite (s). *Reviews in Agricultural Science*, *7*, 1-9.

Dönmez Çavdar, A., Kalaycioğlu, H., & Mengeloğlu, F. (2011). Tea mill waste fibers filled thermoplastic composites: The effects of plastic type and fiber loading. *Journal of Reinforced Plastics and Composites*, *30*(10), 833-844.

EN-113. (2006). Wood Preservatives-Test Method for Determining the Protective Effectiveness Against Wood Destroying Basidiomycetes-Determination of the Toxic Values, European Standard, Brussels, Belgium.

Feist, W. C., & Hon, D. N.-S. (1984). Chemistry of weathering and protection. *The chemistry of solid wood*, *207*, 401-451.

Freeman, M. H., Shupe, T. F., Vlosky, R. P., & Barnes, H. (2003). Past, present, and future of the wood preservation industry. *Forest products journal*, *53*(10), 8.

Fufa, S. M., & Hovde, P. J. (2010). Nano-based modifications of wood and their environmental impact: review. Proceeding of 11th World Conference of Timber Engineering,

González-Laredo, R. F., Rosales-Castro, M., Rocha-Guzmán, N. E., Gallegos-Infante, J. A., Moreno-Jiménez, M. R., & Karchesy, J. J. (2015). Wood preservation using natural products. *Madera y bosques*, *21*(SPE), 63-76.

Goodell, B., Winandy, J. E., & Morrell, J. J. (2020). Fungal degradation of wood: Emerging data, new insights and changing perceptions. *Coatings*, *10*(12), 1210.

Habibzade, S., Taghiyari, H. R., Omidvar, A., & Roudi, H. R. (2016). Effects of impregnation with styrene and nano-zinc oxide on fire-retarding, physical, and mechanical properties of poplar wood. *Cerne*, *22*, 465-474.

Haile, A., Gelebo, G. G., Tesfaye, T., Mengie, W., Mebrate, M. A., Abuhay, A., & Limeneh, D. Y. (2021). Pulp and paper mill wastes: utilizations and prospects for high value-added biomaterials. *Bioresources and Bioprocessing*, *8*, 1-22.

Iejavs, J., & Spulle, U. (2016). Cellular wood material properties–review. *Drewno: prace naukowe, doniesienia, komunikaty*, *59*(198), 1-18.

ISO-7724. (2003). Paints and Varnishes – Colorimetry – Part 1: Principles.

Järvinen, J., Ilgın, H. E., & Karjalainen, M. (2022). Wood preservation practices and future outlook: Perspectives of experts from Finland. *Forests*, *13*(7), 1044.

Jones, D., Kržišnik, D., Hočevar, M., Zagar, A., Humar, M., Popescu, C.-M., Popescu, M.-C., Brischke, C., Nunes, L., & Curling, S. F. (2022). Evaluation of the Effect of a Combined Chemical and Thermal Modification of Wood though the Use of Bicine and Tricine. *Forests*, *13*(6), 834.

Kartal, S. N., & Clausen, C. A. (2001). Leachability and decay resistance of particleboard made from acid extracted and bioremediated CCA-treated wood. *International Biodeterioration & Biodegradation*, *47*(3), 183-191.

Kartal, S. N., Hwang, W.-J., & Imamura, Y. (2007). Water absorption of boron-treated and heat-modified wood. *Journal of Wood Science*, *53*, 454-457.

Kim, J. K., Pal, K., Kim, J. K., & Pal, K. (2011). Overview of wood-plastic composites and uses. *Recent advances in the processing of wood-plastic composites*, 1-22.

Kocaefe, D., Poncsak, S., Dor , G. v., & Younsi, R. (2008). Effect of heat treatment on the wettability of white ash and soft maple by water. *Holz als roh-und werkstoff*, *66*(5), 355-361.

Lebow, S., Winandy, J., & Bender, D. (2004). Treated wood in transition: a look at CCA and the candidates to replace it. *Wood Design Focus*, *14*(2), 4-8.

Lin, C.-Y., & Lu, C. (2021). Development perspectives of promising lignocellulose feedstocks for production of advanced generation biofuels: A review. *Renewable and Sustainable Energy Reviews*, *136*, 110445.

Lykidis, C., Mantanis, G., Adamopoulos, S., Kalafata, K., & Arabatzis, I. (2013). Effects of nano-sized zinc oxide and zinc borate impregnation on brown rot resistance of black pine (Pinus nigra L.) wood. *Wood Material Science & Engineering*, *8*(4), 242-244.

Ives, E. (2001). A Guide to Wood Microtomy, Suffolk Offset, UK.

Mantanis, G., Terzi, E., Kartal, S. N., & Papadopoulos, A. (2014). Evaluation of mold, decay and termite resistance of pine wood treated with zinc-and copper-based nanocompounds. *International Biodeterioration & Biodegradation*, *90*, 140-144.

Marais, B. N., Brischke, C., & Militz, H. (2022). Wood durability in terrestrial and aquatic environments–A review of biotic and abiotic influence factors. *Wood Material Science & Engineering*, *17*(2), 82-105.

Nair, S., Pandey, K. K., Giridhar, B., & Vijayalakshmi, G. (2017). Decay resistance of rubberwood (Hevea brasiliensis) impregnated with ZnO and CuO nanoparticles dispersed in propylene glycol. *International Biodeterioration & Biodegradation*, *122*, 100-106.

Palanti, S., & Feci, E. (2013). A wood preservative based on commercial silica nanodispersions and boric acid against fungal decay through laboratory and field tests. *Open Journal of Forestry*, *3*(2), 57.

Pánek, M., Kubovský, I., Oberhofnerová, E., Štěrbová, I., Niemz, P., Osvald, A., & Kačík, F. (2021). Influence of natural weathering on the ignition and relative burning rate of selected softwoods. *Construction and Building Materials*, *304*, 124615.

Popescu, C. M., & Pfriem, A. (2020). Treatments and modification to improve the reaction to fire of wood and wood based products—An overview. *Fire and Materials*, *44*(1), 100-111.

Schultz, T. P., & Nicholas, D. D. (2000). Naturally durable heartwood: evidence for a proposed dual defensive function of the extractives. *Phytochemistry*, *54*(1), 47-52.

Sedjo, R. A., & Sohngen, B. (2013). Wood as a major feedstock for biofuel production in the United States: impacts on forests and international trade. *Journal of sustainable forestry*, *32*(1-2), 195-211.

Soltani, M., Najafi, A., Yousefian, S., Naji, H. R., & Bakar, E. S. (2013). Water repellent effect and dimension stability of beech wood impregnated with nano-zinc oxide. *BioResources*, *8*(4), 6280-6287.

Taghiyari, H. R., Enayati, A., & Gholamiyan, H. (2013). Effects of nano-silver impregnation on brittleness, physical and mechanical properties of heat-treated hardwoods. *Wood Science and Technology*, *47*, 467-480.

Tomak, E. D., Yazici, O. A., Parmak, E. D. S., & Gonultas, O. (2018). Influence of tannin containing coatings on weathering resistance of wood: Combination with zinc and cerium oxide nanoparticles. *Polymer Degradation and Stability*, *152*, 289-296.

TS-2595. (1977). Determination of Compressive Strength of Wood Parallel to Fibers, Turkish Standards Institute, Ankara. In.

Tshabalala, M. A., Jakes, J., VanLandingham, M. R., Wang, S., & Peltonen, J. (2005). Surface characterization. *Handbook of wood chemistry and wood composites*, 217-252.

Ximenes, F. A., & Evans, P. D. (2006). Protection of wood using oxy-aluminum compounds. *Forest*, *2005*(10075).