

Article

Impact of Thermal Treatment and Accelerated Aging on the Chemical Composition, Morphology, and Properties of Spruce Wood

František Kačík ^{1,*} , Jozef Kúdela ² , Eva Výbohová ¹, Tereza Jurczykova ³ , Iveta Čabalová ¹, Lukáš Adamčík ⁴ , Elena Kmeťová ⁵  and Danica Kačíková ⁵

¹ Department of Chemistry and Chemical Technology, Faculty of Wood Sciences and Technology, Technical University in Zvolen, 96001 Zvolen, Slovakia; vybohova@tuzvo.sk (E.V.); cabalova@is.tuzvo.sk (I.Č.)

² Department of Wood Science, Faculty of Wood Sciences and Technology, Technical University in Zvolen, T. G. Masaryka 24, 960 01 Zvolen, Slovakia; kudela@tuzvo.sk

³ Department of Wood Processing and Biomaterials, Faculty of Forestry and Wood Sciences, Czech University of Life Sciences Prague, Kamýcká 129, 16000 Prague, Czech Republic; jurczykova@fld.czu.cz

⁴ Department of Woodworking, Faculty of Wood Sciences and Technology, Technical University in Zvolen, T. G. Masaryka 24, 960 01 Zvolen, Slovakia; xadamcicl@is.tuzvo.sk

⁵ Department of Fire Protection, Faculty of Wood Sciences and Technology, Technical University in Zvolen, 96001 Zvolen, Slovakia; xkmetovae@is.tuzvo.sk (E.K.); kacikova@is.tuzvo.sk (D.K.)

* Correspondence: kacik@is.tuzvo.sk

Abstract: Thermal modification improves the properties of wood, especially its stability and durability. We thermally treated spruce wood with the Thermowood process at three temperatures (160 °C, 180 °C, and 210 °C) and subjected it to accelerated aging in wet mode. We evaluated the chemical composition (wet chemistry, infrared spectroscopy), color, surface morphology, and wetting of the wood surface with water. Thermal treatment caused a significant decrease in hemicelluloses (up to 72.39% at a temperature of 210 °C), which initiated an increase in the content of more resistant wood components—cellulose and lignin. With accelerated aging, the hemicellulose content decreased by another 5%. The most significant differences between the infrared spectra of thermally modified wood before and after exposure to accelerated aging were in the absorption bands of lignin (1509 and 1596 cm^{−1}) and in the region of carbonyl groups between 1800 and 1630 cm^{−1}. Thermal treatment also caused a change in the color of the wood to dark brown; the overall color difference ΔE increased several times. The thermal-induced shortening of polysaccharide fibers and reduction in their width were even more manifested during accelerated aging. This work contains new knowledge about the properties critical for the reuse of thermally modified wood after accelerated aging, simulating the end of its life cycle.

Keywords: spruce; thermowood; life cycle; recycling; infrared spectroscopy; color; surface morphology; hydrophobicity; carbon footprint



Academic Editors: Athanasios Dimitriou, Anna Sandak and Magdalena Broda

Received: 18 December 2024

Revised: 10 January 2025

Accepted: 17 January 2025

Published: 19 January 2025

Citation: Kačík, F.; Kúdela, J.; Výbohová, E.; Jurczykova, T.; Čabalová, I.; Adamčík, L.; Kmeťová, E.; Kačíková, D. Impact of Thermal Treatment and Accelerated Aging on the Chemical Composition, Morphology, and Properties of Spruce Wood. *Forests* **2025**, *16*, 180. <https://doi.org/10.3390/f16010180>

Copyright: © 2025 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

Thermal modification of wood is a well-established process that offers numerous advantages. The recyclability of thermowood is an important aspect of its environmental performance and sustainability. These benefits, including improved dimensional stability, biological durability, esthetic enhancements, and reduced weight, make thermally modified wood valuable in various applications, from construction to furniture making [1–3]. Well-known technologies, such as thermowood (Finland), retified wood (France), Bois Perdu (France), PLATO process (The Netherlands), OHT process (Germany), together with FWD

(Germany), Timura (Germany), TVT and Termovuoto (Italy), Westwood process (USA), WTT and IWT (USA), and Oleobois (France) [4,5], involve wood heat treatment at high temperatures between 180 °C and 260 °C under an oxygen-free atmosphere to avoid burning involving either the use of steam, nitrogen, or oil [6]. Heat treatment modifies the structure of wood cell wall polymers through different chemical reactions conferring the material's new properties [7,8].

Research on thermally modified wood has been the object of important investigations for several decades [9–11]. Even if the effects of heat treatment on wood durability have been known for a long time, its industrial exploitation and the question of its use after the end of its life cycle and recycling are only recently dated. The interest in thermally modified wood has also expanded due to the decreased production of resistant raw wood materials, the increased interest in durable construction materials, and legislative changes that restrict the use of toxic substances [12], because increasing current environmental pressures have led to important changes in the field of wood protection.

The environmental impact of the thermal modification process itself is relatively low [1,13]. Candelier et al. [14] noted that the heat treatment process generates minimal waste, and any byproducts can be captured and purified for further use. Additionally, thermally modified wood can be recycled at the end of its life cycle without the detrimental effects of chemically treated wood, which often contains biocidal agents. This recyclability contributes to a more sustainable life cycle for wood products. One of the key factors influencing the recyclability of thermowood is the alteration in its chemical composition, particularly lignin. Kačíková et al. [15] highlighted that thermal treatment leads to significant changes in lignin structure, which can affect the properties of wood products and their recyclability. The modifications in lignin can enhance the bonding properties of thermowood, making it suitable for reuse in composite materials or other applications.

The thermal modification process can also improve the esthetic qualities of wood, which may enhance its marketability for recycling. For instance, thermowood exhibits a rich, dark color that is often desirable in decorative applications [16]. The color change not only enhances the visual appeal of the wood but also provides a level of protection against UV radiation, further extending its lifespan [17,18]. The uniformity of color achieved through thermal treatment can be a significant selling point for manufacturers and consumers alike. Perdoch [19] noted that thermowood maintains high color stability, which can be advantageous for its reuse in visible applications where appearance is important. This esthetic appeal can facilitate the recycling of thermowood into new products, as it may attract consumers looking for visually appealing materials.

Thermally modified wood is typical for its reduced hygroscopicity. Studies have shown that thermal treatment can significantly reduce swelling and shrinkage, making thermally modified wood more reliable in varying environmental conditions [20,21]. This is achieved through the degradation of hemicelluloses, one of the major components of wood, that are thermally less stable, and their degradation occurs in the first phase. For instance, Calonego et al. [22] reported that thermal modification of *Shizolobium parahyba* resulted in EMC reductions of up to 51.1% for juvenile wood and 42.7% for mature wood. Similarly, Barbosa et al. [23] and Kozakiewicz et al. [24] highlighted that thermal treatment significantly reduces the wood's ability to exchange water with the outside environment, thereby minimizing dimensional variations. This reduction in moisture absorption not only enhances the dimensional stability of the wood but also contributes to its longevity, as it minimizes the risk of warping and cracking over time [25].

In addition to dimensional stability, thermal modification enhances the biological durability of wood. The process alters the chemical composition of wood, making it less susceptible to decay and insect attacks. Research indicates that thermal treatment reduces

the equilibrium moisture content of wood, which in turn decreases its vulnerability to fungal growth [26,27]. Salman et al. [28] noted that thermal modification could improve the durability of wood against termites, although the effectiveness may vary depending on the wood species. Minkah et al. [29] highlighted that the thermal treatment significantly increases the durability of *Gmelina arborea* wood against biological threats, which is crucial for applications in outdoor environments, where wood is exposed to moisture and pests. The ecological benefits of thermowood are further emphasized by its ability to improve durability without the use of toxic chemicals, making it an environmentally friendly alternative to traditional wood treatments [30]. This increased durability extends the lifespan of wood products, reducing the need for chemical preservatives that can be harmful to the environment [14]. Assuming the preservation of these properties, such as reduced hygroscopicity, improved dimensional stability, and resistance to biological damage, even after the end of the thermal wood life cycle, this material becomes very attractive in various areas of use.

The mechanical properties of thermowood also play a role in its recyclability. They can vary depending on wood species, and specific conditions of the thermal modification process, including temperature, duration, protective atmospheres during treatment, etc. Therefore, optimizing the thermal modification conditions to achieve the desired mechanical properties for specific applications is needed [21,31,32]. While some studies have reported improvements in rigidity and hardness, others indicate a decrease in certain strength parameters [33–35]. For example, Moliński et al. [36] found that while thermal modification improved the rigidity of ash wood at lower temperatures, it led to a significant decrease in the modulus of rupture (MOR) and modulus of elasticity (MOE) at higher temperatures. Korkut and Aydin [37] found that the modulus of elasticity for wild cherry wood decreased by as much as 39.5% when treated at 212 °C for 2.5 h. Similarly, Gennari et al. [38] reported that heat-treated wood generally exhibited lower mechanical properties than untreated wood, confirming a trend observed in various species. Changes in the crystalline and amorphous proportion of cellulose can also greatly affect the mechanical properties, and thermally treated spruce wood exhibits decreased mechanical properties and polysaccharide content, especially hemicelluloses [35]. Winandy and Lebow [39] and Esteves et al. [40] reported the correlation between the hemicellulose content and flexural strength.

The density of thermally modified wood also tends to decrease due to the loss of mass associated with the degradation of its chemical components. Roszyk et al. [41] observed a reduction in density for ash wood, which decreased from 591 kg·m⁻³ to 563 kg·m⁻³ after treatment at 200 °C, alongside a mass loss of approximately 6%. This reduction in density can affect the overall mechanical performance of the wood, as a lower density often correlates with reduced strength.

All these changes can influence how thermowood can be processed and reused. For example, thermowood with preserved mechanical properties may be suitable for structural applications, while wood that has become more brittle may be better suited for non-structural uses, such as in composite materials. Additionally, the recyclability of thermowood can be enhanced by its compatibility with other materials. Demircioğlu et al. [42] explored the use of thermowood in composite structures, where it was combined with rubber cork to create impact-resistant materials. This type of application not only utilizes thermowood effectively but also promotes recycling by integrating it into products that can be easily disassembled and reused at the end of their life cycle.

Unlike earlier studies that primarily explored the influence of the thermal modification process on wood properties, this work investigates the changes in the properties critical for the reuse of thermally modified wood after accelerated aging, simulating the end of its life

cycle. We aim to determine changes in lignin and hemicelluloses during aging, highlighting their role in improving recyclability and the potential for value-added applications such as composite materials and adhesives. By studying how the chemical and physical properties evolve, the research supports sustainable practices, such as extending wood's life cycle and optimizing its recycling potential. This approach also bridges the gap in a better understanding of environmental sustainability in the woodworking industry.

2. Materials and Methods

2.1. Material

The experiments were performed on spruce (*Picea abies*, Karst) from the central region of Czechia. After pine (52%), spruce wood is the second most heat-treated wood species (33%); therefore, it was chosen as the material for investigation. The material consisted of five logs, each 2 m long. The logs were cut at a tree height of 1.3 m above the ground. The log diameters were from 0.4 to 0.5 m. The logs were processed into radial timber, 30 mm in thickness, which was gradually dried to a 16% moisture content. Then, from each log, four radial samples with dimensions 200 mm × 100 mm × 20 mm were obtained. The specimens were sampled without juvenile wood. The samples were assorted into four sets and acclimated to a 12% moisture content.

2.2. Thermal Modification

Four sets of samples were prepared for this purpose. One set consisted of samples without thermal treatment (reference, denoted as REF). The other three sets of samples were thermally treated at 160, 180, and 210 °C temperatures (denoted as 160-TW, 180-TW, and 210-TW) following the Thermowood process according to Sikora et al. [3] (Figure 1). During thermal modification, the samples were protected using steam. Each set contained 10 samples. All samples were conditioned at 65% relative humidity and 20 °C before aging. All surface properties and parameters (chemical properties, color, roughness profiles, contact wetting angles) were measured on the samples before placing them in the Xenotest chamber.

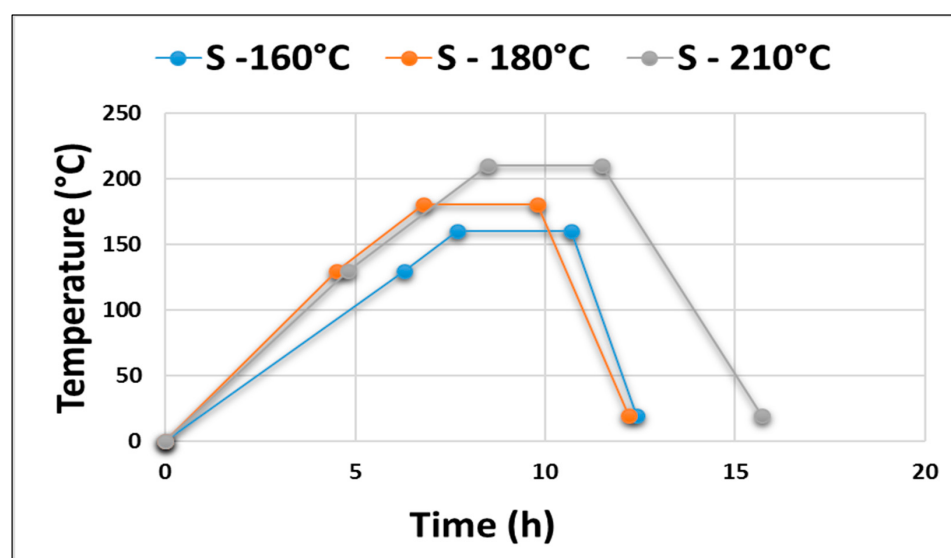


Figure 1. Thermal modification process of spruce wood [3].

2.3. Accelerated Aging

The degradation phenomena associated with the accelerated aging process were studied on test specimens prepared from the thermally treated and from the control samples.

The specimens' dimensions were 100 mm × 50 mm × 20 mm (length × width × thickness)—Figure 2. Each sample set was represented by ten test specimens, two from each log. The specimens in the individual sets were labeled as 160-TW-XE, 180-TW-XE, 210-TW-X, and REF. The degradation phenomena were studied and evaluated on the radial specimens' surfaces (Figure 2). Before being exposed to aging, all the specimens were acclimated under a relative air humidity of 65% and an air temperature of 20 °C. All the specimens were measured to obtain the values of all their studied surface properties and parameters (chemical properties, color, roughness profiles, wetting contact angles), and then the specimens were placed in the Xenotest chamber.

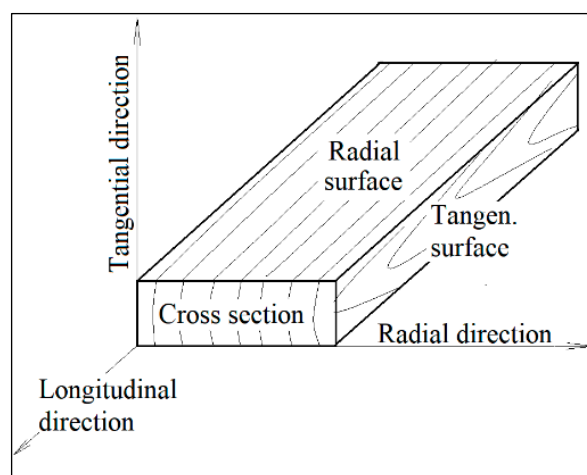


Figure 2. The test specimen of spruce wood.

The accelerated wood aging was realized in a xenon test chamber, Q-SUN Xe-3-HS (Q-Lab Europe, Ltd., Bolton, UK). The experimental material, situated in the xenon test chamber, was regularly shifted according to the recommended schedule, ensuring equal radiation intensity and heat for all the specimens.

The aging conditions in the Xenotest chamber followed the standard ASTM G 155 [43]. This standard is fundamental in determining the conditions for accelerated aging for non-metallic materials with the aid of a xenon charge tube. The exterior, so-called “wet mode” was underway, simulating conditions when wood is exposed to radiation and rain (Table 1).

Table 1. The aging parameters set according to the standard ASTM G 155 “wet mode”.

Step	Mode	Radiation Intensity (W·m ⁻²)	Black Panel Temperature (°C)	Air Temperature (°C)	Relative Air Humidity (%)	Time (min)
1	Radiation	0.35	63	48	30	102
2	Radiation + water spraying	0.35	63	48	90	18

2.4. Chemical Analyses

Samples were ground to a 200–300 µm particle size using a POLYMIX PX-MFC 90D laboratory mill (Kinematica, Luzern, Switzerland). Extractives were determined according to ASTM D1107-21 [44] with a mixture of absolute ethanol for analysis (Merck, Darmstadt, Germany) and toluene for analysis (Merck, Germany) (1.0/0.427, v/v), lignin according to Sluiter et al. [45], cellulose according to Seifert [46], and holocellulose according to Wise et al. [47]. Hemicelluloses were calculated as the difference between the holocellulose and cellulose contents. Measurements were made in four replicates per sample. The results are expressed as oven-dry mass per unextracted wood.

2.5. Color Measurement

The colorimetric values of the coordinates L^* , a^* , and b^* on all specimens were measured with the aid of a spectrophotometer, Spectro-guide 45/0 gloss (BYK-GARDNER GmbH, Geretsried, Germany) before the beginning and after ending of the aging process (600 h). The measurements were taken at ten spots per specimen. The color differences ΔL^* , Δa^* , Δb^* under different irradiation conditions and the total color difference ΔE^* were determined according to the following equations:

$$\Delta L^* = L_2 - L_1, L_3 - L_1, \dots, L_n - L_1 \quad (1)$$

$$\Delta a^* = a_2 - a_1, a_3 - a_1, \dots, a_n - a_1 \quad (2)$$

$$\Delta b^* = b_2 - b_1, b_3 - b_1, \dots, b_n - b_1 \quad (3)$$

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \dots \quad (4)$$

Note as follows: the “from 2 to n” means the color value after wood surface irradiation, and the index “1” denotes the referential value measured on the wood surface before the aging process. For each mode, the color was measured at 10 spots on each specimen, so the total number of measurements for each surface treatment mode was 100.

2.6. Evaluation of Wood Surface Morphology

The surface morphology of all specimens before and after aging was evaluated based on the roughness parameters: R_a (mean arithmetic deviation), R_z (the maximum peak height plus the maximum depression depth within the cut-off, or a sampling length), and R_{Sm} (mean distance between the trenches). The roughness profiles were recorded with a Surfcom 130A profilometer (Carl Zeiss, Oberkochen, Germany), consisting of a measuring unit and an evaluation unit.

Roughness was measured on radial surfaces, parallel to the grain course and perpendicular to the grain course, at two different spots on each specimen. The entire traversing length consisted of a pre-length segment, five sample length segments l_r (cutoff λ_c), and a post-length segment l_p . The basic lengths were chosen from the interval 0.025–8 mm, based on the preliminary measured values of the roughness parameters R_a and R_z .

The morphology of the thermal-treated wood surface structure after having finished the aging process was also studied with the aid of a Keyence VHX 7000 digital microscope (Keyence Corporation, Osaka, Japan). All surfaces were scanned using a VH-Z100R camera (Keyence Corporation, Osaka, Japan) performing at a 200-fold amplification. The scan size was 10×10 mm. The scanned surfaces were processed by applying a topographic height map, and in this way, 3D morphological patterns were generated for each surface.

2.7. Wood Surface Wetting with Water

Wood surface wetting with water was realized with a Krüss DSA30 Standard goniometer (Krüss, Hamburg, Germany). The wetting process was evaluated using the DSA3 software package (Krüss, Hamburg, Germany). Wood wetting was performed by applying a drop of redistilled water with a volume of 0.0018 mL onto the wood surface. From the moment in which the drop attained the wood surface up to the complete soaking into this substrate. The drop profile history was scanned in the grain direction. This profile was used for determining the contact angle as a measure of wetting extent. The scanning frequency per second was adjusted according to the wetting process duration. The drop shape was analyzed, and the contact angle was measured by circle methods.

2.8. FTIR Spectroscopy

The surfaces of solid samples were analyzed by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). The spectra were acquired by accumulating 64 scans at a spectral resolution of 4 cm^{-1} in an absorbance mode from 4000 to 650 cm^{-1} and standardized using the baseline method. Obtained data were analyzed using the OMNIC 9.0 software. Measurements were performed four times per sample.

2.9. Fiber Tester Analysis

A 0.5 g sample of holocellulose was soaked in 500 mL of distilled water for 24 h. The mixture was then pulverized for 5 min at 850 rpm using an IKA RW 20 Digital Mixer equipped with blunt blades (IKA-Werke GmbH & Co. KG, Staufen, Germany). A portion of 300 mL of the mixed sample was used for measurement. Fiber dimensional characteristics were determined using an L & W Fiber Tester analyzer (Lorentzen and Wettre, Kista, Sweden), which uses two-dimensional imaging technology. This automated measurement technology allows frequent and rapid analysis of fiber quality, assessing properties such as fiber length, width, and fine fraction (fiber lengths from 0.1 mm to 0.3 mm). Measurements were performed in a single replicate per sample, with fiber counts in each population ranging from 16,248 to 19,226 cells.

2.10. Evaluation of the Results

The results were processed in the STATISTICA version 10.0 program. The basic statistical characteristics (mean, standard deviation) were determined by using descriptive statistics. The impacts of the studied factors on the given properties were evaluated with the multi-way variance analysis (MANOVA) and Duncan's test.

3. Results and Discussion

3.1. Chemical Analyses

Wood contains especially low-molecular compounds that can be extracted with water vapor or solvents with different polarities—from non-polar to highly polar. They are extractive substances, mainly terpenes, fats, waxes, triglycerides, resin acids, steryl esters, and phenols. Wood extractives can migrate to the surface if mobile under thermal modification conditions. In the temperature range of 100 – $160\text{ }^{\circ}\text{C}$, fats and waxes move along the axial parenchyma cells to the surface of the pine sapwood during the heat treatment. At elevated temperatures (above $180\text{ }^{\circ}\text{C}$), fats and waxes disappeared from the pine sapwood surface [48]. Some extractive substances decompose at elevated temperatures and escape from the wood, while some new ones are created due to the decomposition of polysaccharides, especially hemicelluloses and partially also lignin. Almost all the original extractives disappeared, and new compounds arose such as anhydrosugars and phenolic compounds in heat-treated pine wood at 190 – $210\text{ }^{\circ}\text{C}$ [49]. The wood chemical composition changed with the heat treatment because of the different thermal resistance of the chemical compounds. Heat-treated wood generally had more extractives, apparent lignin and cellulose, and fewer hemicelluloses [50]. Our results are in line with the above findings; the thermal modification of spruce wood causes a decrease in the content of polysaccharides mainly through the degradation of hemicelluloses. The amount of more thermally stable polymers (lignin, cellulose) in modified wood also increases slightly, and the total amount of extractive substances also increases (Table 2). The content of hemicelluloses in the thermally treated wood at a temperature of $210\text{ }^{\circ}\text{C}$ decreased by 72.39%, after accelerated aging, by up to 77.70%. Similarly, greater decreases in hemicelluloses were observed after aging even at lower temperatures (160-TW—7.16%, 180-TW—26.65%, 160-TW-XE—7.37%, and

180-TW-XE—35.02%). Since the aging was in wet mode, the results indicated the leaching of part of the hemicelluloses by water.

Table 2. Chemical composition of untreated, thermally treated, and aged spruce wood (% odw, SD are in the parentheses).

Sample	Extractives	Lignin	Cellulose	Holocellulose	Hemicelluloses
REF	0.98 (0.05)	26.24 (0.04)	45.35 (0.26)	73.43 (0.61)	28.07 (0.68)
160-TW	2.11 (0.07)	26.45 (0.07)	45.48 (0.14)	71.54 (0.31)	26.06 (0.38)
180-TW	2.71 (0.26)	28.65 (0.09)	46.33 (0.21)	66.93 (0.61)	20.59 (0.81)
210-TW	3.49 (0.25)	33.08 (0.05)	50.64 (0.17)	58.39 (0.12)	7.75 (0.26)
160-TW-XE	1.63 (0.10)	27.68 (0.40)	45.38 (0.12)	71.38 (0.36)	26.00 (0.40)
180-TW-XE	2.25 (0.14)	32.14 (0.18)	46.23 (0.37)	64.47 (0.27)	18.24 (0.33)
210-TW-XE	3.07 (0.23)	35.26 (0.43)	52.56 (0.11)	58.82 (0.22)	6.26 (0.12)

3.2. Color Changes

The first changes that were visually observed on the surface of spruce wood during thermal treatment and the aging process were color changes. As the heat treatment temperature changed and after accelerated aging, the values of the color coordinates L^* , a^* , and b^* of the spruce wood changed significantly, which was confirmed by the results of the two-factor analysis of variance. The basic statistical characteristics of the values of the individual color coordinates are shown in Table 3.

Table 3. Basic statistical characteristics of the values of the color coordinates L^* , a^* , and b^* before and after 600 h of aging of thermally treated spruce wood.

Conditions	Color Coordinates	Basic Statistical Characteristics	Temperature (°C)			
			REF	160	180	210
Before Aging (TW)	L^*	$\bar{x}$	85.07	75.99	58.46	32.09
		s	0.74	2.52	2.14	2.03
	a^*	$\bar{x}$	3.44	7.05	12.67	7.02
		s	0.37	0.57	0.65	1.25
	b^*	$\bar{x}$	19.06	26.86	29.79	10.59
		s	0.65	1.14	1.02	2.54
After Aging (TW-XE)	L^*	$\bar{x}$	76.27	71.51	71.71	51.00
		s	1.76	2.89	2.35	10.63
	a^*	$\bar{x}$	3.91	6.50	5.77	6.97
		s	0.64	0.86	0.80	1.82
	b^*	$\bar{x}$	10.60	15.16	14.07	12.93
		s	0.93	2.09	2.00	1.90

The mean value of L^* lightness of the spruce specimens before thermal treatment and before aging was 85, which is in line with the published results [50]. Spruce wood is classified as a light species based on the lightness values and the values of the color coordinates a^* and b^* . These are more susceptible to discoloration in thermal treatment and aging [51,52].

With the increasing thermal modification temperature, the lightness decreased significantly up to a value of 32. The values of the a^* and b^* coordinates increased with the increasing thermal modification temperature up to 180 °C, i.e., they shifted towards a deeper red and yellow color. With the increasing temperature, the wood gradually acquired a more saturated brown color. By heat treatment at 210 °C, the values of the a^* and b^* coordinates decreased significantly again, giving the wood a distinct dark brown color (Figure 3).

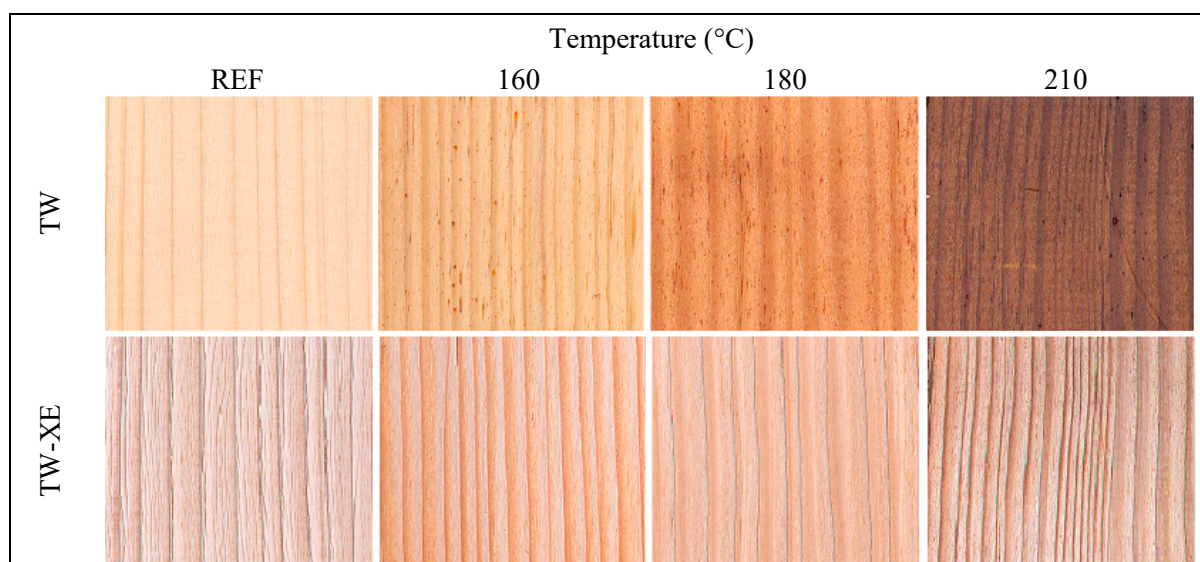


Figure 3. Color variation in spruce wood specimens during thermal treatment and accelerated aging.

Changes in the L^* , a^* , and b^* coordinates were also reflected in the overall color difference ΔE (Figure 4). Already after thermal treatment at 160 °C, the overall average color difference $\Delta E = 12.54$, which already represents a different color compared to the original color [53]. As can be seen from Figure 5, thermal treatment at higher temperatures increased the ΔE values several fold.

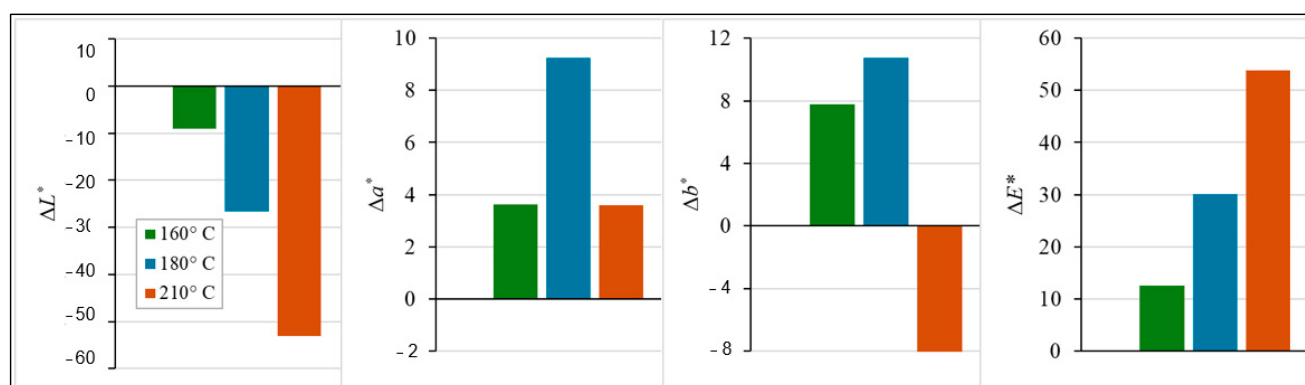


Figure 4. Differences in color coordinates and the total color difference after thermal treatment of spruce wood.

In the accelerated aging process under simulated outdoor conditions with simulated rain, the color changes in the spruce wood surface were qualitatively and quantitatively different compared to the thermal treatment (Table 3). Two factors (radiation and water) interacted in the wet aging mode. As a result of radiation-induced photodegradation, the spruce surface without thermal treatment darkened more intensively, which agrees with works [54,55]. This was also observed for the thermally treated wood at 160 °C. The second factor (water), interacting with the radiation itself, had the opposite effect. The longer the aging process, the greater the influence of the second factor. As a result of the shift in values, particularly of the b^* coordinate, towards achromatic colors (Figure 5), the spruce wood in all cases gradually turned gray and acquired the so-called patina (Figure 3). Likewise, acetylated wood is susceptible to weathering in outdoor conditions and begins to fade and turn gray [56].

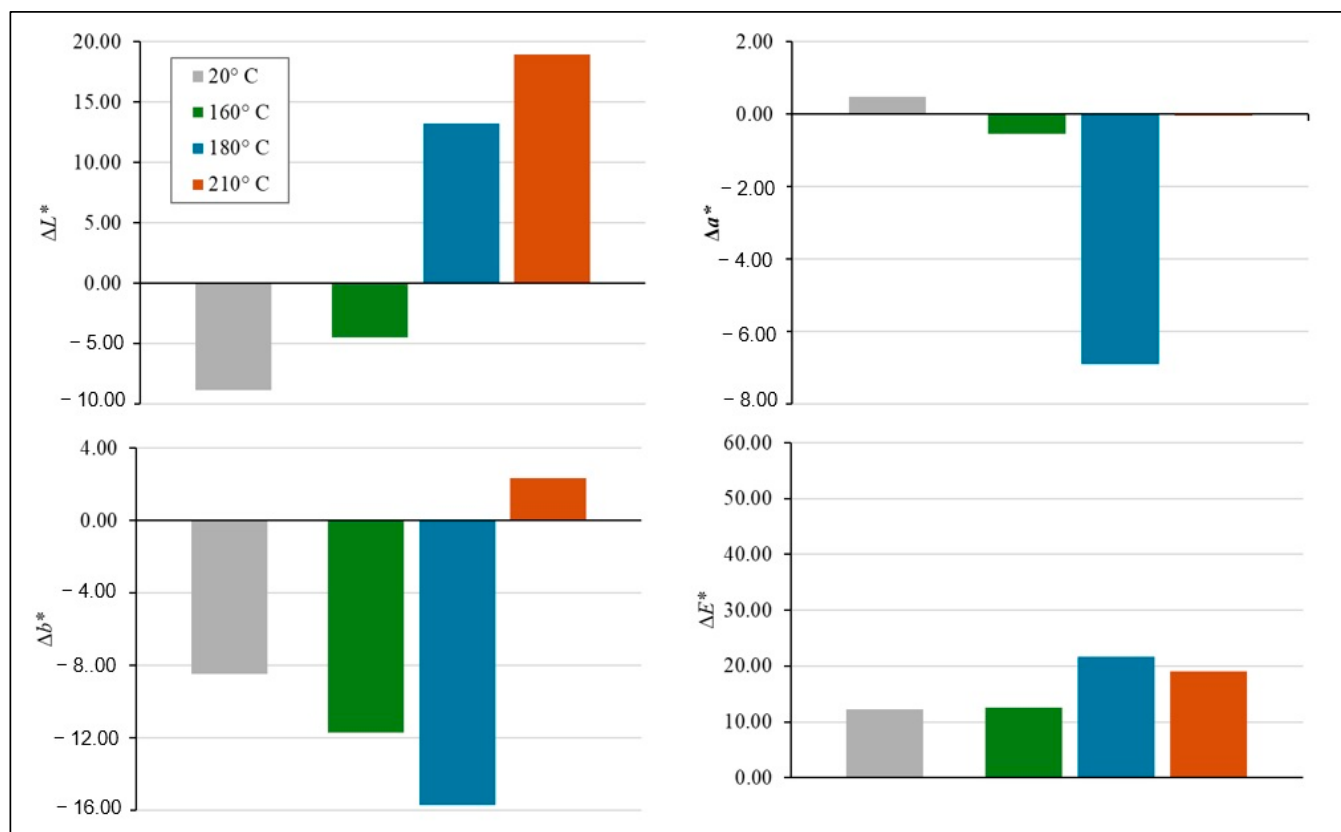


Figure 5. Differences in color coordinates and the total color difference thermal treatment spruce wood after accelerated aging.

3.3. Morphology of Surfaces

The results of the three-factor analysis of variance confirmed the significant influence of all three factors evaluated (thermal treatment, aging, and anatomical direction) and their interactions on the roughness parameters.

Because of the orientation of its cellular elements, the original surface of the spruce wood treated by milling had significantly lower values of roughness parameters in the grain direction than perpendicular to the grain course (Table 4). The results of the spruce wood roughness were in good agreement with those of Gurau [57] and Csanády et al. [58].

The thermal treatment slightly increased the roughness of the radial surfaces of the spruce wood (Table 4). Greater changes in roughness were observed perpendicular to the grain course than in the grain direction and this was due to the different degradation of spring and summer wood [59]. Spring wood is more susceptible to degradation [60,61]. Although this difference was statistically significant, from a practical point of view, we can neglect these differences between thermally untreated and treated spruce wood. This is especially true for roughness in the longitudinal direction. High temperatures cause the degradation of hemicelluloses [62,63], which break down into volatile products that evaporate at high temperatures [64].

Table 4. Statistical characteristics of roughness parameters before and after 600 h of accelerated aging of thermally treated spruce wood.

Temperature (°C)	Statistical Characteristics	Roughness Parameters—Parallel to Fibers (μm)					
		Before Aging (TW)			After Aging (TW-XE)		
		R_a	R_z	R_{Sm}	R_a	R_z	R_{Sm}
20 (REF)	$\bar{x}$	3.16	25.47	487.62	11.57	86.78	1314.90
	s	0.78	6.53	116.91	2.75	15.09	685.25
160	$\bar{x}$	4.07	29.26	696.13	7.68	49.36	2037.03
	s	2.93	15.82	303.12	3.13	20.26	1049.18
180	$\bar{x}$	4.08	26.09	563.62	6.16	41.33	1350.95
	s	1.84	11.29	252.33	2.09	14.06	755.55
210	$\bar{x}$	4.34	27.65	582.96	11.01	75.96	1527.38
	s	1.49	8.62	329.68	5.21	37.32	864.09
		Roughness parameters—perpendicular to fibers (μm)					
		R_a	R_z	R_{Sm}	R_a	R_z	R_{Sm}
20 (REF)	$\bar{x}$	6.09	48.29	251.08	35.20	292.27	1180.421
	s	0.65	5.59	22.20	5.71	47.00	987.25
160	$\bar{x}$	7.99	54.54	522.26	23.46	151.31	1854.32
	s	2.35	16.37	398.98	5.38	32.22	1042.30
180	$\bar{x}$	5.15	43.71	227.50	33.45	149.60	2938.51
	s	1.41	11.49	208.09	7.03	20.70	1339.36
210	$\bar{x}$	5.86	46.76	242.61	48.19	213.55	1180.78
	s	2.10	14.29	235.75	12.85	93.12	1371.42

After the aging process, a decrease in carbonyl groups and hydrolysis reactions affecting mainly the acetyl groups of hemicelluloses occurred in the non-thermally treated spruce wood due to the interaction of radiation with water. These phenomena resulted in a more pronounced degradation of the spruce wood structure. This was reflected in significantly higher values of the roughness parameters and greater changes were found in the perpendicular direction than in the grain direction (Table 4). This is again due to the different densities of spring and summer wood [50]. The average density of spring spruce wood is $300 \text{ kg} \cdot \text{m}^{-3}$, while summer wood is $750 \text{ kg} \cdot \text{m}^{-3}$ [65]. These differences in density resulted in the faster erosion of spring wood during the aging process and a significant increase in roughness measured mainly perpendicular to the grain direction. Our results are in line with the findings of the authors [66,67]. This differential erosion in spring and summer wood resulted in the creation of the so-called “plastic texture”, which is generally typical for conifers [68,69].

The thermal treatment made the spruce wood more hydrophobic. It was more resistant to both air humidity and liquid water. This significantly slowed down the destructive action of radiation in interaction with water in the aging process. This resulted in smaller changes in the values of the roughness parameters. The exception was the thermal treatment at 210 °C. The effect of this high temperature resulted in increased degradation of the coating layers and incipient charring. This degraded wood was less resistant to water in the aging process, which was reflected in a more pronounced change in the roughness parameters (Table 4).

Changes in the surface morphology of the spruce wood caused by the influence of the studied factors can be seen on the topographic elevation map (Figures 6 and 7).

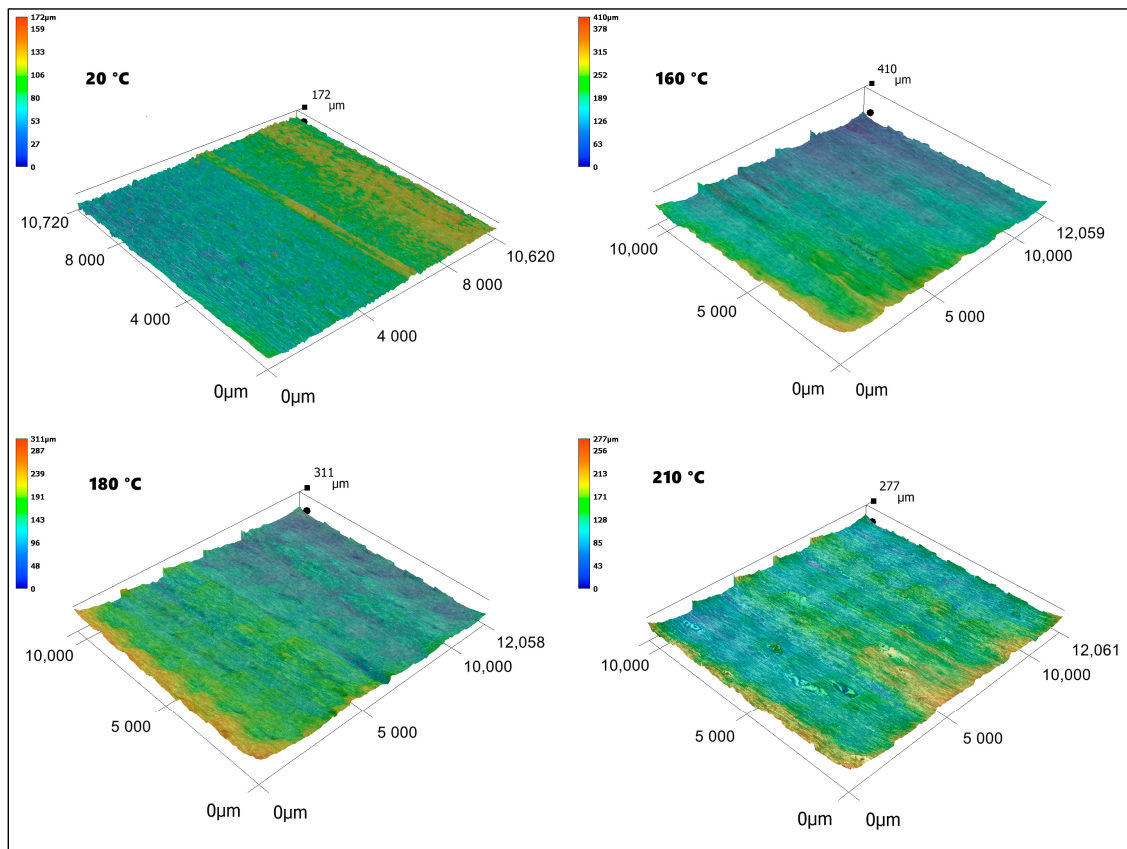


Figure 6. Topographic elevation map of spruce wood surface after different thermal modifications.

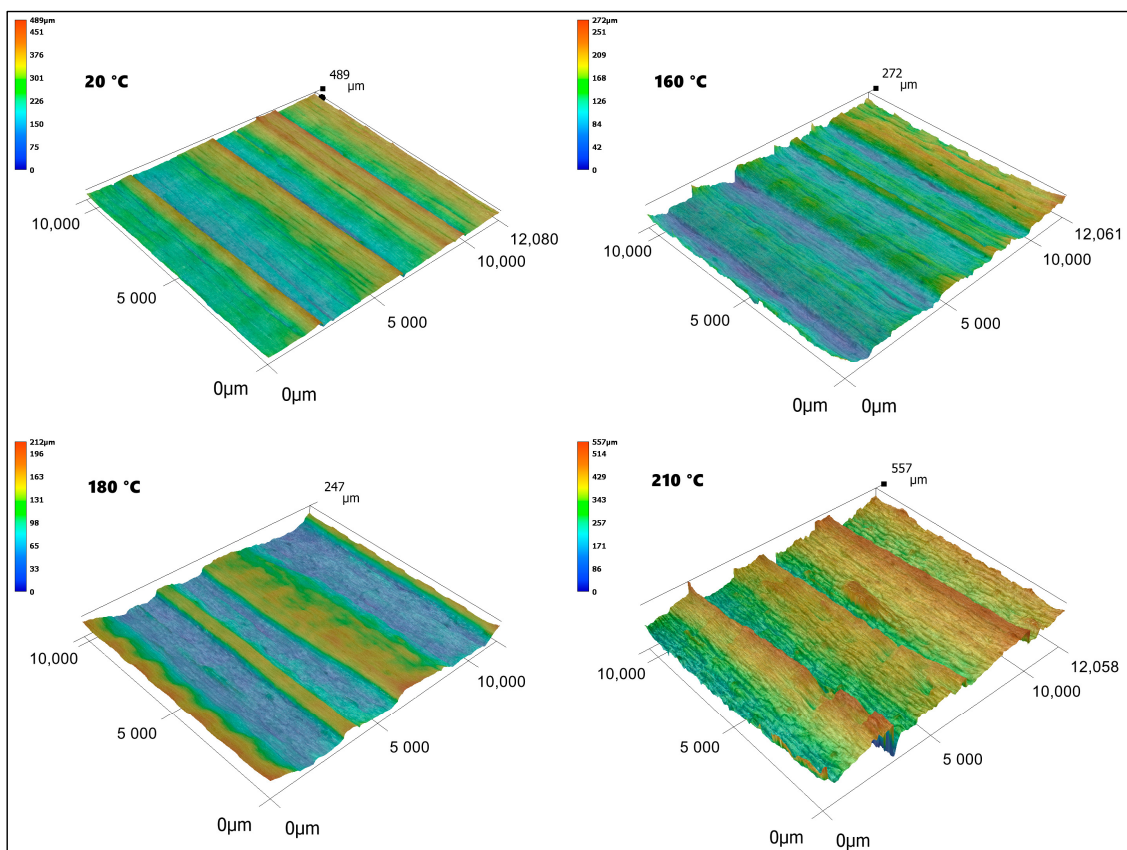


Figure 7. Topographic elevation map of thermally modified spruce wood after 600 h of accelerated aging.

3.4. Wetting of Spruce Wood with Water

The results of the water wetting of the spruce wood carried out with a drop applied to its surface are shown in Table 5. The average contact angle at the beginning of the wetting process was 32° for the untreated spruce wood. After being applied to the wood, the drop spread continuously over the surface and simultaneously soaked into the wood. The average soaking time of the water drop in the spruce wood was 26 s. This was imperfect wetting. The contact angle values throughout the wetting process were the result of the morphology of the wood surface and its chemical composition [70].

Table 5. Basic statistical characteristics of the contact angle θ_0 before and after 600 h of aging of thermally treated spruce wood.

Temperature (°C)	Statistical Characteristics	Wetting Before Aging (TW)		Wetting After Aging (TW-XE)	
		Contact Angle θ (°)	Time of Wetting t (s)	Contact Angle θ (°)	Time of Wetting t (s)
20 (REF)	$\bar{x}$ s	32 7	26 19	9 4	1.2 0.4
160	$\bar{x}$ s	104 5	625 127	72 21	13.8 9.2
180	$\bar{x}$ s	107 8	984 242	32 22	2.5 1.8
210	$\bar{x}$ s	104 7	876 237	2 3	0.3 0.4

Signaled by its color change, chemical changes after thermal treatment of the spruce wood significantly affected its hydrophilicity or hydrophobicity. Thermal treatment at three different temperatures significantly increased the water resistance of spruce, which was also reflected in the contact angle values. The average contact angle values of the thermally treated spruce at the beginning of the wetting process were in all cases above 100° (Table 5). This state of incomplete non-wetting persisted for an average of 3.7 min. The duration of the entire wetting process, until the drop was completely absorbed into the wood, was increased by a factor of 24 to 37 for the thermally treated wood compared to the untreated wood. These facts indicate the hydrophobic character of the surface of the spruce wood after its thermal treatment. Qualitatively similar results of thermally treated wood are also reported by Todaro et al. [71], Miklečić et al. [72], and Bekhta et al. [73].

The changes in chemical composition and morphology that occurred in the spruce wood during accelerated aging were significantly reflected in a reduction in water resistance, as evidenced by significantly lower measured contact angle values and a significantly shortened wetting process (Table 5). Both the wetting angles and the times for complete soaking of the drop in the wood were highly variable, indicating a high heterogeneity of the spruce wood surfaces.

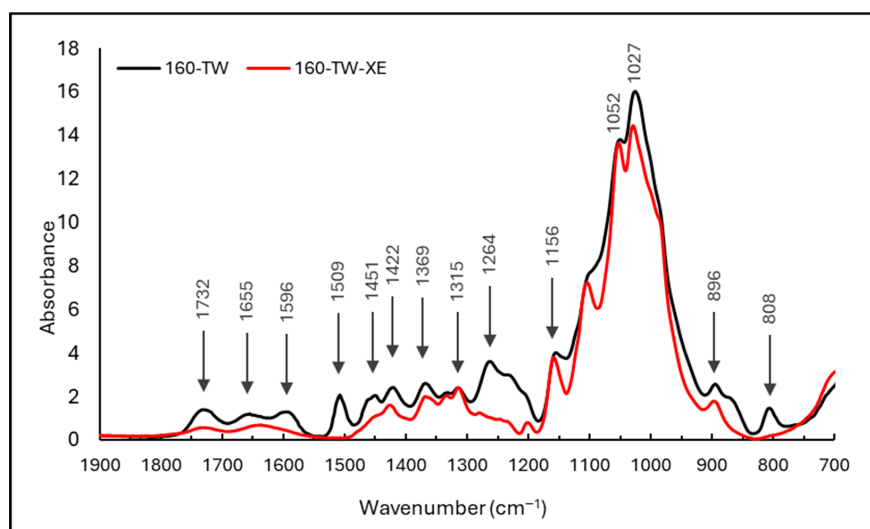
The average value of the contact angle at the beginning of wetting of the untreated thermal wood was 9° and the average duration of this process was 1.2 s. Cases of complete wetting were also recorded. The thermally treated wood at 160 °C was the most resistant to wetting, but the average contact angle after aging dropped to 72°, indicating imperfect wetting of these surfaces. Even better wetting after aging was observed for the wood thermally treated at 180 °C. The contact angle was only half that of the previous case. The wetting time was also significantly reduced. The wood thermally treated at 210 °C lost almost all its water resistance after the accelerated aging process was complete (Table 5). In most cases, this was complete wetting.

The results showed that the wood subject to thermal treatment to increase hydrophobicity against environmental factors gradually loses this property and is prone to degrading effects.

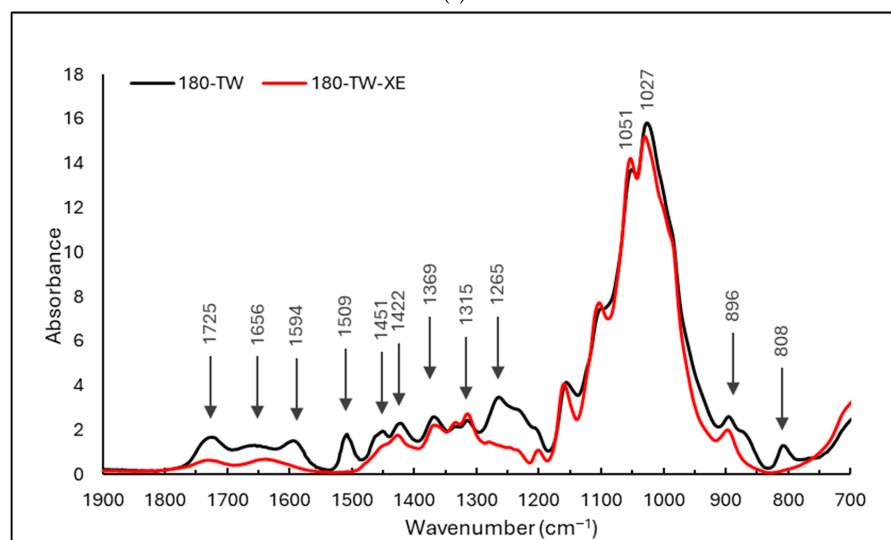
3.5. FTIR Spectroscopy

The most significant differences between the spectra of the thermally modified wood before and after exposure to UV irradiation pertain to absorption bands of lignin (Figure 8a–c). The bands at 1509 and 1596 cm^{-1} (aromatic skeletal vibrations) and at 808 cm^{-1} (C–H out-of-plane aromatic in lignin) completely disappeared. A decrease in the intensity of the absorption bands can also be observed in the region 1485–1440 cm^{-1} (overlapping bands of C–H deformation vibrations in lignin and polysaccharides) and 1300–1185 cm^{-1} ($\text{C}_{\text{aryl}}\text{–O}$, guaiacyl ring breathing with CO stretching at 1264 cm^{-1} , and C–O linkage in guaiacyl aromatic methoxyl groups and acetyl groups in xyloglucan at 1230 cm^{-1}) [74,75]. These findings are consistent with Hoffman et al. [76] and Godinho et al. [77], indicating that thermal modification does not contribute to lignin protection.

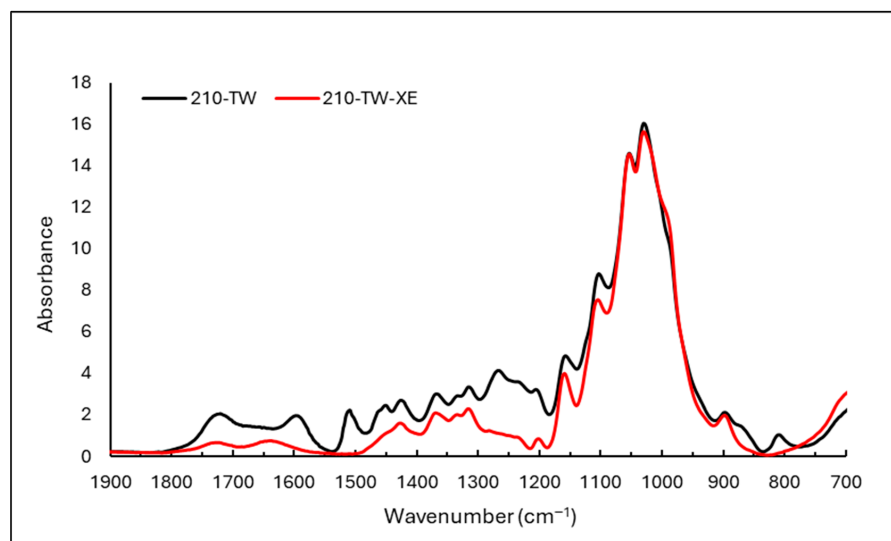
Weathering also caused a significant decrease in the absorption bands' intensity in the carbonyl groups region between 1800 and 1630 cm^{-1} . This is a band around 1655 cm^{-1} , which is assigned to conjugated carbonyl groups in lignin and extractives, and to adsorbed water molecules [78,79]. For the next absorption band in this region, not only a decrease in its intensity can be observed, but also a shift in its maximum. In the case of the sample thermally modified at 160 °C, a decrease of almost 68% and a shift in its maximum from 1732 to 1730 cm^{-1} is recorded; in the case of the sample modified at 180 °C, there is a decrease of about 62% and a shift in the maximum from 1725 to 1731 cm^{-1} and in the case of the sample modified at 210 °C, there is a decrease of up to 72% and a shift in its maximum from 1720 to 1726 cm^{-1} . Various changes in this spectral region caused by weathering or artificial aging are described in the literature. An increase in the intensity of the absorption band of carbonyl compounds was observed by Geffert et al. [80] after exposure of beech and pine wood to intense UV radiation by a Sirius UVIR device with a mercury lamp (125 W) within 150 min, further by Kúdela et al. [50] by accelerated aging of spruce wood during 600 h of simulated outdoor conditions, and by Hofmann et al. [76] after 36 h UV irradiation of spruce wood. On the other hand, like in this work, other authors have observed a decrease in the intensity of carbonyl bands after the artificial aging of wood. Firstly, it was after 800 h UV irradiation of Scots pine wood [81], secondly, after 2000 h of artificial aging of pine sapwood [82], and thirdly, after 24-month natural weathering of unmodified and thermally modified pine and ash wood [77]. During UV irradiation, several processes take place in wood simultaneously with different effects on the absorption in this region. It appears that the primary cause of these changes is lignin degradation due to UV irradiation. By degradation of lignin, macromolecule free radicals are generated, which subsequently react with oxygen to form various carbonyl compounds, which is reflected in an increase in the intensity of their absorption bands. However, lignin degradation increases the exposure of cellulose and hemicelluloses to weathering. It can be assumed that with the increasing duration of UV irradiation, degradation of acetyl groups, esters, and carboxylic acids occurs on the wood surface, resulting in a decrease in the intensity of the absorption band of carbonyl groups [77,82]. Amorphous polysaccharides are preferentially degraded by UV radiation. According to Tornaiainen et al. [79], this is indicated by an increase in the intensity of the absorption band at 1156 cm^{-1} (C–O–C vibration in cellulose and hemicelluloses).



(a)



(b)



(c)

Figure 8. (a). FTIR spectra of spruce wood thermally treated at 160 °C (160-TW) and after accelerated aging (160-TW-XE). (b). FTIR spectra of spruce wood thermally treated at 180 °C (180-TW) and after accelerated aging (180-TW-XE). (c). FTIR spectra of spruce wood thermally treated at 210 °C (210-TW) and after accelerated aging (210-TW-XE).

3.6. Fiber Tester Analysis

The results obtained from the Fiber Tester analysis (Figures 9 and 10) highlight the variations in fiber length and width distribution in the spruce wood samples based on the applied treatment. According to the fiber length distribution, the reference sample (REF) comprised 44.41% fibers longer than 0.5 mm and 42.39% of the fine proportion. Modifications in the treatment of the samples consistently reduced the proportion of fibers exceeding 0.5 mm in length and resulted in an increase in the fine proportion. The most notable changes were observed in the 210-TW-XE samples, where the combination of thermal treatment at 210 °C and subsequent exposure to the Xenotest reduced the content of fibers longer than 0.5 mm by 64%. The fine proportion content in these samples represented a share of 67.03%. As the heat treatment temperature increased, the fraction of longer fibers (>0.5 mm) decreased, while the proportion of shorter fibers (<0.5 mm) increased. The Xenotest caused a further reduction in the fraction of longer fibers.

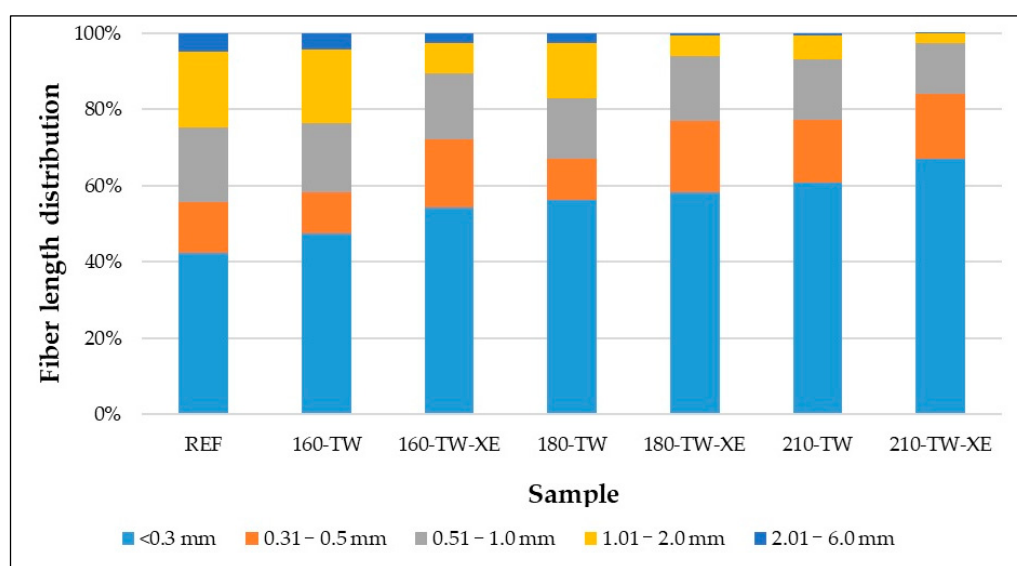


Figure 9. Fiber length distribution of spruce wood samples depends on its treatment.

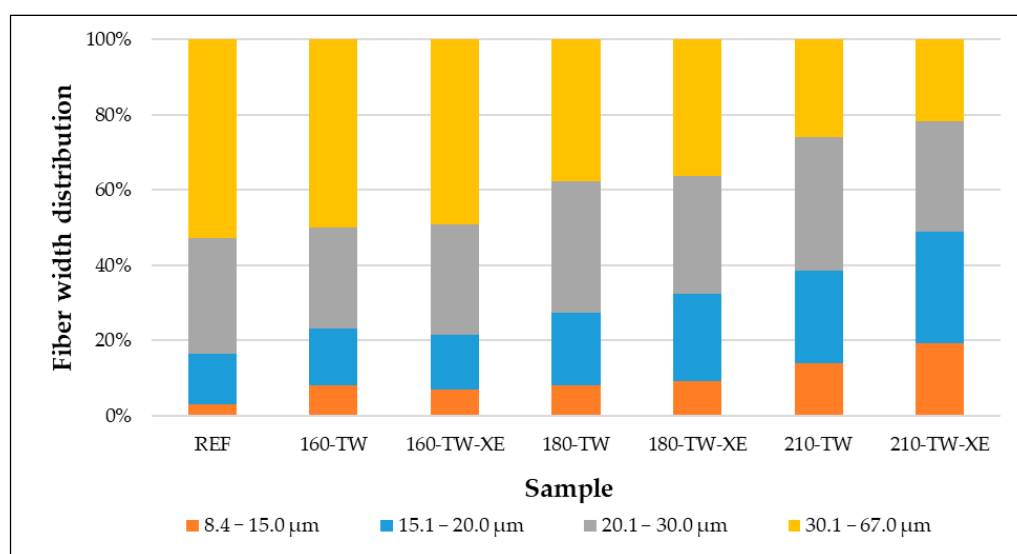


Figure 10. Fiber width distribution of spruce wood samples depends on its treatment.

The thermal treatment and subsequent Xenotest exposure also impacted the fiber width. The reference sample contained 52.79% of fibers wider than 30.1 μm. Thermal

treatment at 160 °C induced only minor changes in the fiber width distribution (Figure 10), and the Xenotest had an insignificant impact on fibers treated at this temperature. At 180 °C, the number of fibers wider than 30.1 μm decreased by 29%, with no substantial additional effect from the Xenotest. However, treatment at 210 °C reduced the fraction of fibers wider than 30.1 μm by 51%, with the Xenotest contributing an additional 8% reduction.

The distribution of the fiber length and width also depends on which part of the tree the wood sample is taken from. A spruce wood sample taken from the trunk contains a larger number of fibers shorter than 0.3 mm (approximately 50%) compared to the wood-top (approximately 35%). During thermal treatment and long-term storage of wood, there is a decrease in the fractions of longer fibers and an increase in the fractions of shorter fibers, which is reflected in a decrease in the average fiber length [83]. According to Sawoszczuk et al. [84], the decrease in the arithmetic mean of the fibers is linearly correlated with a decrease in the cellulose degree of polymerization. It is therefore assumed that these changes will be reflected in a decrease in the mechanical strength of the wood. Tyrväinen [85] stated that longer fibers have a greater number of interfibril bonding opportunities per fiber than shorter fibers. The length of the fibers is a very important parameter in the strength of wooden materials.

The applied treatments caused deformation, or “shrinkage,” of the fibers, resulting in changes to their dimensions, both in length and width. Many of these changes were irreversible, likely due to the structural alterations induced by the combined thermal and Xenotest treatments. Thermal modification places the wood cell wall in a permanently strained state [20,86], which could result in a loss of mechanical strength of the wood. The properties and structure of thermally modified wood are slightly different than untreated woods from the same wood species, and therefore it is necessary to look for suitable modification conditions that will improve the properties and prevent the wood’s mechanical strength loss.

4. Conclusions

The influence of thermal treatment and accelerated aging on the changes in the properties of spruce wood has been studied by wet chemical methods, infrared spectroscopy, color measurement, surface morphology, and wetting of the wood surface with water. The thermal treatment causes a significant decrease in hemicelluloses and a decrease in absorbances in the infrared spectra belonging to the lignin and carbonyl groups. As the temperature of the spruce wood treatment increases, the brightness of the wood decreases significantly, and the wood darkens, acquiring a dark brown color at the highest temperature. Due to the influence of radiation and water during accelerated aging, the spruce wood gradually turned gray. The reduction in the fiber length and width during aging points to opportunities for repurposing wood fibers in composite materials, such as particleboards or fiber-reinforced composites. Due to the improved wetting of the wood with liquids after aging, it is assumed that a better bond between the wood and the adhesive will be formed, which will be suitable for the improved properties of particleboard. The increased lignin content in aged wood provides a basis for extracting valuable chemicals like phenolic compounds, which can be used in adhesives or bio-based materials, or can be utilized in energy recovery processes, such as biomass combustion or pyrolysis.

The findings of this work are a prerequisite for innovative applications in composite materials, adhesives, and energy recovery, contributing to a more circular and environmentally friendly approach to wood processing. In future research, it would be necessary to study the effect of aging on industrially produced samples of heat-treated wood to determine the effect of aging (accelerated and natural) on real samples of the most used

wood species to produce thermowood (e.g., pine, spruce) and also from the perspective of released emissions and energy demand.

Author Contributions: Conceptualization, D.K. and F.K.; methodology, F.K. and E.V.; data curation, F.K., E.V., J.K., L.A. and I.Č.; writing—original draft preparation, F.K., T.J. and D.K.; writing—review and editing, F.K., J.K., E.V., E.K., T.J., L.A., D.K. and I.Č.; supervision, D.K. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Scientific Grant Agency of the Ministry of Education SR and the Slovak Academy of Sciences Grant No. 1/0117/22, and Grant No. 1/0656/23. This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-22-0030. This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-20-0159.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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

References

- Hill, C.A.S. *Wood Modification: Chemical, Thermal and Other Processes*; John Wiley & Sons: Chichester, UK, 2006; ISBN 978-0-470-02172-9.
- Esteves, B.M.; Pereira, H.M. Wood Modification by Heat Treatment: A Review. *BioResources* **2009**, *4*, 370–404. [[CrossRef](#)]
- Sikora, A.; Kačík, F.; Gaff, M.; Vondrová, V.; Bubeníková, T.; Kubovský, I. Impact of Thermal Modification on Color and Chemical Changes of Spruce and Oak Wood. *J. Wood Sci.* **2018**, *64*, 406–416. [[CrossRef](#)]
- Acosta, R.; Arango, J.A.M.; Silva, E.J.D. Technologies Applied to Wood Heat Treatments, a Review: Tecnologías Aplicadas a Los Tratamientos Térmicos En Madera, Una Revisión. *Sci. Technol.* **2021**, *26*, 129–136. [[CrossRef](#)]
- Boonstra, M.J.; Van Acker, J.; Tjeerdsma, B.F.; Kegel, E.V. Strength Properties of Thermally Modified Softwoods and Its Relation to Polymeric Structural Wood Constituents. *Ann. For. Sci.* **2007**, *64*, 679–690. [[CrossRef](#)]
- Militz, H. Heat Treatment Technologies in Europe: Scientific Background and Technological State-of-Art. In Proceedings of the Conference Enhancing the Durability of Lumber and Engineered Wood Products, Kissimmee, FL, USA, 11–13 February 2002; pp. 239–249.
- Baysal, E.; Kart, S.; Toker, H.; Degirmençtepe, S. Some Physical Characteristics of Thermally Modified Oriental-Beech Wood. *Maderas Cienc. Tecnol.* **2014**, *16*, 291–298. [[CrossRef](#)]
- Gérardin, P. New Alternatives for Wood Preservation Based on Thermal and Chemical Modification of Wood—A Review. *Ann. For. Sci.* **2016**, *73*, 559–570. [[CrossRef](#)]
- Jämsä, S.; Ahola, P.; Viitaniemi, P. Long-Term Natural Weathering of Coated ThermoWood. *Pigment Resin. Technol.* **2000**, *29*, 68–74. [[CrossRef](#)]
- Spear, M.J.; Dimitriou, A.; Marriott, R. Chemical Composition of Larch Oleoresin before and during Thermal Modification. *Forests* **2024**, *15*, 904. [[CrossRef](#)]
- Tjeerdsma, B.F.; Boonstra, M.; Pizzi, A.; Tekely, P.; Militz, H. Characterisation of Thermally Modified Wood: Molecular Reasons for Wood Performance Improvement. *Holz Roh Werkst.* **1998**, *56*, 149–153. [[CrossRef](#)]
- Čekovská, H.; Gaff, M.; Osvald, A.; Kačík, F.; Kubš, J.; Kaplan, L. Fire Resistance of Thermally Modified Spruce Wood. *BioResources* **2017**, *12*, 947–959. [[CrossRef](#)]
- Svoboda, T.; Ruman, D.; Gaff, M.; Gašparík, M.; Miftieva, E.; Dundek, L. Bending Characteristics of Multilayered Soft and Hardwood Materials. *BioResources* **2015**, *10*, 8461–8473. [[CrossRef](#)]
- Candelier, K.; Thevenon, M.-F.; Petrissans, A.; Dumarcay, S.; Gerardin, P.; Petrissans, M. Control of Wood Thermal Treatment and Its Effects on Decay Resistance: A Review. *Ann. For. Sci.* **2016**, *73*, 571–583. [[CrossRef](#)]
- Kačíková, D.; Kubovský, I.; Ulbriková, N.; Kačík, F. The Impact of Thermal Treatment on Structural Changes of Teak and Iroko Wood Lignins. *Appl. Sci.* **2020**, *10*, 5021. [[CrossRef](#)]
- Cirule, D.; Sansonetti, E.; Anderson, I.; Kuka, E.; Andersons, B. Enhancing Thermally Modified Wood Stability against Discoloration. *Coatings* **2021**, *11*, 81. [[CrossRef](#)]
- Krauss, A.; Piernik, M.; Pinkowski, G. Cutting Power during Milling of Thermally Modified Pine Wood. *Drv. Ind.* **2016**, *67*, 215–222. [[CrossRef](#)]
- Todaro, L.; Liuzzi, S.; Pantaleo, A.M.; Lo Giudice, V.; Moretti, N.; Stefanizzi, P. Thermo-Modified Native Black Poplar (*Populus nigra* L.) Wood as an Insulation Material. *iForest* **2021**, *14*, 268–273. [[CrossRef](#)]

19. Perdoch, W.; Benc, M.; Mazela, B. Wood from Field Tests as a Model for Assessing the Suitability of Post-Consumer Wood. *Forests* **2023**, *15*, 80. [\[CrossRef\]](#)
20. González-Peña, M.M.; Curling, S.F.; Hale, M.D.C. On the Effect of Heat on the Chemical Composition and Dimensions of Thermally-Modified Wood. *Polym. Degrad. Stab.* **2009**, *94*, 2184–2193. [\[CrossRef\]](#)
21. Majka, J.; Roszyk, E. Swelling Restraint of Thermally Modified Ash Wood Perpendicular to the Grain. *Eur. J. Wood Prod.* **2018**, *76*, 1129–1136. [\[CrossRef\]](#)
22. Calonego, F.; Severo, E.; Sansígolo, C.; de Brito, A. Physical and Chemical Changes in Juvenile and Mature Wood of *Shizolobium Parahyba* Caused by Thermal Modification. *J. Trop. For. Sci.* **2020**, *32*, 333–340. [\[CrossRef\]](#)
23. de Andrade Barbosa, J.; da Silva, B.M.; Ranzini, M.; Longui, E.L.; de Lima, I.L. Effect of thermal modification on wood properties of 38-year-old *Cariniana legalis* cultivated at different spacing. *Sci. Electron. Arch.* **2021**, *14*, 26–31. [\[CrossRef\]](#)
24. Kozakiewicz, P.; Drożdżek, M.; Laskowska, A.; Grześkiewicz, M.; Bytner, O.; Radomski, A.; Mróz, A.; Betlej, I.; Zawadzki, J. Chemical Composition as a Factor Affecting the Mechanical Properties of Thermally Modified Black Poplar (*Populus nigra* L.). *BioResources* **2020**, *15*, 3915–3929. [\[CrossRef\]](#)
25. Park, Y.; Han, Y.; Choi, Y.-S.; Lee, H.-M.; Yoon, S.-M.; Yeo, H.; Eom, C.-D. Correlation Analysis between Mass Loss of Wood Due to Thermal Modification and Equilibrium Moisture Content of Thermally Modified Wood. *BioResources* **2024**, *19*, 1283–1294. [\[CrossRef\]](#)
26. Calonego, F.W.; Severo, E.T.D.; Furtado, E.L. Decay Resistance of Thermally-Modified *Eucalyptus grandis* Wood at 140 °C, 160 °C, 180 °C, 200 °C and 220 °C. *Biores. Technol.* **2010**, *101*, 9391–9394. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Niemz, P.; Hofmann, T.; Rétfalvi, T. Investigation of Chemical Changes in the Structure of Thermally Modified Wood. *Maderas Cienc. Tecnol.* **2010**, *12*, 69–78. [\[CrossRef\]](#)
28. Salman, S.; Thévenon, M.F.; Pétrissans, A.; Dumarçay, S.; Candelier, K.; Gérardin, P. Improvement of the Durability of Heat-Treated Wood against Termites. *Maderas Cienc. Tecnol.* **2017**, *19*, 317–328. [\[CrossRef\]](#)
29. Minkah, M.; Afrifah, K.; Batista, D.; Militz, H. Chemical and Mechanical Characterization of Thermally Modified *Gmelina arborea* Wood. *Les/Wood* **2021**, *70*, 31–44. [\[CrossRef\]](#)
30. Bytner, O.; Drożdżek, M.; Laskowska, A.; Zawadzki, J. Influence of Thermal Modification in Nitrogen Atmosphere on the Selected Mechanical Properties of Black Poplar Wood (*Populus nigra* L.). *Materials* **2022**, *15*, 7949. [\[CrossRef\]](#) [\[PubMed\]](#)
31. Antons, A.; Čirule, D.; Andersone, I.; Verovkins, A.; Kuka, E. Influence of Different Modifications on Bending Strength of Wood. *Key Eng. Mater.* **2019**, *800*, 240–245. [\[CrossRef\]](#)
32. Javed, M.A.; Kekkonen, P.M.; Ahola, S.; Telkki, V.-V. Magnetic Resonance Imaging Study of Water Absorption in Thermally Modified Pine Wood. *Holzforschung* **2014**, *69*, 899–907. [\[CrossRef\]](#)
33. Alén, R.; Kotilainen, R.; Zaman, A. Thermochemical Behavior of Norway Spruce (*Picea abies*) at 180–225 °C. *Wood Sci. Technol.* **2002**, *36*, 163–171. [\[CrossRef\]](#)
34. Gosselink, R.J.A.; Krosse, A.M.A.; van der Putten, J.C.; van der Kolk, J.C.; de Klerk-Engels, B.; van Dam, J.E.G. Wood Preservation by Low-Temperature Carbonisation. *Ind. Crops Prod.* **2004**, *19*, 3–12. [\[CrossRef\]](#)
35. Yildiz, S.; Gezer, E.D.; Yildiz, U.C. Mechanical and Chemical Behavior of Spruce Wood Modified by Heat. *Build. Environ.* **2006**, *41*, 1762–1766. [\[CrossRef\]](#)
36. Moliński, W.; Roszyk, E.; Jabłoński, A.; Puszyński, J.; Cegiela, J. Mechanical Parameters of Thermally Modified Ash Wood Determined by Compression in Radial Direction. *Maderas Cienc. Tecnol.* **2016**, *18*, 577–586. [\[CrossRef\]](#)
37. Korkut, S.; Aydin, A. Evaluation of Physical and Mechanical Properties of Wild Cherry Wood Heat-Treated Using the Thermowood Process. *Maderas Cienc. Tecnol.* **2015**, *17*, 171–178. [\[CrossRef\]](#)
38. Gennari, E.; Picchio, R.; Lo Monaco, A. Industrial Heat Treatment of Wood: Study of Induced Effects on Ayous Wood (*Triplochiton scleroxylon* K. schum). *Forests* **2021**, *12*, 730. [\[CrossRef\]](#)
39. Winandy, J.; Lebow, P. Modeling Strength Loss in Wood by Chemical Composition. Part I. An Individual Component Model for Southern Pine. *Wood Fiber Sci.* **2001**, *33*, 239–254.
40. Esteves, B.M.; Domingos, I.J.; Pereira, H.M. Pine Wood Modification by Heat Treatment in Air. *BioResources* **2008**, *3*, 142–154. [\[CrossRef\]](#)
41. Roszyk, E.; Stachowska, E.; Majka, J.; Mania, P.; Broda, M. Moisture-Dependent Strength Properties of Thermally-Modified *Fraxinus excelsior* Wood in Compression. *Materials* **2020**, *13*, 1647. [\[CrossRef\]](#)
42. Demircioğlu, T.K.; Balıkoğlu, F.; İnal, O.; Arslan, N.; Ay, İ.; Atas, A. Experimental Investigation on Low-Velocity Impact Response of Wood Skinned Sandwich Composites with Different Core Configurations. *Mater. Today Commun.* **2018**, *17*, 31–39. [\[CrossRef\]](#)
43. ASTM-G155-05; Practice for Operating Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials. ASTM International: West Conshohocken, PA, USA, 2005.
44. ASTM D1107-21; Standard Test Method for Ethanol-Toluene Solubility of Wood. ASTM International: West Conshohocken, PA, USA, 2021.

45. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. Determination of Structural Carbohydrates and Lignin in Biomass. In *Laboratory Analytical Procedure (LAP)*; National Renewable Energy Laboratory: Denver, CO, USA, 2012.
46. Seifert, V. Über ein neues Verfahren zur Schnellbestimmung der Rein-Cellulose. (About a New Method for Rapid Determination of Pure Cellulose). *Papier* **1956**, *13*, 301–306.
47. Wise, L.E.; Murphy, M.; d’Addieco, A.A. Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses. *Pap. Trade J.* **1946**, *122*, 35–43.
48. Nuopponen, M.; Vuorinen, T.; Jämsä, S.; Viitaniemi, P. The Effects of a Heat Treatment on the Behaviour of Extractives in Softwood Studied by FTIR Spectroscopic Methods. *Wood Sci. Technol.* **2003**, *37*, 109–115. [[CrossRef](#)]
49. Esteves, B.; Videira, R.; Pereira, H. Chemistry and Ecotoxicity of Heat-Treated Pine Wood Extractives. *Wood Sci. Technol.* **2011**, *45*, 661–676. [[CrossRef](#)]
50. Kúdela, J.; Ihracký, P.; Kačík, F. Discoloration and Surface Changes in Spruce Wood after Accelerated Aging. *Polymers* **2024**, *16*, 1191. [[CrossRef](#)] [[PubMed](#)]
51. Fan, Y.; Gao, J.; Chen, Y. Colour Responses of Black Locust (*Robinia pseudoacacia* L.) to Solvent Extraction and Heat Treatment. *Wood Sci. Technol.* **2010**, *44*, 667–678. [[CrossRef](#)]
52. Chen, Y.; Gao, J.; Fan, Y.; Tshabalala, M.A.; Stark, N.M. Heat-Induces Chemical and Color Changes of Extractive-Free Black Locust (*Robinia pseudoacacia*) Wood. *BioResources* **2012**, *7*, 2236–2248. [[CrossRef](#)]
53. Pandey, K.K.; Vuorinen, T. Comparative Study of Photodegradation of Wood by a UV Laser and a Xenon Light Source. *Polym. Degrad. Stab.* **2008**, *93*, 2138–2146. [[CrossRef](#)]
54. Allegretti, O.; Travan, L.; Cividini, R. Drying Techniques to Obtain White Beech. In Proceedings of the EDG Conference, Bled, Slovenia, 14–17 June 2009; pp. 7–13.
55. Mokrzycki, W.; Tatol, M. Color Difference Delta E—A Survey. *Mach. Graph. Vis.* **2011**, *20*, 383–411.
56. Sandak, A.; Gordobil, O.; Poohphajai, F.; Herrera Diaz, R. Weathering of Wood Modified with Acetic Anhydride—Physical, Chemical, and Aesthetical Evaluation. *Forests* **2024**, *15*, 1097. [[CrossRef](#)]
57. Gurau, L. *Quantitative Evaluation of the Sanding Quality in Furniture Manufacturing*; Transilvania University: Braşov, Romania, 2007; ISBN 978-973-598-126-6.
58. Csanady, E.; Magoss, E.; Tolvaj, L. *Quality of Machined Wood Surfaces*; Springer: Berlin/Heidelberg, Germany, 2015; ISBN 978-3-319-22418-3.
59. Monaco, A.L.; Pelosi, C.; Agresti, G.; Picchio, R.; Rubino, G. Influence Fo Thermal Treatment on Selected Properties of Chestnut Wood and Full Range of Its Vidual Features. *Drewno* **2020**, *63*, 5–24. [[CrossRef](#)]
60. Hamada, J.; Pétrissans, A.; Mothe, F.; Ruelle, J.; Pétrissans, M.; Gérardin, P. Variations in the Natural Density of European Oak Wood Affect Thermal Degradation during Thermal Modification. *Ann. For. Sci.* **2016**, *73*, 277–286. [[CrossRef](#)]
61. Hamada, J.; Pétrissans, A.; Mothe, F.; Ruelle, J.; Pétrissans, M.; Gérardin, P. Intraspecific Variation of European Oak Wood Thermal Stability According to Radial Position. *Wood Sci. Technol.* **2017**, *51*, 785–794. [[CrossRef](#)]
62. Huang, X.; Kocaefe, D.; Kocaefe, Y.; Boluk, Y.; Pichette, A. A Spectrocolorimetric and Chemical Study on Color Modification of Heat-Treated Wood during Artificial Weathering. *Appl. Surf. Sci.* **2012**, *258*, 5360–5369. [[CrossRef](#)]
63. Marino, S.; Gaff, M.; Sethy, A.K.; Kamboj, G.; Rezaei, F.; Kačík, F.; Hosseini, S.B.; Li, H.; Hui, D. Enhancing the Fire Resistance Properties of Thermally Modified *Robinia pseudoacacia* Wood with Natural and Synthetic Flame Retardants: Chemical Characterisation and Fire Behaviour. *Eur. J. Wood Prod.* **2024**, *82*, 1145–1157. [[CrossRef](#)]
64. Korkut, S.; Kocaefe, D. Effect of Heat Treatment on Wood Properties. *Duzce Univ. J. For.* **2009**, *5*, 11–34.
65. Moliński, W.; Cunderlik, I.; Krauss, A.; Fabisiak, E.; Jurek, P. Gradient of Density and Tensile Strength along the Grains of Spruce Wood (*Picea abies*) within Individual Annual Rings. *Ann. Wars. Univ. Life Sci. SGGW For. Wood Technol. SGGW For. Wood Technol.* **2009**, *69*, 87–92.
66. Hazneza, S.; Evans, P.D. End-Grain Erosion of Douglas Fir Wood during Natural Weathering. *Int. Wood Prod. J.* **2016**, *7*, 3–11. [[CrossRef](#)]
67. Preklet, E.; Tolvaj, L.; Tsuchikawa, S.; Varga, D. Photodegradation Properties of Earlywood and Latewood Spruce Timber Surfaces. *Acta Silv. Lignaria Hung.* **2021**, *17*, 9–20. [[CrossRef](#)]
68. Andersone, I.; Andersons, B.; Avramidis, G.; Barbu, M.; Bergland, L.; Clemons, C.; Diitenberger, M.; Evans, P.; Frihart, C.; Ibach, R.; et al. *Handbook of Wood Chemistry and Wood Composites*, 2nd ed.; Rowell, R.M., Ed.; CRC Press: Boca Raton, FL, USA, 2012; ISBN 978-0-429-10909-6.
69. Williams, R.S.; Feist, W.C. *Water Repellents and Water-Repellent Preservatives for Wood*; FPL-GTR-109; U.S. Department of Agriculture, Forest Service, Forest Products Laboratory: Madison, WI, USA, 1999.
70. Chu, D.; Mu, J.; Avramidis, S.; Rahimi, S.; Liu, S.; Lai, Z. Functionalized Surface Layer on Poplar Wood Fabricated by Fire Retardant and Thermal Densification. Part 1: Compression Recovery and Flammability. *Forests* **2019**, *10*, 955. [[CrossRef](#)]
71. Todaro, L.; Rita, A.; Moretti, N.; Cuccui, I.; Pellerano, A. Assessment of Thermo-Treated Bonded Wood Performance: Comparisons among Norway Spruce, Common Ash, and Turkey Oak. *BioResources* **2015**, *10*, 772–781. [[CrossRef](#)]

72. Miklečić, J.; Jirouš-Rajković, V. Influence of Thermal Modification on Surface Properties and Chemical Composition of Beech Wood (*Fagus sylvatica* L.). *Drv. Ind.* **2016**, *67*, 65–71. [[CrossRef](#)]
73. Bekhta, P.; Krystofiak, T.; Proszkyk, S.; Lis, B. Evaluation of Dynamic Contact Angle of Loose and Tight Sides of Thermally Compressed Birch Veneer. *Drv. Ind.* **2018**, *69*, 387–394. [[CrossRef](#)]
74. Zou, W.; Wang, Z.; Sun, Z.; Jiang, X.; Yu, M.; Song, L.; Sun, D. A thermochromic wood that can change colour at 24–40 °C and collect heat for heating flooring. *Ind. Crops Prod.* **2022**, *186*, 115293. [[CrossRef](#)]
75. Zou, W.; Deng, J.; Wang, Z.; Sun, D.; Zou, N. Encapsulation of thermochromic tetradecyl myristate/methyl red compo-site via full poplar-based cellulose/lignin/SiO₂ framework for preparation of thermochromic wood with thermal response and storage. *Int. J. Biol. Macromol.* **2024**, *276*, 133881. [[CrossRef](#)] [[PubMed](#)]
76. Hofmann, T.; Tolvaj, L.; Visi-Rajczi, E.; Varga, D. Chemical Changes of Steamed Timber during Short-Term Photodegradation Monitored by FTIR Spectroscopy. *Eur. J. Wood Prod.* **2022**, *80*, 841–849. [[CrossRef](#)]
77. Godinho, D.; Ferreira, C.; Lourenço, A.; de Oliveira Araújo, S.; Quilhó, T.; Diamantino, T.C.; Gominho, J. The Behavior of Thermally Modified Wood after Exposure in Maritime/Industrial and Urban Environments. *Heliyon* **2024**, *10*, e25020. [[CrossRef](#)] [[PubMed](#)]
78. Horikawa, Y.; Hirano, S.; Mihashi, A.; Kobayashi, Y.; Zhai, S.; Sugiyama, J. Prediction of Lignin Contents from Infrared Spectroscopy: Chemical Digestion and Lignin/Biomass Ratios of *Cryptomeria japonica*. *Appl. Biochem. Biotechnol.* **2019**, *188*, 1066–1076. [[CrossRef](#)]
79. Tornaiainen, P.; Popescu, C.-M.; Jones, D.; Scharf, A.; Sandberg, D. Correlation of Studies between Colour, Structure and Mechanical Properties of Commercially Produced ThermoWood® Treated Norway Spruce and Scots Pine. *Forests* **2021**, *12*, 1165. [[CrossRef](#)]
80. Geffert, A.; Geffertová, J.; Výbohová, E. Surface Changes of Beech and Pine Wood under the Influence of UV Radiation. *Acta Fac. Xylogologiae Zvolen* **2020**, *62*, 5–18. [[CrossRef](#)]
81. Temiz, A.; Terziev, N.; Jacobsen, B.; Eikenes, M. Weathering, Water Absorption, and Durability of Silicon, Acetylated, and Heat-Treated Wood. *J. Appl. Polym. Sci.* **2006**, *102*, 4506–4513. [[CrossRef](#)]
82. Lionetto, F.; Del Sole, R.; Cannoletta, D.; Vasapollo, G.; Maffezzoli, A. Monitoring Wood Degradation during Weathering by Cellulose Crystallinity. *Materials* **2012**, *5*, 1910–1922. [[CrossRef](#)]
83. Čabalová, I.; Zachar, M.; Kačík, F.; Tribulová, T. Impact of Thermal Loading on Selected Chemical and Morphological Properties of Spruce ThermoWood. *BioResources* **2019**, *14*, 387–400. [[CrossRef](#)]
84. Sawoszczuk, T.; Wandelt, P.; Barański, A.; Łagan, J.M.; Łojewski, T.; Perlińska-Sipa, K. Degradation of Paper as Studied by Fiber Length Measurements After Hydrodynamical Treatment. In Proceedings of the International Conference Durability of Paper and Writing, Ljubljana, Slovenia, 16–22 November 2004; pp. 78–80.
85. Tyrväinen, J. Wood and Fiber Properties of Norway Spruce and Its Suitability for Thermomechanical Pulping. *Acta For. Fenn.* **1995**, *249*, 7511. [[CrossRef](#)]
86. He, L.; Zhang, T.; Zhao, Y.; Gao, J.; Zhang, Y.; Yang, Y.; He, Z.; Yi, S. Effect of Natural Tung Oil on Wood Shrinkage during the Thermal Modification Process. *J. Clean. Prod.* **2022**, *379*, 134450. [[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.