



Article Enhancing Surface Characteristics and Combustion Behavior of Black Poplar Wood through Varied Impregnation Techniques

Abdullah Beram 匝

Department of Industrial Design, Faculty of Architecture and Design, Pamukkale University, 20160 Denizli, Türkiye; abdullahberam@pau.edu.tr

Abstract: The objective of this work was to improve the thermal stability, flame resistance, and surface properties of black poplar (*Populus nigra* L.) wood via different impregnation methods. The impregnation methods were employed through two distinct modalities: vacuum impregnation and immersion impregnation. Here, poplar wood was impregnated with calcium oxide solutions (1%, 3% and 5%). Fourier-transform infrared spectroscopic analysis revealed a shift in the typical peaks of cellulose, hemicellulose, and lignin depending on the impregnation method and solution ratio. Thermogravimetric analysis and the limiting oxygen index indicated that the samples impregnated with lime solutions exhibited higher thermal stability than the unimpregnated wood. Both impregnation methods caused a decrease in water absorption and thickness swelling of the sample groups. Using a scanning electron microscope, the effect of the impregnation process on the structure of the wood was examined. In terms of surface properties, it was determined that the surface roughness value increased. On the contrary, it was observed that the contact angle value also increased. A significant difference emerged between the applied methods. In conclusion, the applied lime minerals are suitable substances to increase the flame resistance and thermal stability of black poplar wood.

Keywords: black poplar; impregnation; surface properties; thermal stability; wood protection



Citation: Beram, A. Enhancing Surface Characteristics and Combustion Behavior of Black Poplar Wood through Varied Impregnation Techniques. *Appl. Sci.* **2023**, *13*, 11482. https://doi.org/10.3390/ app132011482

Academic Editors: Alena Očkajová, Martin Kučerka and Richard Kminiak

Received: 20 September 2023 Revised: 17 October 2023 Accepted: 17 October 2023 Published: 19 October 2023



Copyright: © 2023 by the author. 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

Wood, a fundamental natural resource, has been employed in various applications since time immemorial. Its versatility, renewable nature, and wide availability have rendered it an indispensable material in industries such as construction, furniture, and manufacturing [1–3]. However, one of the perennial challenges associated with wood products is their susceptibility to combustion. The threat of fire not only poses safety concerns but also has substantial economic and ecological ramifications. Hence, there has been an enduring quest to enhance the fire-resistant properties of wood [4–10].

Among the numerous wood species available, poplar wood (*Populus* spp.) stands out for its fast growth rate and ease of cultivation. Poplar is widely distributed across temperate regions, and its utilization has surged in recent years, particularly in applications where rapid growth is essential [11]. Black poplar (*Populus nigra* L.) is one of these species. Black poplar is distributed in North Africa, Central and Western Asia, and Europe, especially in wetlands along riverbanks [12]. The distribution of poplar species in the world is more than 100 million ha. Türkiye ranks fourth in the world in terms of poplar plantation area [13]. More than 3 million m³ of wood are obtained annually from this species alone in Türkiye [14]. Although black poplar wood is widely used in furniture production, it can also find a place as a raw material in the packaging industry (boxes, crates, pallets, etc.) and in the production of models, plywood, matches, composite panels, and prostheses [15,16]. Nevertheless, like many other wood varieties, poplar wood is inherently vulnerable to fire, necessitating innovative approaches to improve its fire-resistant characteristics.

In this context, the impregnation of wood with fire-retardant chemicals has emerged as a promising avenue for enhancing its fire resistance. Impregnation involves the penetration of wood with fire-retardant substances, which can alter the wood's surface properties and combustion behavior [17–19]. The choice of impregnation technique and the type of fire retardant used are important factors in determining the effectiveness of this process. Therefore, it becomes imperative to explore the influence of diverse impregnation techniques on the surface characteristics and combustion behavior of poplar wood [20–25].

The practice of impregnating wood with various substances to enhance its properties is a method that has been used for many years. It has been employed for centuries, albeit with rudimentary techniques. Modern wood impregnation techniques have evolved significantly [26–30]. One of the earliest methods involved simply soaking wood in a solution containing fire-retardant chemicals. While this method is straightforward, it often results in uneven impregnation and inadequate penetration of fire retardants into the wood's cellular structure. To address these limitations, vacuum impregnation and pressure impregnation techniques were developed. Vacuum impregnation, in particular, involves subjecting wood to reduced pressure before immersing it in a fire-retardant solution [24,31–34].

The choice of fire-retardant chemicals is a critical determinant of the efficacy of wood impregnation. Fire retardants can be categorized into several classes, including inorganic compounds, organic compounds, and intumescent agents [35–38]. Inorganic fire retardants, such as ammonium phosphate and aluminum hydroxide, work by releasing water vapor when exposed to heat, thereby reducing the wood's temperature and retarding combustion. One of these, calcium oxide (CaO), is a white, corrosive, and alkaline solid [39]. Calcium oxide is used in the construction industry and in the production of paper, among many other applications, such as the manufacture of various types of glass [39,40]. These compounds are known for their non-toxic nature and widespread use in wood impregnation.

In this study, black poplar wood was subjected to different impregnation methods with calcium hydroxide in order to improve its physical properties and resistance to burning. Solutions prepared at different concentrations (1%, 3% and 5%) were used in the vacuum method and the immersion method. The chemical and thermal changes caused by the impregnation process in the samples were evaluated by comparison with the control samples. The effects of different impregnation methods at different durations and concentrations on the physical and fire properties of the samples were investigated.

2. Materials and Methods

2.1. Materials

2.1.1. Wood Material

The material of black poplar used in the study was obtained from Denizli Kırgız Timber Company, Türkiye. According to TS 2470 standards [41], the samples were made from sapwood and first-class timber materials that are smooth fiber, knotless, crack-free, without color or density differences, and with yearly rings perpendicular to the surfaces. A total of 30 samples were taken for each experimental group.

2.1.2. Impregnation Material (Calcium Hydroxide (Ca(OH)₂))

Calcium oxide (CaO), often known as quicklime, is a substance that is frequently utilized as a commercial product. At room temperature, it is an alkaline solid that is white and caustic. In addition to CaO, quicklime contains magnesium oxide (MgO) and silicon dioxide (SiO₂), with minor traces of aluminum oxide (Al₂O₃) and iron oxide (Fe₂O₃). This phenomenon is attributed to the inherent presence of these contaminants in the raw material, 'limestone' [42,43] (Table 1). CaO powder was purchased from Ayteks Chemical Industry Ltd. Denizli/Türkiye. Prior to its application in the impregnation process, calcium oxide necessitates slaking (adding water to the lime). Afterwards, the powdered lime was weighed to 1%, 3%, and 5% (w/v); the solutions were prepared through the slaking of lime to Equation (1) [43].

CAS number	1305-78-8
PubChem CID	14778
UN number	1910
Molecule formula	CaO
Molecular mass	56.0774 g/mol
Appearance	White to yellow/brown powder
Odor	odorless
Density	3.34 gr/cm^3
Melting point	2613 °C
Boiling point	3850 °C (100 hPa)
Solubility	(in water) reacts to form calcium hydroxide
Acidity (pKa)	12.8

Table 1. Identifiers and properties of calcium oxide [43].

Calcium hydroxide exhibits a relatively low water solubility. Investigating its solubility, it was determined [44] that it amounts to 0.0222 molal at 25 $^{\circ}$ C, corresponding to a low solubility of 1.6 g in 1 kg of water.

$$CaO + H_2O \to Ca(OH)_2 \tag{1}$$

2.2. Methods

2.2.1. Impregnation Methods (Immersion Method and Vacuum Method)

Calcium hydroxide (Ca(OH)₂) solutions at concentrations of 1%, 3%, and 5% (w/v) were prepared. According to the ASTM D 1413 standard, samples were impregnated with these solutions using the medium-term (120 min) immersion method.

The vacuum method of impregnation of the test samples was carried out under the conditions specified in ASTM D 1413. In this impregnation process, the samples were subjected to pre-vacuum treatment at 760 mmHg⁻¹ with a compressor in a closed container for 30 min. Then, the samples were removed from the closed container and impregnated in solution at atmospheric pressure for 30 min [45].

The samples in wet weights were held in the air-conditioning cabinet at a temperature of 20 ± 2 °C and a relative humidity of $65 \pm 5\%$ until they reached equilibrium humidity after impregnations. After being impregnated, the samples were maintained in an oven set at 103 ± 2 °C until they were entirely dry. After these steps, the characterization was conducted. The experimental design of the samples used in the study is given in Table 2.

Method	Sample Type	Concentration of Solution (%)	Impregnation Time (min)	
Control	А	-	-	
	В	1	120	
Immersion	С	3	120	
	D	5	120	
	Е	1	30 + 30	
Vacuum	F	3	30 + 30	
	G	5	30 + 30	

Table 2. Experimental design of immersion and vacuum methods.

2.2.2. Preparation of Samples

Density (D), thickness swelling (TS) and water absorption (WA) experiments were carried out with samples of $20 \times 20 \times 30 \text{ mm}^3$ (L \times T \times R) volume. The density, dimensional change, and water uptake determinations of the samples were conducted in compliance with TS 2472, TS 4084, and TS EN 317 standards, respectively [46–48]. For each treated wood sample, the weight percent gain (WPG) was calculated according to Equation (2). The oven-dry weight of each specimen was recorded before and after impregnation. The assessment of surface and fire properties adhered to relevant criteria. The residues left on

the wood surface from the impregnation process were removed before the tests to ensure they did not affect the results.

$$WPG = \frac{(Wa - Wb)}{Wb} \times 100\%$$
 (2)

where W_b is the oven-dry weight of specimens before treatment (g), and W_a is the oven-dry weight of specimens after treatment (g).

2.2.3. Testings of Surface and Burning Properties

Surface roughness test

Surface roughness measurements were conducted in accordance with the DIN 4768 (1990) standard [49], employing a stylus-type profilometer (Mitutoyo SJ-301, Mitutoyo Corp., Kawasaki, Japan). The measurement was taken on the wood surfaces in parallel to the grain direction (||). The roughness values were captured with a sensitivity of 0.5 μ m, ensuring precision in the measurements. The key instrument parameters included a measuring speed of 10 mm/min, a pin diameter of 4 μ m, and a pin top angle set at 90 degrees. The points selected for roughness measurements were conducted parallel to the direction of the wood fibers. Three standard roughness parameters were determined: average roughness (Ra); mean peak-to-valley height (Rz); and maximum roughness (Rmax). Ra values were specifically employed for statistical evaluations. Additionally, measurements were repeated whenever the scanning needle's tip entered the cell spaces within the wood sample.

Water contact angle test

According to GB/T 30693 (2014), the water contact angle of the surface of wood was calculated. KRUSS DSA30 water contact angle meter (KRÜSS, Hamburg, Germany) was used. The size of the water drop was 4 μ L. The data were obtained 15 s after the water droplet made contact with the wood surface. The contact angles were obtained at five separate sites on the same sample surface using five replicates for each group, and the mean value was calculated.

FTIR analysis

The samples were finely ground, falling within the 40–100 mesh size range, in preparation for their utilization in Fourier-transform infrared (FTIR) spectroscopy and thermogravimetric analyses (TGA). Following the grinding process, pellets were created by subjecting 10 mg of wood flour and KBr to a 1:100 (w/w) ratio for each sample group. These pellets were formed by applying a pressure of 602 N/mm². For the FTIR analysis, a Perkin Elmer BX FTIR spectrometer instrument (PerkinElmer U.S. LLC, Shelton, CT, USA) was employed, operating at ambient temperature. The instrument covered a wavenumber range of 4000 to 400 cm⁻¹, with a spectral resolution of 4 cm⁻¹.

• DTG/TGA analysis

To assess the thermal stability of the samples, thermogravimetric analysis (TGA) was conducted using an Exstar SII TG DTA 7200 (Exstar, SII NanoTechnology In., Tokyo, Japan) instrument. The analysis was carried out under a nitrogen gas atmosphere, with the samples experiencing a gradual temperature increase at a rate of 10 °C per minute, spanning from 25 to 600 °C. Each sample was weighed at approximately 5 mg.

LOI analysis

A flammability test to determine the limiting oxygen index (LOI) of wood samples was carried out using a flammability tester (S.C. Dey Co., Kolkata, India). This test was conducted in accordance with the ASTM D-2863 method [50]. The LOI value expresses the minimum amount of oxygen required to start combustion. In the LOI apparatus, the wood sample was positioned vertically and subjected to ignition for a minimum duration

of 30 s. Throughout the ignition process, the ratio between nitrogen and oxygen in the environment was carefully monitored and recorded.

SEM analysis

A scanning electron microscope (FESEM, Zeiss Gemini Sigma 300, Jena, Germany) equipped with an energy dispersive spectrometer (EDS) system (Bruker XFlash 6I100) was employed to reveal the effect of impregnation on the particles.

• Statistical analysis

Statistical analysis was performed on the study's findings using SPSS[®] 20.0 for Windows[®] software. The data were subjected to an analysis of variance (ANOVA) test. A Duncan test was used to identify the various groups in cases where the ANOVA test revealed statistical differences via SPSS[®] 20.0 for Windows[®] (IBM Corp., Armonk, NY, USA).

3. Results and Discussion

The physical properties

The physical characteristics of the samples of black poplar with different impregnation methods are presented in Table 3. Using the ANOVA test, it was found that there was a statistically significant difference between the control and impregnated sample sets in terms of the physical characteristics of the experimental specimens. After applying the Duncan test, four homogeneous clusters were delineated within each of the datasets corresponding to D_0 , TS-2, and TS-24 h and five homogeneous clusters were delineated within each of the datasets corresponding to WA-2, WA-24, and WPG.

Table 3. The physical properties of impregnated wood samples.

Sample Type	D ₀ (g/cm ³)	WA-2 h	WA-24 h	TS-2 h	TS-24 h	WPG (%)
А	0.36 (0.09) ¹ a ²	38.21 (3.57) a	72.89 (5.88) a	14.86 (2.43) a	17.26 (3.45) a	-
В	0.41 (0.13) b	33.83 (3.26) b	67.86 (6.11) b	13.23 (1.31) b	15.08 (3.04) b	0.62 (0.09) a
С	0.44 (0.09) c	29.42 (2.61) c	63.22 (5.67) c	11.38 (1.14) c	13.77 (2.14) c	0.73 (0.21) b
D	0.45 (0.11) c	26.55 (1.93) d	59.49 (4.93) d	10.75 (0.81) cd	12.13 (1.86) cd	0.91 (0.18) b
Е	0.42 (0.12) b	31.26 (2.79) c	63.92 (4.55) c	11.49 (1.05) c	14.86 (2.11) b	1.12 (0.30) c
F	0.46 (0.14) c	24.12 (2.44) d	58.32 (5.22) d	9.08 (1.27) d	12.22 (1.37) cd	1.79 (0.35) d
G	0.49 (0.09) d	22.07 (1.66) e	54.11 (4.83) e	8.83 (0.95) d	11.45 (1.96) d	2.28 (0.51) e

¹: Standard deviation, ²: The same letters in a column of D0, WA-2, WA-24, TS-2, TS-24, and WPG are not significantly different ($p \le 0.01$). The post hoc tests (Duncan) for the D0, WA-2, WA-24, TS-2, TS-24, and WPG were analyzed separately because the interaction factor was significantly different.

It was found that the density (D_0) and weight percent gain (WPG) rose when the lime ratio increased in the two impregnation methods. When 1%, 3%, and 5% lime were added, respectively, the D_0 values were found to be between 0.41 and 0.49 g/cm³. Depending on this, the WPG increased between 0.62% and 2.28%. Applied impregnation methods with lime progressively decreased water absorption and thickness swelling in the samples. It was observed that WA-2, WA-24, TS-2, and TS-24 values decreased when 1%, 3%, and 5% lime were added, respectively.

The WA-2 decreased between 11.5% and 30.5%, the WA-24 values decreased between 6.9% and 18.4%, the TS-2 values decreased between 10.9% and 27.6%, and the TS-24 values decreased between 12.6% and 29.7% in the immersion method. In the vacuum method, which is the other method applied, the WA-2 decreased between 18.2% and 42.2%, WA-24 values decreased between 12.3% and 25.7%, TS-2 values decreased between 22.6% and 40.5%, and TS-24 values decreased between 13.9% and 33.6% (Table 3). These data are consistent with earlier research, which found that adding lime to wood increased its physical qualities and made it more stable dimensionally [5,8,9,33]. In addition, there appear to be obvious differences in physical properties between the applied methods. It is seen that the vacuum method provides more stability to the wood material compared to the immersion method [51–53].

• The surface roughness, contact angle, and LOI properties

Table 4 displays the surface roughness, contact angle, and LOI characteristics of samples of black poplar treated with various impregnation methods. According to the ANOVA test, a statistically significant difference was detected in the physical properties of both control and impregnated sample groups. Following the implementation of the Duncan test, we identified four consistent and similar groups within each dataset associated with surface roughness, contact angle, and LOI.

Sample Type	Surface Roughness (Ra) (\parallel)	Changes (%)	Contact Angle (°)	Changes (%)	LOI (%)	Changes (%)
А	2.77 (0.31) ¹ a ²	-	41 (4.66) a	-	23.16 (2.55) b	-
В	3.36 (0.99) b	21.3	54 (4.34) b	31.7	26.75 (3.07) b	15.5
С	3.90 (0.83) c	40.8	59 (5.27) c	43.9	28.44 (2.43) b	22.8
D	4.12 (0.46) d	48.7	62 (4.02) d	51.2	30.08 (1.94) b	29.8
Е	3.58 (0.60) c	29.2	61 (3.95) c	48.8	28.27 (1.64) b	22.0
F	4.35 (0.97) d	57.0	66 (6.26) e	60.9	30.62 (2.44) b	32.2
G	5.22 (0.44) e	88.4	68 (6.31) e	65.8	31.23 (2.74) b	34.8

Table 4. Surface roughness, contact angle, and LOI properties of impregnated wood samples.

¹: Standard deviation, ²: The same letters in a column of surface roughness, contact angle, and LOI are not significantly different ($p \le 0.01$). The post hoc tests (Duncan) for the surface roughness, contact angle, and LOI were analyzed separately because the interaction factor was significantly different.

The average roughness parameter (Ra) increased with an increase in the solution ratio. The values were found to be between 2.77 and 5.22. Compared to the control group, the B group exhibited the smallest alteration, registering a 21.3% change, while the G group displayed the most substantial variation with an 88.4% shift. Ra increases the surface roughness of the impregnation process. It is explained that this situation is related to the increase in the amount of substance on the surface as the amount of retention increases [54–56].

The contact angle values of the groups included in the study are shown in Table 4. It has been determined that as the lime concentration ratio increases, the contact angle increases. The values were found to be between 41° and 68° . It has been determined that the highest hydrophobic sample group with a contact angle of 68° is obtained with group G, which increases hydrophobicity by 65.8% compared to group A. Similar to the findings for water absorption, increasing lime particles increased the contact angle, which was significantly higher in woods treated and impregnated [57–60].

The LOI values of the sample groups are summarized in Table 4. The values were found to be between 23.16% and 31.23%. It has been determined that the highest fireproof sample group with a LOI of 31.23% is obtained with group G, which increases fire resistance by 34.8% compared to group A. In wood impregnated with lime minerals, the LOI value increased as the lime ratio increased. LOI values were found to be between 26.75% and 30.08% in the immersion method and between 28.27% and 31.23% in the vacuum method. The vacuum method is posited to yield a superior insulating effect against heat transfer compared to the immersion method. The retardation of flame propagation appears to stem from the lime's capacity to facilitate the generation of char. This ensuing coal coating forms an insulative barrier, impeding the passage of combustible gases that sustain the flame and displaying resistance to heat transfer [61–63].

FTIR analysis

FTIR analysis was employed to discern the functional groups and chemical interactions among the materials. The FTIR spectrum exhibited observable shifts in the characteristic peaks of cellulose, hemicellulose, and lignin, contingent upon the impregnation method and the ratio of lime additive. FTIR spectra encompassing the impregnated black poplar samples, as well as the control samples, were recorded over the wavelength range of 4000 to 400 cm⁻¹. The control group and the groups impregnated with both impregnation methods show absorbance peaks for wood fibers at 876 cm⁻¹ (Si–O–C), 1060 cm⁻¹ (C–O–C),

2910 cm⁻¹ (C–H), and 3450 cm⁻¹ (O–H). In addition, the impregnated groups showed a new increase at 1450 cm⁻¹ for C=O stretching vibration. The lack of a drop in the strength of the band at 1060 cm⁻¹ indicates that the cellulose's C–O–C bonds have not been harmed by the procedure. It may be argued that the impregnated lime particles are to blame for this phenomenon (Table 5 and Figure 1). The absorption bands over 1450 cm⁻¹ can be assigned to the stretching vibrations of (CO₃)- anions present in the carbonate phase in the sample. The behavior of Ca(OH)₂ adsorbed on the surface was monitored, showing that Ca(OH)₂ continuously transformed into the carbonate phase and crystallization proceeded first through the formation of aragonite-like and then calcium-like carbonates [64].

Spectrum Band Position, cm^{-1}	Active Wood Mass Group	Type of Vibration
3450–3400 2970–2850 1462–1425 1060–1025 876	O-H of alcohols, phenols and acids CH ₂ , CH- and CH ₃ CH ₂ cellulose, lignin C-O-C Anti-symmetric out-of-phase stretching in pyranose ring	O-H stretching C-H stretching C-H deformations Deformation Stretching in pyranose ring
Absorbance	000 000 000 000 000 000 000 000 000 00	

Table 5. Match of wood functional groups to IR bands of spectra [65,66].

Figure 1. FTIR Spectra of the impregnated and unimpregnated black poplar samples.

The presence of a band at 3450 cm^{-1} signifies a reduction in the quantity of OH groups, leading to a further decrease compared to the control group. An examination of the FTIR spectroscopy peaks reveals notable alterations in cellulose, hemicellulose, and lignin due to the processing [23,66,67]. In contrast to the control group, the peak observed at 2910 cm⁻¹ is notably diminished. This decrease can be attributed to the asymmetric stretching of C–H methyl and methylene groups [68–70]. Conversely, a noticeable increase is evident in the peak at 1450 cm⁻¹ compared to the control group. This peak is characteristic of lignin components and signifies symmetrical tension vibrations in C=O and –COO groups within aromatic rings [71–73]. Moreover, these changes elucidate the influence of functional groups in the added lime minerals on the wood. Another significant observation is the increase in the 873 cm⁻¹ band relative to the control group, which can be attributed to the Si–O–Al stretching mode associated with CaO [74,75]. Additionally, distinct peak bands are discernible at 430 cm⁻¹ [23,76]. Those findings suggest that lime minerals were successfully grafted into the poplar wood fibers.

• DTG/TGA analysis

The TGA and DTG thermograms of the control and impregnated black poplar samples are plotted in Figures 2 and 3.



Figure 2. TGA thermograms of the control and impregnated black poplar samples.



Figure 3. DTG thermograms of the control and impregnated black poplar samples.

The provided data in Table 6 summarize the initial decomposition temperature (T_0), maximum degradation temperature (T_{max}), final temperature (T_f), and residual weight (RW, %) for the wood samples, both impregnated and control, with calcium hydroxide. The onset of degradation occurred at 140 °C for both the impregnated and non-impregnated black poplar samples, signifying the removal of water and certain extractive components from the specimens up to this temperature [77,78]. After 140 °C, the decomposition process

continued until 476 °C in the control sample, between 494 and 531 °C in the samples impregnated with the immersion method, and between 532 and 584 °C in the samples impregnated with the vacuum method. The highest final temperature was determined in the G sample at 584 °C. The maximum degradation temperature is the lowest value in the control sample at 329 °C and the highest value in the G sample at 347 °C. From 140 °C to 476 °C, and 584 °C, hemicellulose, the remaining extractives, lignin, and cellulose were decomposed [22,79]. The residue weight varied depending on the method of impregnation. The rate of RW at 600 °C in the samples was 16.2% in the control sample (A), between 18.3 and 22.3% in the samples impregnated with the immersion method, and between 19.8 and 24.9% in the samples impregnated with the vacuum method. The TGA study results showed that as the concentration of calcium hydroxide increased, the heat resistance of the fibers gradually increased. Additionally, the amount of residue detected in the vacuum method is slightly higher than in the immersion method. These values are relatively low when compared with the literature results [80–84].

 Table 6. Thermal degradation temperatures and residue weight of black polar samples.

Sample Type	T ₀ (°C)	T _{max} (°C)	T _f (° C)	RW at 600 $^{\circ}$ C (%)
А	140	329	476	16.2
В	140	332	494	18.3
С	140	337	503	18.5
D	140	338	531	22.3
Е	140	339	532	19.8
F	140	342	576	24.4
G	140	347	584	24.9

T₀: Initial decomposition temperature, T_{max}: maximum degradation temperature, T_f: Final temperature.

• SEM analysis

Observation under SEM at high magnifications showed the samples of impregnated and unimpregnated black poplar (Figures 4 and 5).



Figure 4. SEM topographs of black poplar: (A) control $(500 \times)$; (E) impregnated sample $(1000 \times)$.



Figure 5. SEM micrographs of impregnated samples of black poplar: (B–D) (500×), (E–G) (1000×).

SEM analysis of impregnated wood material revealed the presence of impregnation substances concentrated along the wood lumen cell and transition edges. Additionally, nanoparticles were observed to form clusters within certain regions of the trachea [85]. It can be seen that the amount of impregnation filling the lumen cell is related to the change in concentration.

4. Conclusions

This study was undertaken to enhance the surface characteristics and fire-resistant properties of black poplar wood, a rapidly growing tree species. In pursuit of this objective, two distinct methods were employed for the impregnation of calcium hydroxide. In comparison to the immersion method, the vacuum impregnation method produced better results, showing lower water absorption and thickness swelling values. This resulted in an increase in hydrophobic characteristics of the wood. Notably, an increase in the weight percent gain (WPG) ratio corresponded with a successful impregnation process and a concurrent elevation in limiting oxygen index (LOI) values, suggesting improved fire resistance. The Fourier-transform infrared (FTIR) analysis findings aligned with the thermogravimetric analysis-differential thermal gravimetry (TGA-DTG) results, demonstrating an augmentation in residue content as the concentration rate of impregnation increased. These analyses affirm enhanced fireproof properties. Examination of scanning electron microscopy (SEM) images revealed some deposits in lumen cell occupancy, indicative of a successful impregnation process. Additionally, it was observed that while porosity decreased, surface roughness increased due to the disintegration of structural elements. This effect, however, led to an increase in contact angle values and the filling of surface gaps on the poplar wood. In conclusion, calcium hydroxide emerges as an auspicious candidate for augmenting the fire-resistant attributes of wood materials. The applicability of this approach should be considered in accordance with specific use cases and the structural

limitations inherent to poplar wood, thereby facilitating the production of more efficacious end products.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

References

- Asif, M. Sustainability of timber, wood and bamboo in construction. In Sustainability of Construction Materials; Khatib, J.M., Ed.; Woodhead Publishing: Oxford, UK, 2009; pp. 41–54. [CrossRef]
- 2. Rosillo-Calle, F.; Woods, J. The Biomass Assessment Handbook; Routledge: London, UK, 2012.
- Aristri, M.A.; Lubis, M.A.R.; Yadav, S.M.; Antov, P.; Papadopoulos, A.N.; Pizzi, A.; Fatriasari, W.; Ismayati, M.; Iswanto, A.H. Recent developments in lignin-and tannin-based non-isocyanate polyurethane resins for wood adhesives—A review. *Appl. Sci.* 2021, 11, 4242. [CrossRef]
- Slimak, K.M.; Slimak, R.A. Enhancing the Strength, Moisture Resistance, and Fire-Resistance of Wood, Timber, Lumber, Similar Plant-Derived Construction and Building Materials, and Other Cellulosic Materials. U.S. Patent No. 6,146,766, 21 March 2000.
- 5. Östman, B.; Voss, A.; Hughes, A.; Jostein Hovde, P.; Grexa, O. Durability of fire-retardant treated wood products at humid and exterior conditions review of literature. *Fire Mater.* **2001**, *25*, 95–104. [CrossRef]
- 6. Pereyra, A.M.; Giudice, C.A. Flame-retardant impregnants for woods based on alkaline silicates. *Fire Saf. J.* **2009**, *44*, 497–503. [CrossRef]
- Wen, M.Y.; Kang, C.W.; Park, H.J. Impregnation and mechanical properties of three softwoods treated with a new fire-retardant chemical. J. Wood Sci. 2014, 60, 367–375. [CrossRef]
- Fu, Q.; Medina, L.; Li, Y.; Carosio, F.; Hajian, A.; Berglund, L.A. Nanostructured wood hybrids for fire-retardancy prepared by clay impregnation into the cell wall. ACS Appl. Mater. Interfaces 2017, 9, 36154–36163. [CrossRef] [PubMed]
- Madyaratri, E.W.; Ridho, M.R.; Aristri, M.A.; Lubis, M.A.R.; Iswanto, A.H.; Nawawi, D.S.; Antov, P.; Kristak, L.; Majlingová, A.; Fatriasari, W. Recent advances in the development of fire-resistant biocomposites—A review. *Polymers* 2022, 14, 362. [CrossRef]
- 10. Yu, Z.L.; Ma, Z.Y.; Yao, H.X.; Qin, B.; Gao, Y.C.; Xia, Z.J.; Huang, Z.H.; Yin, Y.C.; Tu, H.; Ye, H.; et al. Economical architected foamy aerogel coating for energy conservation and flame resistance. *ACS Mater. Lett.* **2022**, *4*, 1453–1461. [CrossRef]
- Ercan, M. Poplar Research Institute from its Establishment to the Present 1962–2014; (T.R. Ministry of Forestry and Water Affairs, General Directorate of Forestry, Poplar and Fast-Growing Forest Trees Research Institute. Directorate Publication No: 270); Various Publications Series No: 25: Izmit, Türkiye, 2014. Available online: https://kutuphane.tarimorman.gov.tr/vufind/Record/10258 (accessed on 5 August 2023).
- 12. Marchi, M.; Bergante, S.; Ray, D.; Barbetti, R.; Facciotto, G.; Chiarabaglio Pier, M.; Nervo, G. Universal reaction norms for the sustainable cultivation of hybrid poplar clones under climate change in Italy. *Iforest Biogeosciences For.* **2022**, *15*, 47. [CrossRef]
- 13. Atmaca, C. Performance of Various Poplar Clones in the Early Years. Master's Thesis, Düzce University, Institute of Science and Technology, Düzce, Türkiye, 2018.
- 14. Birler, A.S. Poplar Cultivation in Türkiye: Nursery-Afforestation-Protection-Revenue-Economy-Wood Characteristics; Poplar and Fast-Growing Forest Trees Research Directorate of the Ministry of Environment and Forestry: Ankara, Türkiye, 2010.
- 15. Bozkurt, Y.; Erdin, N. Wood Anatomy; İstanbul University, Publishing of Faculty of Forestry: Istanbul, Türkiye, 2000.
- 16. Gaudet, M.; Jorge, V.; Paolucci, I.; Beritognolo, I.; Scarascia Mugnozza, G.; Sabatti, M. Genetic linkage maps of *Populus nigra* L. including AFLPs, SSRs, SNPs, and sex trait. *Tree Genet. Genomes* **2008**, *4*, 25–36. [CrossRef]
- 17. Uysal, B.; Yapıcı, F.; Kol, H.Ş.; Özcan, C.; Esen, R.; Korkmaz, M. Determination of thermal conductivity finished on impregnated wood material. In Proceedings of 6th International Advanced Technologies Symposium (IATS'11), Elazığ, Türkiye, 6–18 May 2011.
- 18. Kesik, H.İ.; Keskin, H.; Temel, F.; Öztürk, Y. Bonding Strength and Surface Roughness Properties of Wood Materials Impregnated with VacsolAqua. *Kastamonu Univ. J. For. Fac.* **2016**, *16*, 181–189. [CrossRef]
- 19. Demir, A.; Aydin, İ. Effects of Treatment with Fire Retardant Chemicals on Technologic Properties of Wood and Wooden Materials. *Duzce Univ. Fac. For. J. For.* **2016**, *12*, 96–104.
- Göker, Y.; Ayrılmış, N. Performance characteristicsand thermal degredation of wood and wood-based products in fire. J. Fac. For. Istanb. Univ. 2002, 52, 1–22.
- 21. He, X.; Li, X.J.; Zhong, Z.; Mou, Q.; Yan, Y.; Chen, H.; Liu, L. Effectiveness of impregnation of ammonium polyphosphate fire retardant in poplar wood using microwave heating. *Fire Mater.* **2016**, *40*, 818–825. [CrossRef]
- 22. Kong, L.; Guan, H.; Wang, X. In situ polymerization of furfuryl alcohol with ammonium dihydrogen phosphate in poplar wood for improved dimensional stability and flame retardancy. *ACS Sustain. Chem. Eng.* **2018**, *6*, 3349–3357. [CrossRef]
- 23. Liu, Q.; Chai, Y.; Ni, L.; Lyu, W. Flame retardant properties and thermal decomposition kinetics of wood treated with boric acid modified silica sol. *Materials* **2020**, *13*, 4478. [CrossRef]

- 24. Kuai, B.; Wang, Z.; Gao, J.; Tong, J.; Zhan, T.; Zhang, Y.; Lu, J.; Cai, L. Development of densified wood with high strength and excellent dimensional stability by impregnating delignified poplar by sodium silicate. *Constr. Build. Mater.* **2022**, *344*, 128282. [CrossRef]
- 25. Cheng, X.; Lu, D.; Yue, K.; Lu, W.; Zhang, Z. Fire resistance improvement of fast-growing poplar wood based on combined modification using resin impregnation and compression. *Polymers* **2022**, *14*, 3574. [CrossRef]
- As, N.; Akbulut, T. Odunun fiziksel özelliklerini iyileştiren işlemler ve mekanik özellikler üzerine olan etkisi. J. Fac. For. Istanb. Univ. 1989, 39, 98–112.
- 27. LeVan, S.L.; Winandy, E.J. Effect of fire retardant treatment on wood strenght: A Rewiev. Wood Fiber Sci. 1990, 22, 113–131.
- Ayrılmış, N. Effects of Various Fire Retardants on Fire and Technological Properties of Some Wood Based Panel Products. Ph.D. Thesis, Istanbul University, Institute of Science, İstanbul, Türkiye, 2006.
- 29. Demir, A. The Effects of Fire Retardant Chemicals on Thermal Conductivity of Plywood Produced from Different Wood Species. Master's Thesis, Karadeniz Technical University, Institute of Science, Trabzon, Türkiye, 2014.
- Gökmen, K. The Effect of Heat Treatment with Tall Oil Impregnation on the Properties of Wood Material. Master's Thesis, Bartin University, Institute of Science and Technology, Bartin, Türkiye, 2017.
- Wang, Y.; Wang, T. Effect of vacuum impregnation on mechanical properties of fast-growing poplar. J. Northeast For. Univ. 2019, 47, 53–56.
- 32. Cao, S.; Cai, J.; Wu, M.; Zhou, N.; Huang, Z.; Cai, L.; Zhang, Y. Surface properties of poplar wood after heat treatment, resin impregnation, or both modifications. *BioResources* 2021, *16*, 7562–7577. [CrossRef]
- 33. Yang, H.; Gao, M.; Wang, J.; Mu, H.; Qi, D. Fast Preparation of high-performance wood materials assisted by ultrasonic and vacuum impregnation. *Forests* **2021**, *12*, 567. [CrossRef]
- 34. Zhang, Y.; Guan, P.; Zuo, Y.; Li, P.; Bi, X.; Li, X. Preparation of highly-densified modified poplar wood by evacuating the micro-pores of wood through a gas expansion method. *Ind. Crops Prod.* **2023**, *194*, 116374. [CrossRef]
- 35. Kausar, A.; Rafique, I.; Anwar, Z.; Muhammad, B. Recent developments in different types of flame retardants and effect on fire retardancy of epoxy composite. *Polym. Plast. Technol. Eng.* **2016**, *55*, 1512–1535. [CrossRef]
- Blanchet, P.; Pepin, S. Trends in chemical wood surface improvements and modifications: A review of the last five years. *Coatings* 2021, 11, 1514. [CrossRef]
- Kawalerczyk, J.; Walkiewicz, J.; Dziurka, D.; Mirski, R. Nanomaterials to Improve Fire Properties in Wood and Wood-Based Composite Panels. In *Emerging Nanomaterials: Opportunities and Challenges in Forestry Sectors*; Taghiyari, H., Morrell, J.J., Husen, A., Eds.; Springer International Publishing: Cham, Switzerland, 2022; pp. 65–96. [CrossRef]
- 38. Tan, H.; Şirin, M.; Baltaş, H. Ecological structure: Production of organic impregnation material from mussel shell and combustion. *Polímeros* **2022**, *32*, 1–8. [CrossRef]
- 39. Zumdahl, S.S.; DeCoste, D.J. Chemical Principles, 7th ed.; Cengage Learning: Belmont, MA, USA, 2012.
- 40. Haynes, W.M. CRC Handbook of Chemistry and Physics, 95th ed.; CRC Press: New York, NY, USA, 2014.
- 41. *TS* 2470; Methods and General Properties of Sampling from Wood for Physical and Mechanical Experiments. TSE: Ankara, Türkiye, 1976.
- Kılıç, Ö.; Anıl, M. The effects of limestone characteristic properties and calcination temperature to the lime quality. *Asian J. Chem.* 2006, 18, 655–666.
- 43. Ropp, R.C. Encyclopedia of the Alkaline Earth Compounds; Elsevier: Amsterdam, The Netherlands, 2012.
- 44. Duchesne, J.; Reardon, E.J. Measurement and prediction of portlandite solubility in alkali solutions. *Cem. Concr. Res.* **1995**, 25, 1043–1053. [CrossRef]
- 45. ASTM D 1413-99; Standard Method of Testing Wood Preservatives by Laboratory Soil Block Cultures. Annual Book of ASTM Standards: West Conshohocken, PA, USA, 1995.
- TS EN 2472; Wood—Determination of Density for Physical and Mechanical Tests. Turkish Standards Institution: Ankara, Türkiye, 1972.
- 47. TS 4084; Wood—Determination of Radial and Tangential Swelling. Turkish Standard Institution: Ankara, Türkiye, 1983.
- TS EN 317; Particleboards and Fibreboards–Determination of Swelling in Thickness after Immersion in Water. TSE: Ankara, Türkiye, 1999.
- DIN 4768; Determination of Values of Surface Roughness Parameters, Ra, Rz, Rmax, Using Electrical Contact (Stylus) Instruments. Concepts and Measuring Conditions. Deutsches Institut f
 ür Norming: Berlin, Germany, 1990.
- ASTM D 2863; Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index). ASTM International: West Conshohocken, PA, USA, 2006.
- 51. Habibzade, S.; Taghiyari, H.R.; Omidvar, A.; Roudi, H.R. Effects of impregnation with styrene and nano-zinc oxide on fireretarding, physical, and mechanical properties of poplar wood. *Cerne* **2016**, *22*, 465–474. [CrossRef]
- 52. Chen, C.; Chen, J.; Zhang, S.; Cao, J.; Wang, W. Forming textured hydrophobic surface coatings via mixed wax emulsion impregnation and drying of poplar wood. *Wood Sci. Technol.* **2020**, *54*, 421–439. [CrossRef]
- 53. Holy, S.; Temiz, A.; Köse Demirel, G.; Aslan, M.; Amini, M.H.M. Physical properties, thermal and fungal resistance of Scots pine wood treated with nano-clay and several metal-oxides nanoparticles. *Wood Mater. Sci. Eng.* **2022**, *17*, 176–185. [CrossRef]
- 54. Sogutlu, C.; Dongel, N. The effect of the impregnate process of wooden material to color changes and surface roughness. *J. Polytech.* **2009**, *12*, 179–184.

- 55. Keskin, H.; Bülbül, R. Impacts of impregnation with Tanalith-E on surface roughness of solid wood materials. *Furnit. Wooden Mater. Res. J.* **2019**, *2*, 67–78. [CrossRef]
- Aykaç, S.; Sofuoğlu, S.D. A study on the comparison of surface roughness parameters in bamboo material applied with cellulosic, synthetic, polyurethane and water-based varnishes. *Furnit. Wooden Mater. Res. J.* 2020, *3*, 84–92. [CrossRef]
- 57. Kartal, S. Wettebality, water absorption and thickness swelling of particleboard made from remediated CCA-treated wood. *J. Fac. For. Istanb. Univ.* **2001**, *51*, 53–62.
- 58. Kamal, M.R.; Calderon, J.U.; Lennox, B.R. Surface energy of modified nanoclays and its effect on polymer/clay nanocomposites. *J. Adhes. Sci. Technol.* **2009**, *23*, 663–688. [CrossRef]
- Zaidi, S.J.; Fadhillah, F.; Saleem, H.; Hawari, A.; Benamor, A. Organically modified nanoclay filled thin-film nanocomposite membranes for reverse osmosis application. *Materials* 2019, 12, 3803. [CrossRef] [PubMed]
- 60. Emampour, M.; Khademieslam, H.; Faezipour, M.M.; Talaeipour, M. Effects of coating *Populus nigra* wood with nanoclay. *Bioresources* **2020**, *15*, 8026. [CrossRef]
- 61. Alhuthali, A.; Low, I.M.; Dong, C. Characterisation of the water absorption, mechanical and thermal properties of recycled cellulose fibre reinforced vinyl-ester eco-nanocomposites. *Compos. Part B Eng.* **2022**, *43*, 2772–2781. [CrossRef]
- 62. Mandal, M.; Maji, T.K. Comparative study on the properties of wood polymer composites based on different modified soybean oils. *J. Wood Chem. Technol.* **2017**, *37*, 124–135. [CrossRef]
- Kaya, A.I. Fire performance of thermally modified wood impregnated with clay nanomaterials. *Feb. Fresenius Environ. Bull.* 2022, 31, 5292–5296.
- Janotka, I.; Madejova, J.; Števula, L.; Frt'Alová, D.M. Behaviour of Ca(OH)₂ in the presence of the set styrene-acrylate dispersion. *Cem. Concr. Res.* 1996, 26, 1727–1735. [CrossRef]
- 65. Bodirlau, R.; Teaca, C.A. Fourier transform infrared spectroscopy and thermal analysis of lignocellulose fillers treated with organic anhydrides. *Rom. J. Phys.* **2009**, *54*, 93–104.
- Esteves, B.; Velez Marques, A.; Domingos, I.; Pereira, H. Chemical changes of heat-treated pine and eucalypt wood monitored by FTIR. *Maderas Cienc. Y Tecnol.* 2013, 15, 245–258. [CrossRef]
- 67. Wada, K. A structural scheme of soil allophane. Am. Mineral. 1967, 52, 690–708.
- 68. Bellamy, L.J. The Infra-Red Spectra of Complex Molecules; John Wiley & Sons: New York, NY, USA, 1966.
- Wang, X.; Romero, M.Q.; Zhang, X.Q.; Wang, R.; Wang, D.Y. Intumescent multilayer hybrid coating for flame retardant cotton fabrics based on layer-by-layer assembly and sol–gel process, RSC Adv. 2015, 5, 10647–10655. RSC Adv. 2015, 5, 10647–10655. [CrossRef]
- 70. Beram, A.; Yaşar, S. Performance of brutian pine (*Pinus brutia* Ten.) particles modified with NaOH in board production. *J. Grad. Sch. Nat. Appl. Sci. Mehmet Akif Ersoy Univ.* **2018**, *9*, 187–196. [CrossRef]
- Faix, O.; Meier, D.; Fortmann, I. Thermal degradation products of wood. A collection of electron-impact (EI) mass spectra of monomeric lignin derived products. *Holz. Als. Roh. Werkst.* 1990, 48, 351–354. [CrossRef]
- Kotilainen, R.; Toivannen, T.; Alén, R. FTIR monitoring of chemical changes in softwood during heating. J. Wood Chem. Technol. 2000, 20, 307–320. [CrossRef]
- Windeisen, E.; Strobel, C.; Wegener, G. Chemical changes during the production of thermotreated beech wood. *Wood Sci. Technol.* 2007, 41, 523–536. [CrossRef]
- Moser, F.; Trautz, M.; Beger, A.L.; Löwer, M.; Jacobs, G.; Hillringhaus, F.; Wormit, A.; Usadel, B.; Reimer, J. Fungal mycelium as a building material. In Proceedings of the Annual Symposium of the International Association for Shell and Spatial Structures, IASS 2017, Hamburg, Germany, 25–28 September 2017.
- 75. Xu, F.; Zhong, L.; Zhang, C.; Wang, P.; Zhang, F.; Zhang, G. Novel high-efficiency casein-based P–N-containing flame retardants with multiple reactive groups for cotton Fabrics. *ACS Sustain. Chem. Eng.* **2019**, *7*, 13999–14008. [CrossRef]
- Abidin, Z.; Matsue, N.; Henmi, T. Nanometer-scale chemical modification of nanoball allophane. *Clays Clay Miner.* 2007, 55, 443–449. [CrossRef]
- Jiang, J.; Li, J.; Hu, J.; Fan, D. Effect of nitrogen phosphorus flame retardants on thermal degradation of wood. *Constr. Build. Mater.* 2010, 24, 2633–2637. [CrossRef]
- Lowden, L.A.; Hull, T.R. Flammability behaviour of wood and a review of the methods for its reduction. *Fire Sci. Rev.* 2013, 2, 1–19. [CrossRef]
- Zhang, L.L.; Xu, J.S.; Shen, H.Y.; Xu, J.Q.; Cao, J.Z. Montmorillonite-catalyzed furfurylated wood for flame retardancy. *Fire Saf. J.* 2021, 121, 103297. [CrossRef]
- Ghosh, P.; Siddhanta, S.K.; Chakrabarti, A. Characterization of poly (vinyl pyrrolidone) modified polyaniline prepared in stable aqueous medium. *Eur. Polym. J.* 1999, 35, 699–710. [CrossRef]
- Sun, J.X.; Xu, F.; Sun, X.F.; Xiao, B.; Sun, R.C. Physico-chemical and thermal characterization of cellulose from barley straw. *Polym. Degrad. Stab.* 2005, *88*, 521–531. [CrossRef]
- Vazquez, A.; Foresti, M.L.; Cerrutti, P.; Galvagno, M. Bacterial cellulose from simple and low cost production media by Gluconacetobacter xylinus. J. Polym. Environ. 2013, 21, 545–554. [CrossRef]
- Kozakiewicz, P.; Drożdżek, M.; Laskowska, A.; Grześkiewicz, M.; Bytner, O.; Radomski, A.; Zawadzki, J. Effects of thermal modification on selected physical properties of sapwood and heartwood of black poplar (*Populus nigra* L.). *BioResources* 2019, 14, 8391–8404. [CrossRef]

- 84. Yaşar, S.; Güler, G. Chemical characterization of black poplar (*Populus nigra* L.) sawdust hemicelluloses esterified with acyl chlorides. *Turk. J. For.* **2021**, *22*, 426–431. [CrossRef]
- 85. Aydemir, D.; Çivi, B.; Alsan, M.; Can, A.; Sivrikaya, H.; Gündüz, G.; Wang, A. Mechanical, morphological and thermal properties of nano-boron nitride treated wood materials. *Maderas. Cienc. Y Tecnol.* **2016**, *18*, 19–32. [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.