forests

MDPI

Article

Surface Treatment of Oak Wood with Silica Dioxide Nanoparticles and Paraloid B72

Andromachi Mitani [1], Vasiliki Kamperidou [2,*] and Paschalina Terzopoulou [1]

[1] Laboratory of Wood Science and Technology, Department of Forestry, Wood Science and Design, University of Thessaly, 431 00 Karditsa, Greece; amitani@uth.gr (A.M.); terzopouz@for.auth.gr (P.T.)
[2] Laboratory of Wood Technology, Department of Harvesting and Technology of Forest Products, Forestry and Natural Environment Faculty, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece
* Correspondence: vkamperi@for.auth.gr; Tel.: +30-2310-992747

Abstract: Wood is a valuable material with incomparable advantages, though it is susceptible to biotic and abiotic factors action that affect it adversely and shorten its service life. In the current study, the surface modification of oak wood is carried out through brief immersion in a solution of acrylic polymer Paraloid B72, in which silica dioxide nanoparticles in the form of nanopowder were dissolved at different contents (1, 2, 3, and 4% *w*/*v* of the solution) aiming at the elimination of wood material hygroscopicity, and the protection and improvement of other properties. Specifically, the modified and unmodified wood specimens were characterized in terms of physical characteristics (density, equilibrium moisture content, colour, and surface roughness), hygroscopic properties (swelling and absorption percentage) and accelerated weathering performance using xenon light and cycles of moisturizing and drying. The results revealed the dimensional stability of the samples and a significant increase in the hydrophobicity of the modified wood, as well as a significant increase in the resistance to the ageing/weathering factors of oak wood, which was proportional to the increase in the presence of nanoparticles in the Paraloid B72 solution. The colour of the treated samples slightly changed towards darker shades, more reddish and yellowish (with *L** to decrease, while *a** and *b** to slightly increase), though the treated wood revealed higher colour stability. The surface roughness parameters (*Ra*, *Rq*, and *Rz*) increased significantly, restricting the wide application of the treated wood in indoor or outdoor applications where surface roughness constitutes a critical factor. The findings of the current work contribute not only to the production of longer-lasting wood and timber structures, but also to the conservation of the existing weathered heritage timber structures.

Keywords: coating; hydrophobicity; modification; nanotechnology; preservation; surface; treatment; wood

check for updates

Citation: Mitani, A.; Kamperidou, V.; Terzopoulou, P. Surface Treatment of Oak Wood with Silica Dioxide Nanoparticles and Paraloid B72. *Forests* **2024**, *15*, 1842. https://doi.org/10.3390/f15111842

Academic Editor: Miha Humar

Received: 25 September 2024
Revised: 18 October 2024
Accepted: 21 October 2024
Published: 22 October 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Towards the increase in wood use as a construction material, and to take advantage of its numerous benefits, in recent decades, efforts have been implemented to improve the properties of wood and reduce its drawbacks. Most of the disadvantages of wood are related to its hygroscopic nature, such as the dimensional changes (shrinkage and swelling) due to the relative humidity fluctuation, the creation of stresses in the mass of the wood tissue, and the subsequent creation of distortions and microcracks, degradation caused by wood-destroying microorganisms, such as fungi, bacteria, insects, etc. [1].

The choice of the applied wood protective method should be carried out taking into account the wood species, its chemical composition and anatomical characteristics, the type of construction applied (whether it is a load-bearing element, and if the wood is to be glued/jointed using metal connections), the conditions under which it is to be exposed, and the purpose it will serve.

Especially in the last decades, several surface treatment methods have become commonplace serving as wood protection processes. Acrylic polymers, such as Paraloid B72,

have been used extensively in the protection of wood, as well as the preservation and stabilization of degraded wood of historical monuments and artefacts, due to their resistance to oxidation, mechanical forces, and transparency [2]. Paraloid can be dissolved effectively in several solvents, such as acetone, ethanol, or toluene, depending on the desirable rate of solvent evaporation, the viscosity of the preservative, and the available processing time, while it can be applied in wooden elements through immersion or impregnation processes [3]. The preparation and application processes of this acrylic polymer are not considered complicated or laborious. The temperature, the potential pressure applied, and the duration of treatment (impregnation or immersion), as well as the permeability of wood, are significant factors closely related to total preservative retention and its effectiveness [4]. The uniformity of the final distribution of this protective solution and the depth of its penetration into the wood also constitute critical factors for its effectiveness [5]. Paraloid-based solutions have a tendency not only to spread on the surface, but also to penetrate the wood mass and fill its voids [6]. Henriques et al. [7] refer that although this acrylic polymer does protect wood against dimensional stability, it does not protect wood adequately against the wood-destroying microorganisms' action. Therefore, the incorporation of additives that would provide biological durability to wood substrates is considered imperative.

Nanoparticles exhibit several advantages, such as high durability, commercial availability, affinity to the cellulosic substrate and coating properties, and acid neutralization ability [8,9]. Traistaru et al. [10] studied wood modification with Paraloid B-72, combined with zinc oxide nanoparticles (nano-ZnO), aiming to improve the effectiveness of stabilization treatments, examining the aspects of dispersion and retention in wood substrates. When applied to wooden constructions, nano-ZnO demonstrated resistance to decay, mould, and leaching, while also strengthening the wood surface's resilience to water and UV radiation [11]. Additionally, superhydrophobic surfaces with enhanced biological resistance against insect action were generated by utilizing nano-ZnO as an additive [12]. A variety of nanoparticles that have previously been employed in wood modification (either in their pure form or combined with another additive), such as SiO_2, TiO_2, CeO_2, ZnO, Fe_2O_3, etc., have been investigated. The capacity of copper-, mercury-, and other compound-based nanoparticles to strengthen resistance against microorganisms, insects, and fungi that degrade wood has been evaluated. Nanoparticles have the ability to increase the chemical's penetration in wood, mostly because of their size. Because of their unique structure, nanoparticles with a size range of 1–100 nm exhibit new and superior properties and functionalities. They contribute to a low viscosity and a high surface area along with higher stability [8]. In the literature, it has been proposed to add SiO_2 nanoparticles to different materials substrates in order to enhance their ability to prevent weathering brought on by ultraviolet radiation (UV) [13]. If silica nanoparticles (SiO_2) are mixed with a polymer, such as Paraloid B-72, the surface roughness could be increased, increasing as well the hydrophobicity of the polymer and ultimately resulting in superhydrophobicity [6]. A wide variety of organo-silicon compounds has also been studied for application on wood [4,14].

The goal of the current study is to improve the properties and eliminate the hygroscopicity of wood materials by briefly immersing them in a solution of Paraloid B72 containing dissolved silica dioxide nanoparticles at varying contents. More specifically, Paraloid B72, dissolved in acetone, was used as a protective coating on the surface of the wood specimens of the hardwood species of oak (chosen due to its availability), for which no relevant data have been detected so far in the literature. Furthermore, Paraloid polymer has been examined as pure, as well as combined with the action of the nanoparticles of silica dioxide in the form of nanopowder examining different ratios of nanoparticles (1, 2, 3, and 4% w/v), towards the generation of protective coatings on wood surfaces against moisture and weathering factors. The modified and unmodified wood specimens were characterized in terms of physical properties (density, equilibrium moisture content, colour, and surface roughness), hygroscopic properties (swelling and absorption percentage), and accelerated weathering performance using xenon light and cycles of moisturizing and drying to assess the response of wood to such modification processes.

2. Materials and Methods

2.1. Preparation of the Materials

Oak wood (*Quercus pubescens*) material was used for the purpose of the current study, which constitutes a preliminary experimental work, and oak wood was chosen as a widely available species, as well as typically used outdoors in wooden structures exposed under heavy conditions, because of its density, natural biological durability, and mechanical strength. Furthermore, it is a species widely used in the past in wood structures that need to be preserved. Specifically, two trunks of this species were harvested from the area of North Greece (AUTh Forest in Taxiarchis Halkidiki) of around 25 and 38 years for the two trunks, respectively, which were chosen based on straightness, soundness, and the absence of obvious defects, and brought into the laboratory and cut into pieces (boards). Sound boards without apparent defects were chosen and stored under stable conditions of relative humidity (65% ± 1%) and temperature (20 ± 2 °C) until the achievement of constant weight (8.7%–9.8% moisture content—MC). Then, they were prepared into the final specimens' nominal dimensions, preferable for their surface treatment and characterization, namely 20 × 20 × 10 mm (the wider surface was the tangential surface). Only pure wood without apparent defects was selected to participate in the experimental processes. A total of 12 wood specimens were prepared for each material category (reference and treated specimens). The weight and dimensions of all the specimens were measured in accuracy using an analytical laboratory scale (4 decimal places) and a digital clliper (Mitutoyo 500-196-30, Mitutoyo, Kawasaki, Japan) of 0.0005″/0.01 mm resolution. The samples were oven-dried in a drying chamber (75 °C, >24 h) in order to calculate their initial dry weight and were stored in closed air-tight bags to maintain them in this state until the time of immersion.

2.2. Surface Treatment Application

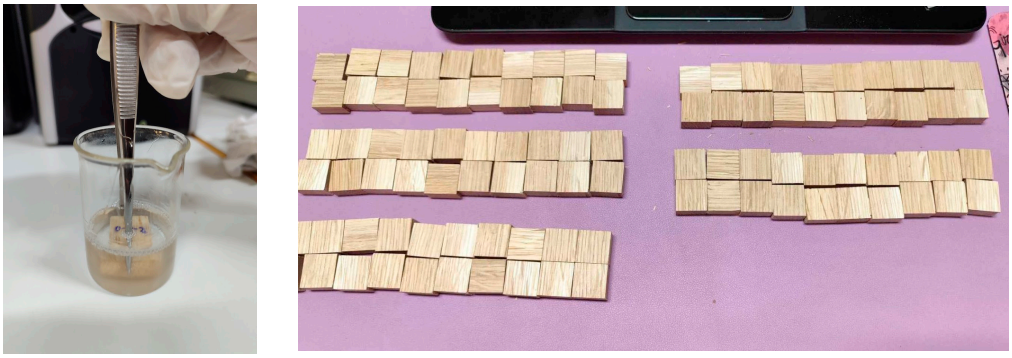
Paraloid B72 (Ethyl Methacrylate-co-Methyl Acrylate) was purchased in the form of solid pellets. The Paraloid pellets were dissolved in acetone (C_3H_6O, ≥99.5%, Honeywell, Sigma Aldrich, St. Louis, MO, USA), considered a useful, fast-evaporating and low-toxicity solvent, at a specific concentration (20:80), optimum in order to ensure the satisfying dilution of Paraloid in acetone and good penetration in the cell walls [15], so that the viscosity of the resin mixture is low and it can be introduced into the wood mass, aiming to achieve a satisfying and appropriate solubility of Paraloid for its utilization in wood surface treatment [16,17]. Furthermore, such low contents of silica nanoparticles may keep the cost of the proposed protective mixtures at a rational, acceptable level.

The method of full immersion of the specimens in the Paraloid solution was utilized (Figure 1). Low concentrations of silica nanoparticles (5–20 nm in the form of nanopowder of silicon dioxide, 99.5% trace metals, Sigma Aldrich) were chosen to be applied and studied in the present experiment in order to ensure an adequate penetration into the cell walls, even of the outer layers on the wood surface, and to avoid the excessive increase in the production cost of these coatings/surface preservatives of wood and therefore, the cost of the final material.

The immersion time of each specimen was 1 min in order to keep the whole process brief and the weight percent gain low (WPG) as well. At the end of immersion, each sample was weighed to record the WPG and retention of the Paraloid–nanoparticle solution (Table 1). The equation used for the calculation of WPG was as follows:

$$WPG\ (\%) = [(m_{of} - m_{oi})/m_{oi})] \times 100$$

where m_{of} is the final oven-dry mass of the treated sample, while the m_{oi} is the initial oven-dry mass of the untreated sample.



(**A**) (**B**)

Figure 1. (**A**). Treatment process (the immersion of the sample in the Paraloid–nanoparticle solution); (**B**). the view of the samples before treatment.

Table 1. Treatment conditions, coding explanation, and the resultant weight percent gain (WPG) of the respective impregnation treatments.

Treatment	Impregnation Conditions	Paraloid (%)	Acetone (%)	Nano-SiO_2 (%)	Weight Percent Gain—WPG (%)
OR	Reference—Untreated	-	-	-	-
O0	Paraloid solution	20	80	0	5.14
O1	Paraloid with 1% SiO_2	20	80	1	5.16
O2	Paraloid with 2% SiO_2	20	80	2	4.59
O3	Paraloid with 3% SiO_2	20	80	3	3.86
O4	Paraloid with 4% SiO_2	20	80	4	4.02

2.3. Characterization of Materials

A Minolta Colourimeter (ASTM D 1536-58 T1964 [18]) was used to analyze the specimens' surface colour in order to assess how it was affected by the surface treatment process/substances. In three-dimensional colour space, the colour is specified by the colourimeter as three coordinates (Figure 2A). This approach, known as CIE $L^*a^*b^*$, offers a consistent scale for comparing colour values and operates in accordance with the CIE standard. The chromatic coordinates on the green–red and blue–yellow axes, respectively, are described by the a^* and b^* coordinates, which have no set numerical boundaries. The L^* coordinate specifies the lightness and varies between 100, which represents a perfect reflecting diffuser, and 0, which indicates dark colour. Before and after each immersion treatment, the three colour coordinates—L^*, a^*, and b^* were recorded.

As regards the examination of surface roughness, and in order to ensure that the results of the wood surface roughness measurements would be comparable, all the measurements were implemented on an axis perpendicular to the grain, on a marked circle area of 10 mm radius in the cenre of each sample surface, ensuring the inclusion of various growth rings encountered on the wood surface. The surface roughness was measured before and after the treatment on each of the samples (as well as on the control/reference material). The measurements were conducted in accordance with the standard methodology of ISO 21920 [19] and the manual instructions of the specific profilometer used, as well as the practice followed in previous studies [20,21]. On the points of interest, at least 12–15 measurements were taken. A "Mitutoyo Surftest SJ-301" fine stylus-type profilometer was used to apply a contact method to the wood surface in order to assess the surface roughness. Since this approach yields precise results, it was considered much more convenient (Figure 2B). The pin tool's highest angle was 90 degrees, its diameter was 4 μm, and its measuring speed

was 10 mm/min. The measurements were taken using a 4.5 mm sampling length, vertically to the grain direction. Three roughness indexes, the mean arithmetic deviation of profile (*Ra*), the mean peak to valley height (*Rz*), and the maximum defect height index within the assessed profile, in other words, the maximum roughness (*Rq*), were assessed. These three features, which have also been established by the relevant edition of ISO 21920-2 [22], have been used in the literature in recent years [13]. Prior to the profilometer operating, it was necessary to perform a calibration using the device's calibration reference plate at an ambient temperature of 20 ± 2 °C.



(**A**) (**B**) (**C**)

Figure 2. (**A**). View of the colour measurement process, (**B**). surface roughness measurement, and (**C**). artificial weathering process of the specimens.

2.4. Artificial Weathering of Materials

The ageing/weathering phenomenon concerns simultaneous and complex processes that take place in the material mass. In the present work, the modified and unmodified wood specimens of oak wood were exposed to accelerated artificial weathering processes in a closed chamber that employed fluctuating climate (temperature and relative humidity) and xenon radiation (Table 2). The artificial xenon light irradiation was performed in accordance with ISO 4892-2 [23] using a soft irradiation source. The experiment was conducted in a commercial chamber (Atlas Material Testing Technology LLC-SUNTEST (Model: XLS+), Atlas Material Testing Technology, Mt Prospect, IL, USA) employing a xenon light at 200 W/m^2, 290 to 400 nm, at 65 °C (black panel), and 50% relative humidity (Figure 2C). The samples were placed approximately 500 mm away from the xenon lamp. The test and the respective exposure process of the samples were shortly interrupted in 3 weeks for the implementation of the first characterization process, while the whole exposure period lasted in total for 4 weeks.

Table 2. Exposure cycles with temperature control by black-standard thermometer.

Exposures Using Daylight Filters (Artificial Weathering)					
Cycle No	**Exposure Period**	**Irradiance Broadband (300 nm to 400 nm) W/m^2**	**Black-Standard Temperature °C**	**Chamber Temperature °C**	**Relative Humidity %**
1	102 min dry 18 min water spray	60 ± 2 60 ± 2	65 ± 3	38 ± 3	50 ± 10 b
2	102 min dry 18 min water spray	60 ± 2 60 ± 2	65 ± 3	Not controlled	Not controlled
3	102 min dry 18 min water spray	60 ± 2 60 ± 2	100 ± 3	65 ± 3	20 ± 10
4	102 min dry 18 min water spray	60 ± 2 60 ± 2	100 ± 3	Not controlled	Not controlled

Therefore, after 3 and 4 weeks of artificial weathering exposure, the specimens were characterized in terms of their dimensions (longitudinal, radial, and tangential), weight, colour, and surface roughness in order to draw conclusions for their durability against abiotic factors (moisture and light impact). The measurement process methodology of these properties has been described in previous subchapters.

2.5. Statistical Analysis

Utilizing the statistical package of SPSS (IBM SPSS Statistics, version 29.0.1.0), a one-way ANOVA analysis was performed to determine which values of these categories differ from one another in a statistically significant way for each examined property. This simple method of statistical analysis was applied to the results of the current research because of the nature of the variables and the design of the experiment. A significance level of p-value = 0.05 was used for the statistical analysis.

3. Results and Discussion

3.1. Changes Induced by the Treatment

According to the results (Figure 3), the dimensions of the samples regarding their length, width, and thickness did not change significantly due to the application of the various impregnation treatments (with the solution of Paraloid and Paraloid combined with the nanoparticles of silica dioxide) compared to the initial dimensions prior to the treatment. Therefore, the short-term immersion of the samples in the Paraloid and nanoparticle solutions did not cause any apparent or statistically significant dimensional changes, a fact particularly crucial for the preservation of the wood quality of the material and the utilization of the modified wood in various high-quality constructions and the utilization of these preservatives in already existent wooden structures of historical value.

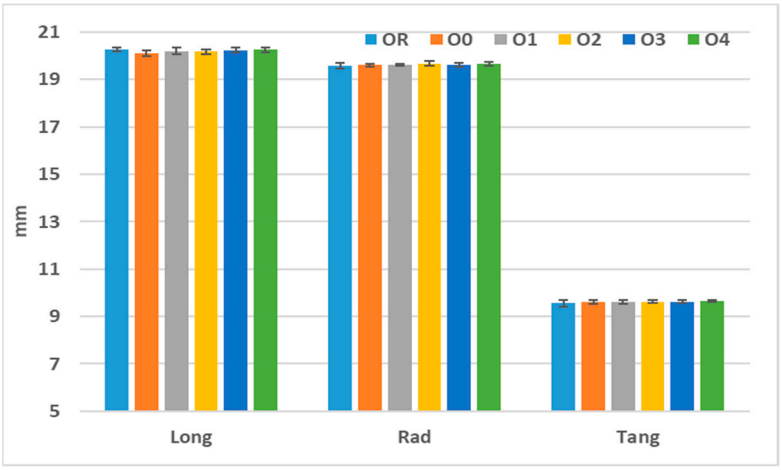
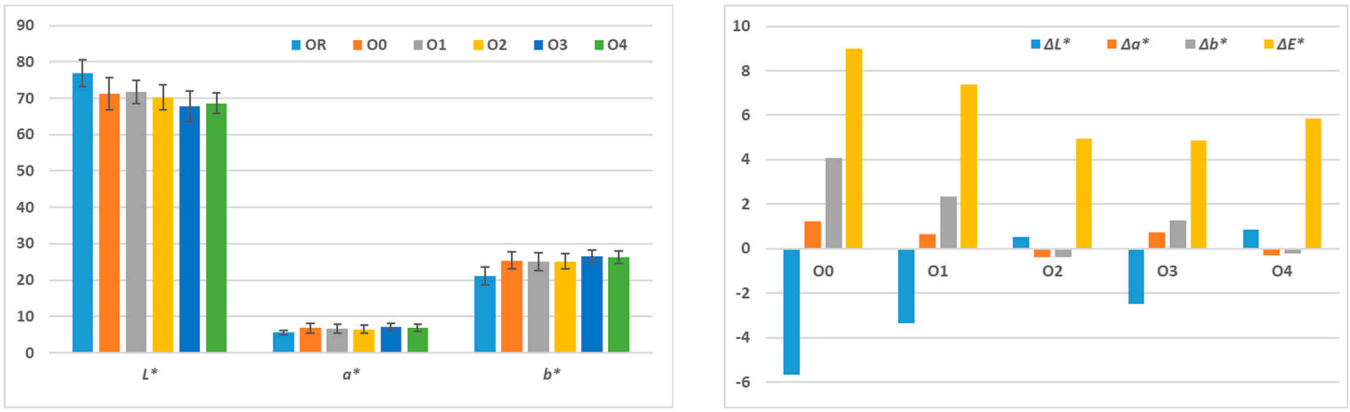


Figure 3. Dimensional changes among the different categories due to different treatments (OR: untreated; O0: Paraloid only; O1: impregnated with 1% SiO_2; O2: impregnated with 2% SiO_2; O3: impregnated with 3% SiO_2; O4: impregnated with 4% SiO_2).

The measurements of the colour parameters (L^*, a^*, and b^*) implemented on the surfaces of the oak wood samples (referring to the tangential surfaces) showed that a significant difference in colour induced by the application of the protective impregnation treatments was observed, both referring to pure Paraloid and the solution of Paraloid combined with silica nanoparticles, compared to the initial colour of the samples before immersion. In particular, the L^* index that corresponds to the surface lightness decreased, marking a progress from the reference sample colour towards the colour of the samples treated intensively with the highest percentage of silica nanoparticle–Paraloid solution of the current work (Figure 4). In contrast, the surface colour parameters of a^* and b^* of the modified samples increased compared to the control samples, showing an increasing trend as the intensity of

the modification increased. Nevertheless, according to the statistical analysis results, the increasing trend in the a^* and b^* values was not found to be statistically significant among the treated specimens, though statistically significant differences were recorded between those of the reference samples' (OR) and the treated samples' respective values.



(**A**) (**B**)

Figure 4. (**A**). Colour indexes (L^*, a^*, and b^*) of the oak wood species, and (**B**). the respective colour changes (ΔL^*, Δa^*, Δb^*, and ΔE^*) on the right among the different categories due to different treatments (OR: without any treatment; O0: Paraloid only; O1: impregnated with 1% SiO_2; O2: impregnated with 2% SiO_2; O3: impregnated with 3% SiO_2; O4: impregnated with 4% SiO_2).

All the modified samples (even those without the presence of silica particles, employing only pure Paraloid) exhibited statistically significantly higher roughness values of the studied specimens, with a trend of increasing roughness as we progressed from the modification of lower intensity (0% silica presence) towards the one of highest intensity (4% silica content). The tangential surfaces presented much lower surface roughness compared to the radial surfaces in each of the cases of treatments, which is attributed to the higher number of annual ring transition zones encountered in the case of the radial surfaces [14,24]. Additionally, the standard deviation values were recorded to be much higher in the *Rz* surface roughness parameter values of both surfaces (tangential and radial) (Figure 5). This increase in the surface roughness of the modified wood should be taken into consideration before use in applications where surface quality is critical. Abdelmouleh et al. [25] observed as well that silane (used in their study as a coupling agent between fibres and different matrices) was efficiently held on the fibre surface through both condensation with cellulose hydroxyl groups and self-condensation between silanol groups. This phenomenon resulted in bio-fibre surface property change after the modification, and the silane functional groups that were appended to the fibre surface participated in the chain growth of appropriate monomers to give a covalent continuity between the fibres, increasing the surface roughness of the fibres. Therefore, the nanosilane particles seem to increase the surface micro-roughness of wood and wood fibres (Figure 6).

According to the statistical analysis, 42.6% of the L^* (lightness) value variability is affected by the type of treatment applied. The mean value of L^* of the untreated specimens was found to differ statistically significantly from the respective values of L^* recorded by all the other treated specimens' values, while the L^* values of the differently treated samples did not provide any statistically significant difference to one another. The statistical analysis revealed that the surface roughness of the samples was affected by the applied treatments by 41.4%. The roughness of the untreated samples presented similar values to the next two categories of treated wood (pure Paraloid O0 and Paraloid with the 1% nanosilica compound O1). The next three groups of higher contents of silica nanoparticles (O2, O3, and O4) did not differ significantly from a statistical point of view, while all of these 3 categories' mean roughness values were found to differ significantly from the

untreated (OR) and the samples treated only with Paraloid (O0) or Paraloid with 1% silica nanoparticles (O2).

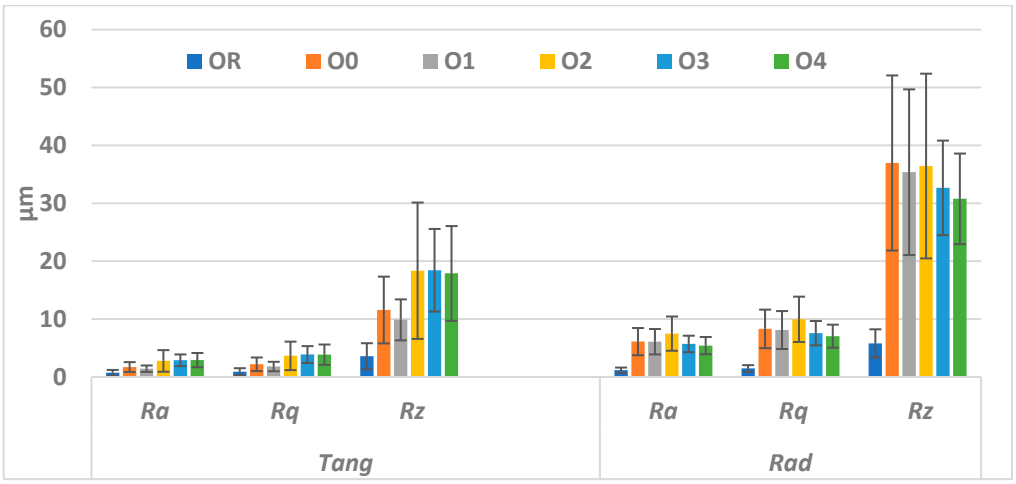


Figure 5. Mean values of surface roughness parameters (*Ra*, *Rq*, and *Rz*) (μm) measured on oak wood samples (treated and untreated ones).

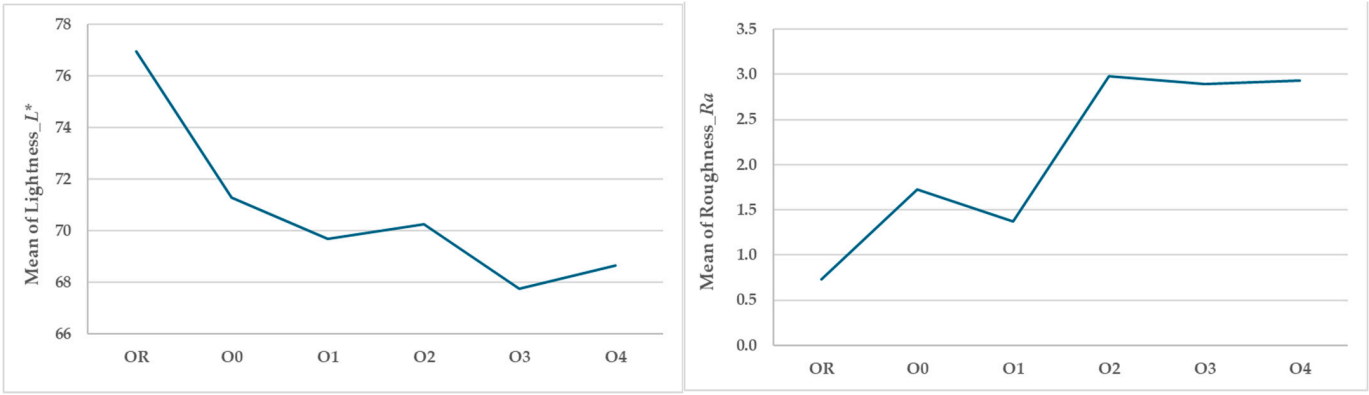


Figure 6. Indicative view of the impact of treatments on the lightness *L** (on the **left**) and surface roughness *Ra* (on the **right**) mean values of the specimens.

3.2. Impact of Artificial Weathering

To review and summarize the effects of the wood sample treatment with SiO_2 nanoparticles combined with Paraloid at different concentrations and exposing them to xenon light for 3 and 4 weeks, we would typically look at several key parameters, such as dimensional changes, colour, and surface roughness changes.

The dimensions increased after the xenon treatment due to the application of different cycles of wetting and drying, with the changes to be recorded particularly in the tangential surface/direction as well as its weight. The radial dimension followed the tangential, while the longitudinal dimension remained more or less stable, which seems to be normal given the structural characteristics of wood [26]. Therefore, as it was expected, the wood samples (independently of the treatment type) tend to change dimensionally (swell and shrink) at a higher extent in the tangential direction [14,26,27]. Indeed, here in the case of the samples of this study, in the tangential direction, the highest swelling percentage was observed. The lowest swelling percentages were, in general, recorded in the longitudinal direction of the specimens. Nevertheless, the observed dimensional changes in this wood species could not be considered high, which seems to be expected since the species of oak wood presents, in general, low dimensional changes [28]. In the period of 3 weeks, the samples presented higher rates of swelling during the exposure to artificial weathering compared

to the respective percentages of swelling at the end of the exposure period (at 4 weeks). This could be attributed to the stabilization of the wood samples in accordance with the chamber conditions. Higher dimensional changes were recorded, in the current work, in the measurement of 3 weeks of exposure to xenon light and artificial weathering, compared to the 4-week period (Figure 7). Significantly lower absorption percentages were recorded by the treated samples, both with Paraloid and Paraloid–silica nanoparticle treatments (Figure 8). At the time of the measurement of the absorption rate of the specimens at the 3-week exposure period, higher values of absorption were recorded compared to the final measurement at the end of the 4-week artificial weathering exposure period.

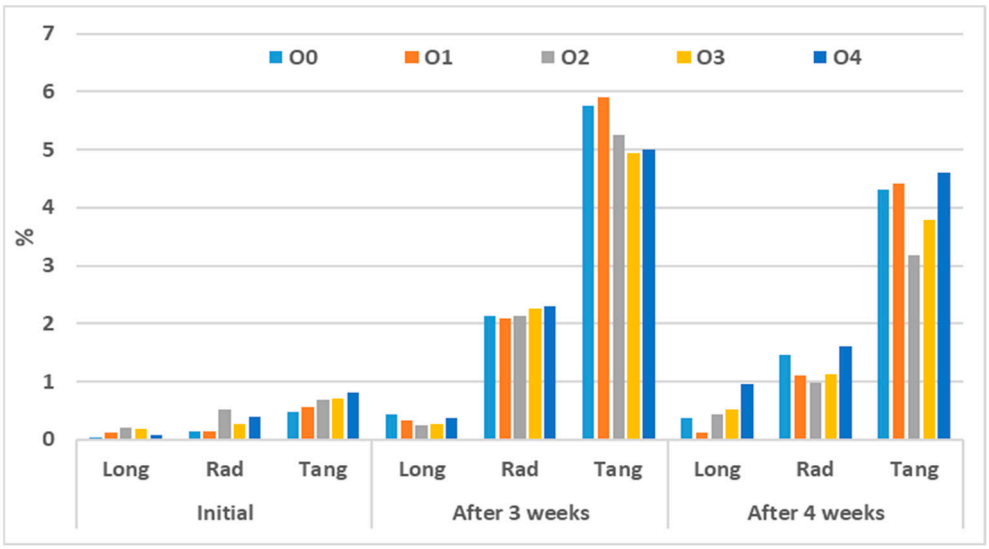


Figure 7. Dimensional changes (%) of the specimens of the different treatments in the longitudinal, radial, and tangential directions due to the exposure to artificial weathering process (OR: without any treatment O0: Paraloid only; O1: impregnated with 1% SiO_2; O2: impregnated with 2% SiO_2; O3: impregnated with 3% SiO_2; O4: impregnated with 4% SiO_2) after 3 and 4 weeks of artificial weathering.

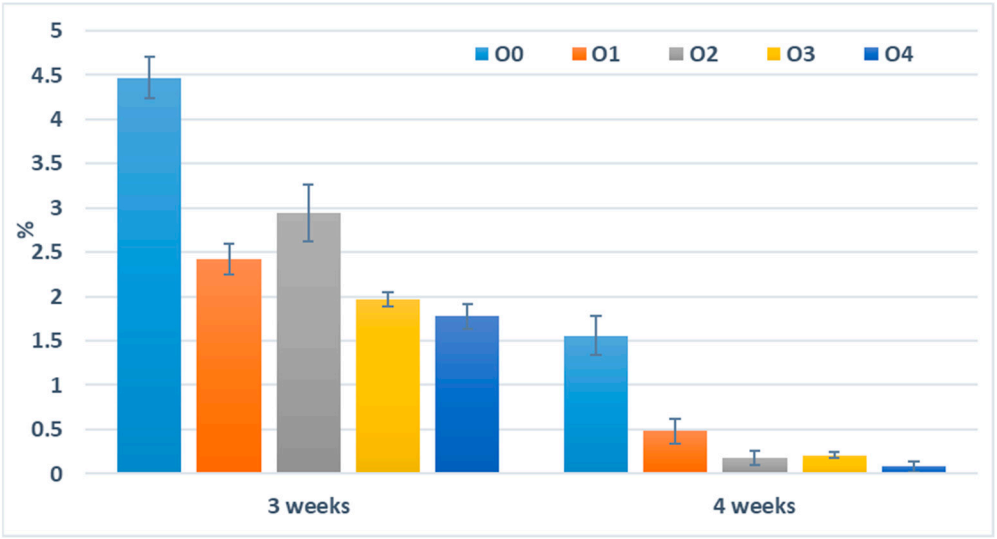


Figure 8. Absorption percentage (%) of the oak specimens (treated and untreated) during the exposure to artificial weathering, determined in 3- and 4-week periods.

Silanes have been utilized for a long time as modifying agents in various applications, such as trying to make materials like glass, textiles, ceramics, etc., more hydrophobic.

Because of their superior qualities, silanes are also appealing for non-mineral substrates like wood [29]. Silicones provide water resistance without decreasing the permeability of water vapur, which is an essential feature when using them as protective coatings for mineral substrates [30]. The hydroxyl groups of cell wall polymers and the silanol groups of silanes can react to generate a strong covalent link across the Si–O–C contact, which separates the silicon compound from the cell wall polymers. These bonds have been suggested to be hydrolyzable but have the ability to reform, which allows them to act as a stress-relaxing agent at the organic/inorganic interface. Improved durability and adhesion are the outcomes [29].

In general, the addition of SiO_2 nanoparticles combined with Paraloid generally enhances the wood's resistance to colour changes when exposed to xenon light and cycles of wetting and drying process. Higher concentrations of the nanoparticles of silica dioxide (especially 3% and 4%) provided the highest protection, minimizing changes in colour, preserving surface morphology, probably maintaining mechanical strength, and reducing chemical degradation (Figure 9).

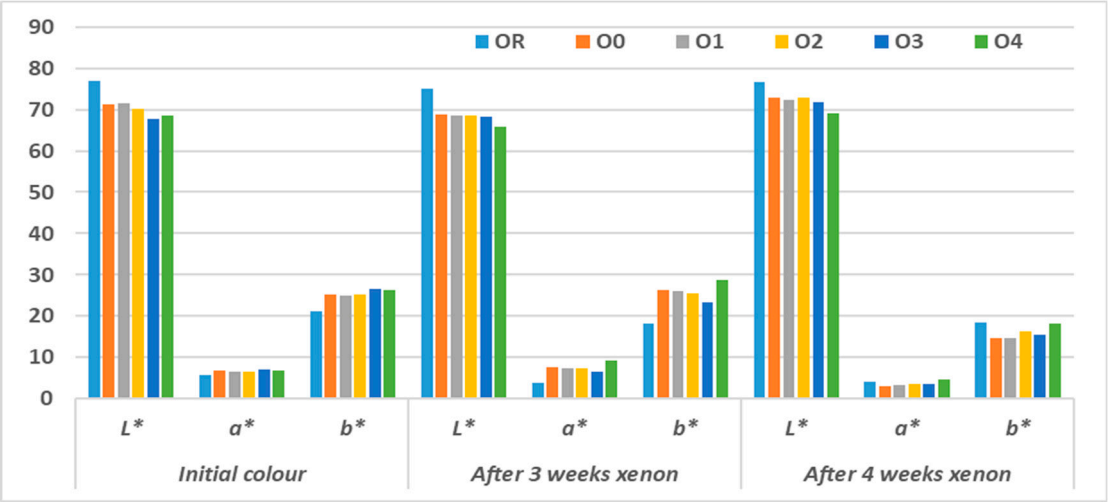


Figure 9. Changes in colour indexes (L^*, a^*, and b^*) of the oak wood species specimens of the different categories of treatment due to the exposure to the artificial weathering factors of 3 and 4 weeks (OR: without any treatment; O0: Paraloid only; O1: impregnated with 1% SiO_2; O2: impregnated with 2% SiO_2; O3: impregnated with 3% SiO_2; O4: impregnated with 4% SiO_2).

The total colour difference (ΔE^*) represents the magnitude of colour change, and in this case of the artificial weathering test, it varied across the samples. In general, the colour changes after 3 and 4 weeks of exposure to artificial weathering were depicted as well in the ΔE^* values that increased notably (Figure 10). Colour stability was achieved until the time of 3 weeks of exposure to artificial weathering by the treated/protected specimens, while at the end of exposure and under the prevailing conditions inside the chamber, the colour of specimens was proven to be quite less stable. In the 3-week measurement, all the ΔE^* values were found to be lower than those recorded in both the 0-week and 4-week exposure duration cases. Therefore, the colour of the specimens tended to become a little darker, more reddish and yellowish after the exposure to artificial weathering at 3- and 4-week duration of exposure. Certain samples exhibited significant colour changes after 4 weeks of exposure, with the ΔE^* values as high as 18.25, suggesting substantial shifts in colour. The data suggest that different samples exhibit varying degrees of colour stability over time. Some materials show significant colour change, while others remain relatively stable, since the changes in colour could be attributed to both changes in the chemical compounds of wood (extractive transfer, oxidation, lignin photodegradation, the depolymerization of hemicelluloses, etc.) combined with the existent anatomical characteristics of wood (cell wall thickness, shape, earlywood–latewood ratio, etc.) [31–33]. The overall trend appears

to be a darkening of the samples over time, with shifts in the red–green and yellow–blue axes depending on the specific sample and treatment applied.

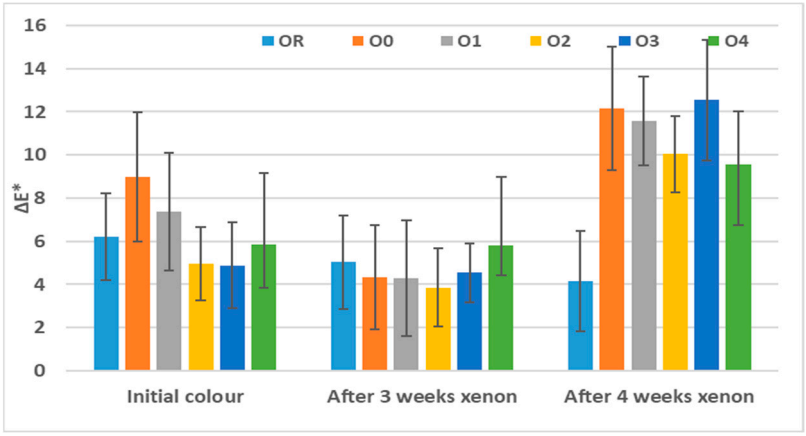


Figure 10. Colour difference (Δ*E**) marked between the oak specimens tangential surfaces initial colours prior to the implementation of any treatment or exposure to artificial weathering process (called in the graph "initial colour") to the respective difference marked after 3 and 4 weeks of artificial weathering.

Concerning the surface roughness of the specimens exposed to artificial weathering (from 0 to 4 weeks), all three surface roughness parameters demonstrated a gradual increase over time, going from 0 to 4 weeks period, indicating a potential degradation of surface (probable presence of cracks and surface damage though not apparent with the naked eye in the case of these specimens) (Figure 11). The samples of O2 (impregnated with 2% SiO_2) consistently exhibited the highest roughness values over time due to the exposure to artificial weathering, making this category of samples the roughest ones of the current study. The values of the parameters *Ra*, *Rq*, and *Rz* have marked a similar trend, which are in line with each other, with *Rz* to present the most pronounced changes recorded. These findings suggest that the surface of the specimens becomes rougher and potentially more irregular over time, which could be due to erosion, fibres rising due to the wetting–drying cycles, material wear, or other simultaneously interacting environmental factors.

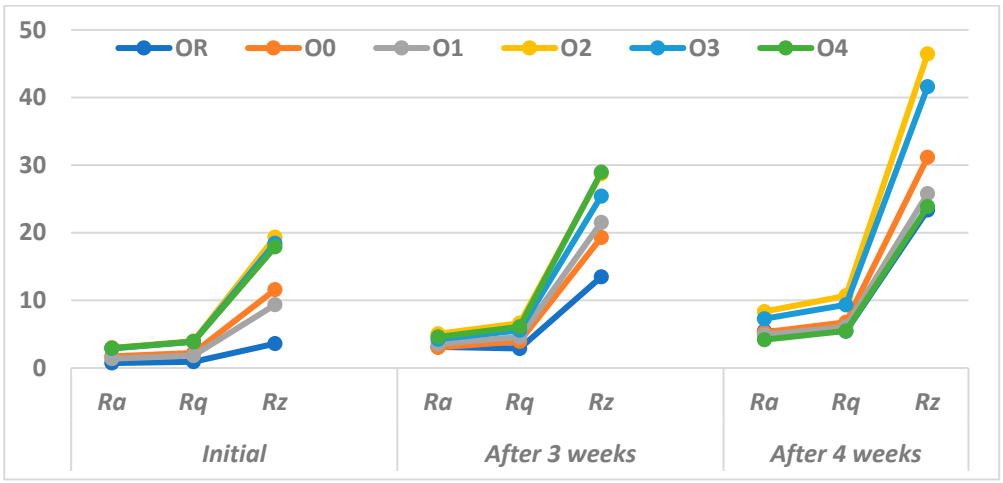


Figure 11. Surface roughness parameters (*Ra*, *Rz*, and *Rq*) recorded during the artificial weathering process of oak wood specimens.

According to the literature, Traistaru et al. [10], who applied on aspen wood samples nano-ZnO diluted in Paraloid, observed that the uptake and retention of the consolidant

was slightly increased within the wooden structure and led to hydrophobic surfaces. Nevertheless, the impact of nano-ZnO additives on water absorption was not conclusive. Soytürk et al. [34] refer that the treatment with pure Paraloid B72 increased the hydrophobicity of wood, whereas the boric acid has limited the effect on the surface wetting properties. The thermal stability of the specimens was enhanced considerably with the incorporation of Paraloid B72 and boric acid, while the treatment by both vacuum and dipping did not improve boron leaching considerably. Furthermore, Ntelia and Karapanagiotis [6], respectively, reported that the superhydrophobicity of several materials, such as glass, marble, brass, and wood, can be induced in Paraloid coatings by embedding silica (SiO_2) nanoparticles into the polymer matrix at appropriate concentrations. They referred that nanoparticles form microscale clusters which enhance the roughness of the polymer surfaces, even though the results of the current work are not in total agreement with this finding. The nanoparticles provided in their study moderate effects on the colour of the treated wood, respectively, and ensure good chemical stability.

4. Conclusions

According to the findings of the current study:

- The oak samples' brief immersion in the solutions containing Paraloid B72 and silica nanoparticles did not induce any detectable dimensional changes, which is highly critical for maintaining the wood quality and applying the modified wood in a variety of structural applications.
- The protective treatments induced a noticeable change in hue (L^* decreased, and a^* and b^* increased), making the wood appear slightly darker, more reddish, and yellowish.
- The roughness of all the modified samples, including those without silica particles, significantly increased, with the increase in silica particles' presence resulting in even higher surface roughness. This should be taken into account prior to the use of modified wood in applications where surface quality is critical.
- The tangential dimension and weight revealed the most significant changes during the exposure to artificial weathering, while the highest dimensional changes were evident after a 3-week exposure.
- All the treatments with Paraloid or Paraloid–silica nanoparticles significantly decreased the absorption rate of specimens during the weathering process and improved the wood resistance to colour changes during the weathering process, especially until the first 3 weeks, with higher concentrations of silica dioxide nanoparticles (3%–4%) providing higher colour stability.

The benefits of using silica dioxide nanoparticles in combination with Paraloid in the preservation of wood seem to be the increase in colour, UV, biological, and moisture resistance, while the surface roughness necessitates further studies to be addressed.

Author Contributions: Investigation A.M., V.K., and P.T.; writing—original draft preparation, A.M., V.K., and P.T.; methodology, A.M. and V.K.; resources, A.M. and V.K., writing—reviewing and editing, V.K. and A.M.; supervision, V.K. and A.M.; conceptualization, A.M. and V.K.; visualization, A.M., V.K., and P.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Available upon request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Mitani, A.; Barboutis, I. Determination of some mechanical properties and nails withdrawal resistance of heat treated fir wood (*Abies borrisi*-regis). *Pro-Ligno* **2015**, *11*, 344–350.
2. Pantoja, M.; Abenojar, J.; Martinez, A.J. Influence of the type of solvent on the development of superhydrophobicity from silane-based solution containing nanoparticles. *Appl. Surf. Sci.* **2017**, *397*, 87–94. [CrossRef]

3. Mankowski, P.; Bogusław, A. Compressive Strength of Wood Pinus Sylvestris Decayed by Coniophora Puteana Fungi and Reinforced with Paraloid B-72. *Wood Res.* **2015**, *60*, 409–415.
4. Liu, Z.; Cao, J. Fabrication of Superhydrophobic wood surface with a Silica/Silicone Oil complex emulsion. *Wood Res.* **2017**, *63*, 353–364.
5. Lionetto, F. Effect of novel consolidants on mechanical and absorption properties of deteriorated wood by insect attack. *J. Cult. Herit.* **2012**, *13*, 195–203. [CrossRef]
6. Ntelia, E.; Karapanagiotis, I. Superhydrophobic Paraloid B72. *Prog. Org. Coat.* **2020**, *139*, 105224. [CrossRef]
7. Henriques, J.D.; Nunes, L.M.R.; Brito, J.Z. Performance of Paraloid B72® combined with the application of biocides on wood degraded by fungi. *COST Action* **2010**, IE0601. Available online: http://repositorio.lnec.pt:8080/jspui/handle/123456789/1001130 (accessed on 30 August 2024).
8. Muhcu, D.; Terzi, E.; Kartal, S.N.; Yoshimura, T. Biological performance, water absorption, and swelling of wood treated with nano-particles combined with the application of Paraloid B72®. *J. For. Res.* **2016**, *28*, 381–394. [CrossRef]
9. Mantanis, G.; Terzi, E.; Kartal, S.N.; Papadouplos, A.N. Evaluation of mold, decay and termite resistance of pine wood treated with zinc- and cooper-based nano-compounds. *Int. Biodeterior. Biodegrad.* **2014**, *90*, 140–144. [CrossRef]
10. Trăistaru, A.T.; Sandu, I.C.A.; Timar, M.C.; Dumitrescu, G.L.; Sandu, I. SEM-EDX, Water Absorption, and Wetting Capability Studies on Evaluation of the Influence of Nano-Zinc Oxide as Additive to Paraloid B72 Solutions Used for Wooden Artifacts Consolidation. *Microsc. Res. Tech.* **2013**, *76*, 209–218. [CrossRef]
11. Zhang, L.; Jiang, Y.; Ding, Y.; Daskalakis, N.N.; Jeuken, L.J.C.; Povey, M.J.W.; O'Neill, A.J.; York, D. Mechanistic investigation into antibacterial behaviour of suspensions of ZnO nanoparticles against E. coli. *J. Nanopart. Res.* **2010**, *12*, 1625–1636. [CrossRef]
12. Shuppe, T.; Piao, C.; Lucas, C. The termiticidal properties of super-hydrophobic wood surfaces treated with ZnO nanorods. *Eur. J. Wood Prod.* **2012**, *70*, 531–535. [CrossRef]
13. Li, T.; Yong-Li, F.; Wang, K.; Song, S.; Liu, X.; Bu, N.; Li, R.; Zhen, Q.; Bashir, S. Methyl-modified silica hybrid fluorinated Paraloid B-72 as hydrophobic coatings for the conservation of ancient bricks. *Constr. Build. Mater.* **2021**, *299*, 123906. [CrossRef]
14. Magoss, E. General Regularities of Wood Surface Roughness. *Acta Silv. Lignaria Hung.* **2008**, *4*, 81–93. [CrossRef]
15. Vinçotte, A.; Beauvoit, E.; Boyard, N.; Guilminot, E. Effect of solvent on PARALOID® B72 and B44 acrylic resins used as adhesives in conservation. *Herit Sci.* **2019**, *7*, 42. [CrossRef]
16. Manoudis, P. Study and Evaluation of Protective Coatings for the Surface Preservation and Protection Cultural Heritage Monuments. Doctoral Dissertation, Aristotle University of Thessaloniki, Thessaloniki, Greece, 2009.
17. Bi, W.; Li, H.; Hui, D.; Gaff, M.; Lorenzo, R.; Corbi, I.; Corbi, O.; Ashraf, M. Effects of chemical modification and nanotechnology on wood properties. *Nanotechnol. Rev.* **2021**, *10*, 978–1008. [CrossRef]
18. *ASTM D 1536-58 T1964*; Tentative Method of Test for Color Difference Using the Colormaster Differential Colorimeter. ASTM International: Washington, DC, USA, 1964.
19. *ISO 21920-1:2021*; Geometrical Product Specifications (GPS)—Surface Texture: Profile Part 1: Indication of Surface Texture. ISO: Geneva, Switzerland, 2021.
20. Kamperidou, V.; Aidinidis, E.; Barboutis, I. Impact of structural defects on the surface quality of hard-wood species sliced veneers. *Appl. Sci.* **2020**, *10*, 6265. [CrossRef]
21. Li, G.; Wu, Q.; He, Y.; Liu, Z. Surface roughnessof thin wood veneers sliced from laminated green woodlumber. *Maderas. Cienc. Tecnol.* **2018**, *20*, 3–10. [CrossRef]
22. *ISO 21920-2*; Geometrical Product Specifications (GPS)—Surface Texture: Profile. Part 2: Terms, Definitions and Surface Texture Parameters. ISO/TC 213: Geneva, Switzerland, 2021.
23. *ISO 4892-2:2013+A1:2021*; Plastics—Methods of Exposure to Laboratory Light Sources—Part 2: Xenon-arc Lamps. ISO: Geneva, Switzerland, 2021.
24. Kastridis, A.; Kamperidou, V.; Stathis, D. Dendroclimatological Analysis of Fir (*A. borisii-regis*) in Greece in the frame of Climate Change Investigation. *Forests* **2022**, *13*, 879. [CrossRef]
25. Abdelmouleh, M.; Boufi, S.; Belgacem, M.N.; Duarte, A.P.; Ben Salah, A.; Gandini, A. Modification of cellulosic fibres with functionalised silanes: Development of surface properties. *Int. J. Adhes. Adhes.* **2004**, *24*, 43–54. [CrossRef]
26. Tsoumis, G. *Wood Science and Technology, Wood Structure and Properties*; Aristotle University of Thessaloniki: Thessaloniki, Greece, 2002; p. 346.
27. Koutsianitis, D.; Ninikas, K.; Mitani, A.; Ntalos, G.; Miltiadis, N.; Vasilios, A.; Taghiyari, H.R.; Papadopoulos, A.N. Thermal Transmittance, Dimensional Stability, and Mechanical Properties of a Three-Layer Laminated Wood Made from Fir and Meranti and Its Potential Application for Wood-Frame Windows. *Coatings* **2021**, *11*, 304. [CrossRef]
28. Leal, S.; Sousa, V.B.; Pereira, H. Cork oak (*Quercus suber* L.) wood hygroscopic properties and dimensional stability. *For. Syst.* **2012**, *21*, 355–363. [CrossRef]
29. Kamperidou, V.; Ratajczak, I.; Perdoch, W.; Mazela, B. Impact of thermal treatment combined with silicon compounds treatment on wood structure. *Wood Res.* **2022**, *67*, 773–784. [CrossRef]
30. Ghosh, S.C.; Militz, H.; Mai, C. The efficacy of commercial silicones against bluestain and mould fungi in wood. *Eur. J. Wood Wood Prod.* **2009**, *67*, 159–167. [CrossRef]
31. Witucki, L.G. A silane primer: Chemistry and applications of alkoxysilanes. *J. Coat. Technol.* **1993**, *65*, 57–60.

32. Tolvaj, L.; Nemeth, R.; Pasztory, Z.; Bejo, L.; Takats, P. Colour stability of thermally modified wood during short-term photodegradation. *BioRes* **2014**, *9*, 6644–6651. [CrossRef]
33. Arpaci, S.S.; Tomak, E.D.; Ermeydan, M.A.; Yildirim, I. Natural weathering of sixteen wood species: Changes on surface properties. *Polym. Degrad. Stab.* **2021**, *183*, 109415. [CrossRef]
34. Soytürk, E.; Kartal, N.; Terzi, E.; Önses, S.; Şarkdemir, K.; Çelik, N. Evaluation of wood treated with Paraloid B72® and boric acid: Thermal behavior, water absorption and mold resistance. *Eur. J. Wood Wood Prod.* **2023**, *81*, 923–934. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.