

Article

The Impact of Paraffin-Thermal Modification of Beech Wood on Its Biological, Physical and Mechanical Properties

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Abstract: The European beech (*Fagus sylvatica* L.) wood was thermally modified in the presence of paraffin at the temperatures of 190 or 210 °C for 1, 2, 3 or 4 h. A significant increase in its resistance to the brown-rot fungus *Poria placenta* (by 71.4%–98.4%) and the white-rot fungus *Trametes versicolor* (by 50.1%–99.5%) was observed as a result of all modification modes. However, an increase in the resistance of beech wood surfaces to the mold *Aspergillus niger* was achieved only under more severe modification regimes taking 4 h at 190 or 210 °C. Water resistance of paraffin-thermally modified beech wood improved—soaking reduced by 30.2%–35.8% and volume swelling by 26.8%–62.9% after 336 h of exposure in water. On the contrary, its mechanical properties worsened—impact bending strength decreased by 17.8%–48.3% and Brinell hardness by 2.4%–63.9%.

Keywords: beech; paraffin; thermal modification; fungi; swelling; mechanical properties

1. Introduction

European beech (*Fagus sylvatica* L.) is one of the most popular commercial broad leaved tree species in Central Europe [1,2]. Beech wood is preferred due to its properties; especially because it is easily workable and impregnable. On the contrary, beech wood suffers from low resistance to fungi and insects, and also from high volume shrinking, i.e., during drying it warps and splits, and under changing weather conditions its dimensions change significantly [3]. Low decay and mold resistance is considered one of the basic disadvantages of beech wood. According to the Standard EN 350 [4], it is non-durable and in exterior cannot be used without convenient treatments, mainly for structural elements.

In comparison to traditional chemical treatment of wood with toxic biocides, the processes of its thermal, biological and chemical modification do not usually affect the environment; therefore, investigation of new wood modification modes is very prospective [5,6].

Thermal modification of wood at high temperatures is connected with changes in its molecular structure. These changes are associated primarily with the hemicelluloses degradation, creation of hemicelluloses–lignin linkages and extinction of some hydroxyl groups [7–9]. An increase in the resistance of wood to water and biotic agents is the main aim of its thermal modification [5,10]. Types and extent of changes in molecular structure and subsequently in properties of thermally modified wood depend not only on the temperature and its duration, but also on the wood species, its initial moisture content, as well as on parameters of air, nitrogen, plant oil or other heating medium [5,6,10,11]. Biological resistance of wood is not affected positively by the thermal modification carried out in the atmosphere at lower temperatures ranging from 130 to 160 °C [10,12,13]. In practice, an increase in wood resistance to wood-decaying fungi and insects results from the application of higher temperatures of air ranging from 160 to 220 °C, or also from temperatures up to 260 °C at the limited

quantity of oxygen present [5,12,14,15].

In comparison to standard thermal modification of wood in hot air, higher resistance to decaying-fungi and water is ensured when hot plant oils and other hydrophobic agents are applied [12–14,16–18].

Waxes are due to hydrophobic properties used to protect wood against water, as the water sorption kinetics of wood is reduced and dimensional stability is improved [19]. Waxes also improve resistance of wood to termites [20,21]. Mechanical properties, as compressive strength [22], bending strength [21] and hardness [21,22], of wood treated with waxes do not change or increase slightly. Moreover, waxes are almost non-toxic and environmentally acceptable, so they can also be used in other sectors, e.g., pharmaceutical, beauty and food-processing industries.

Paraffin belongs to the group of waxes. It is a mixture of solid linear aliphatic hydrocarbons, especially straight chain alkanes synthesized from crude oil using Fischer–Tropsch synthesis or from coal tar. Paraffin is cheap, healthy clean and hydrophobic substance used in beauty industry, candle-making business, civil engineering, as well as in preservation of wood materials in order to reduce the hygroscopicity and to improve the dimensional stability. Paraffin and paraffin emulsions have been used to reduce water soaking and to improve dimensional stability of particleboards [23,24] and in hydrophobic treatment of solid wood [19,21,25] over a long period. Combining the technology of paraffin impregnation of wood with subsequent thermal modification in paraffin can have a synergic effect resulting in an effective improvement of selected wood properties [21,26,27].

The aim of the experiment was to determine the effect of thermal modification of European beech wood in the presence of paraffin in order to increase its resistance to rot, mold and water and at the same time to evaluate the effect of modification on selected mechanical properties of wood.

2. Materials and Methods

2.1. Wood

European beech (*Fagus sylvatica* L.) heart-wood specimens of high quality, i.e., without rot, insect gallery, growth defects, tension wood and red-false wood were or reaction—red-false wood were prepared from the sawn timber naturally seasoned to a moisture content of $13.5\% \pm 2\%$. Three types of specimens were used in the experiment—type (a): 25 mm × 25 mm × 5 mm in mycological tests and in testing the Brinell hardness; type (b): 5 mm × 50 mm × 25 mm in testing the soaking and swelling, and type (c): 120 mm × 10 mm × 10 mm in testing the impact bending strength (Figure 1). The top and bottom surfaces of specimens of the type (a) and type (b) were milled.

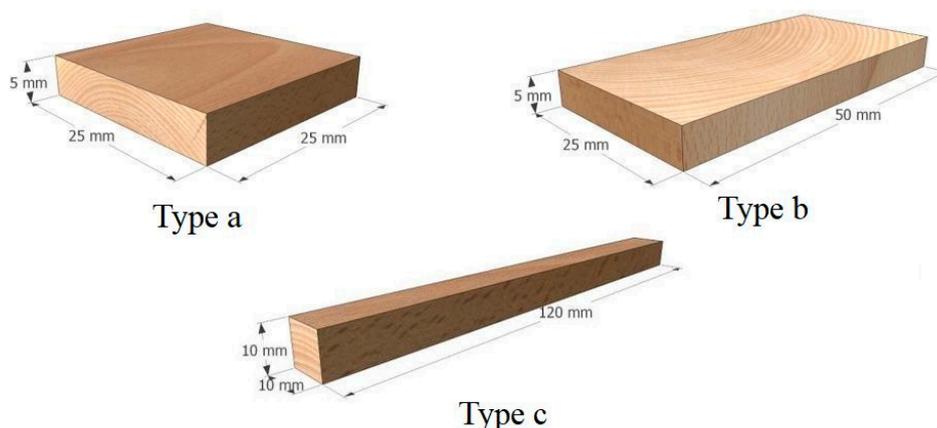


Figure 1. Types of beech wood specimens used in the paraffin-thermal modification and for testing the selected properties. Note: Type (a): 64 modified and 32 reference specimens for attack by wood-decaying fungi; 32 modified and 16 reference specimens for attack by the mold *Aspergillus niger*; 54 modified and six reference specimens for testing the Brinell hardness. Type (b): 54 modified and six reference specimens for testing the soaking and swelling. Type (c): 54 modified and six reference specimens for testing the impact bending strength.

Prior to modification, the beech specimens were dried at 103 ± 1 °C to the oven-dry state in the kiln Memmert UNB 100 (Memmert, Schwabach, Germany), and subsequently cooled in desiccators to a temperature of 20 ± 2 °C and weighed with an accuracy of 0.001 g.

2.2. Paraffin

Clear paraffin wax (MOL, Hungary) with the melting point ranging from 60 to 62 °C was used to modify the beech specimens.

2.3. Paraffin-Thermal Modification

The beech specimens were thermally modified with hot paraffin in the kiln Memmert UNB 100. In the first phase, paraffin melted in stainless steel containers at the temperatures from 80 to 100 °C/1 h. In the second phase, beech wood specimens were impregnated in the melt of paraffin wax at atmospheric pressure and at a temperature of 100 °C/1 h. In the third phase, the temperature of paraffin increased continuously to 190 °C (or 210 °C) during 1 h. In the fourth phase, the temperature in the containers with paraffin and beech specimens remained at 190 °C (or 210 °C) for 1, 2, 3 or 4 h. In the last fifth phase, non-absorbed hot paraffin ran off surfaces of beech specimens. The process of modification is shown in Figure 2a..

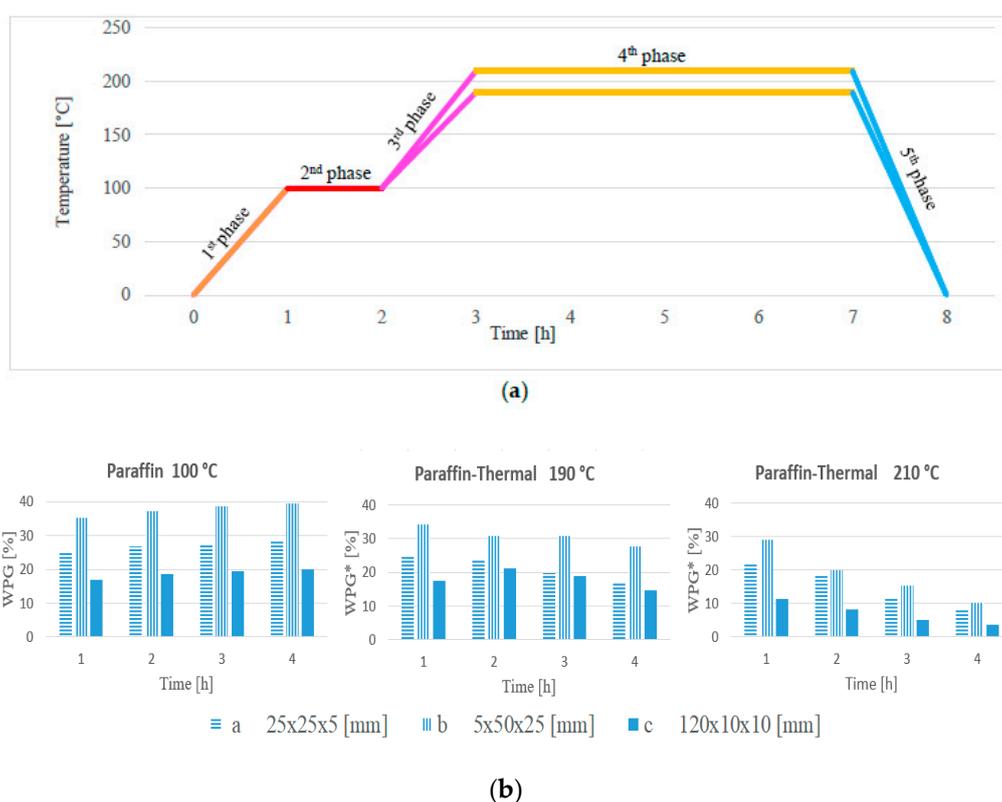


Figure 2. Phases of the paraffin-thermal modification of beech specimens (a) and weight percent gain (WPG) values of the paraffin modified specimens and also so-called real WPG* values of the paraffin-thermally modified specimens—within the 4th phase lasting from 1 to 4 h (b). Note: WPG values of paraffin at the end of the 2nd modification phase: Type (a) 23.91%; Type (b) 33.37% and Type (c) 13.98%. Calculation of the theoretical weight losses ($\Delta m_{\text{Thermal}} = \text{WPG} - \text{WPG}^*$) of paraffin-thermally modified specimens caused by thermal effects in the 4th phase could be performed as well, for example, for specimens of Type (a): $\Delta m_{\text{Thermal}}$ at 190 °C/1 h = 0.10%; 2 h = 3.14%; 3 h = 7.82%; 4 h = 12.02%; and $\Delta m_{\text{Thermal}}$ at 210 °C/1 h = 2.72%; 2 h = 8.68%; 3 h = 15.78%; 4 h = 20.81%.

Modified specimens of beech wood were cooled in desiccators to a temperature of 20 ± 2 °C, weighed with an accuracy of 0.001 g, their dimensions were determined with an accuracy of 0.01 mm, and transferred were to the desiccators again.

The weight percent gain (WPG, and also WPG*) values of paraffin into beech wood specimens were affected by their dimension, at which the lowest WPG (or WPG*) values had specimens of Type (c) 120 mm × 10 mm × 10 mm (L × T × R) with the smallest portion of axial surfaces (Figure 2b). The so-called WPG* ($WPG - \Delta m_{\text{Thermal}}$) values were simultaneously affected by weight losses of specimens caused by degradation of hemicelluloses and other components of wood at the high temperatures of 190 or 210 °C acting from 1 to 4 h (Figure 2b).

Specimens used in mycological tests (i.e., resistance to wood-decaying fungi and molds) and in testing the mechanical properties (i.e., impact bending strength and hardness) were air-conditioned at a temperature of 20 ± 2 °C and a relative air humidity of $60\% \pm 5\%$ for 14 days. Oven-dry specimens with 0% moisture content were used in soaking and swelling tests.

2.4. Attack by Wood-Decaying Fungi

The specimens (25 mm × 25 mm × 5 mm) were subjected to attack by the brown-rot fungus *Poria placenta* (Fries) Cooke sensu J. Eriksson, strain FPRL 280 (Building Research Establishment, Garston-Watford-Herst, UK) or to attack by the white-rot fungus *Trametes versicolor* (Linnaeus ex Fries) Pilat, strain BAM 116 (Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany).

Fungal attack of specimens was performed in Petri dishes with a diameter of 100 mm according to modified Standard EN 113 [28], i.e., specimens with another shape and another method of sterilization were used, and their exposition in fungal mycelia at a temperature of 24 ± 2 °C and a relative air humidity of $90\% \pm 5\%$ lasted for 6 weeks instead of 16 weeks, according to the rapid screening test by Van Acker et al. [29].

Two replicates of the equally modified beech specimen and one replicate of the reference beech unmodified specimen were placed into each Petri dish in the vaccination box (Merci Ferrera, Italy) (Figure 3). Specimens were deposited on plastic mats under which a fungal mycelium had already been grown on a sterilized 4.5 wt% malt agar medium (HiMedia, Ltd., Mumbai, India) with a thickness from 3 to 4 mm. After the fungal attacks, mycelium was carefully cleaned from the surface of specimens. Specimens were then air-conditioned for 14 days at a temperature of 20 ± 2 °C and a relative air humidity of $60\% \pm 5\%$, and weighed to determine the weight loss (Δm), using Equation (1):

$$\Delta m = \frac{m_0 - m_{0deg}}{m_0} \times 100 (\%) \quad (1)$$

where: m_0 —mass of specimen in the conditioned state before mycological test (g) and m_{0deg} —mass of specimen in the conditioned state after mycological test (g).

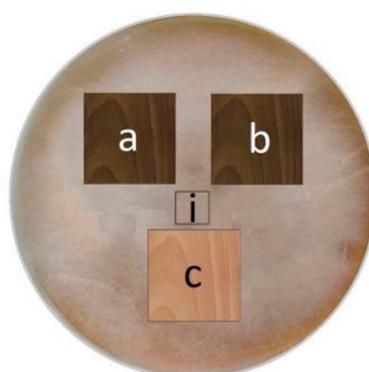


Figure 3. Petri dish with three beech wood specimens (a, b—modified by the same mode, c—reference) and fungal inoculum (i).

2.5. Attack by the Mold *Aspergillus niger*

The mold resistance test of the specimens (25 mm × 25 mm × 5 mm) was performed with the microscopic fungus *Aspergillus niger* Tiegh. according to modified Standard EN 15457 [30], i.e., specimens with other shape and other methods of sterilization were used. Firstly, all surfaces of specimens were sterilized with the 30 W germicidal lamp (Chirana, Medical, a. s., Stará Turá, Slovakia) from a distance of 1 m at a temperature of 22 ± 2 °C/0.5 h. Sterilized specimens were placed into Petri dishes with a diameter of 100 mm on a sterilized 4.9 wt% Czapek-Dox agar medium (HiMedia, Ltd., Mumbai, India) with a thickness from 3 to 4 mm and inoculated with a spore suspension of *A. niger* in a sterile water (10⁶–10⁷ spores/mL). Incubation of inoculated specimens in the thermostat Nahita 636 Plus (Nahita, France) took 21 days at a temperature of 24 ± 2 °C and a relative air humidity of 90%–95%. Growth activity of the mold *A. niger* on the top surfaces of specimens was evaluated on the 7th, 14th and 21th day by these criteria: 0 → growth 0% = no growth of the mould on the top surface of specimen; 1 → growth ≤10%; 2 → growth >10% and ≤30%; 3 → growth >30% and ≤50% and 4 → growth >50%.

2.6. Soaking and Swelling

In order to determine the ability of the reference and modified beech wood specimens (5 mm × 50 mm × 25 mm) to absorb distilled water (S_i), the soaking test according to the Standard STN 49 0104 [31] was performed, using Equation (2):

$$S_i = \frac{m_i - m_0}{m_0} \times 100 (\%) \quad (2)$$

where: m_i —mass of the moist specimen at the defined time of soaking (g) and m_0 —mass of the oven-dry specimen (g).

At the same time, volume swelling of wood (β_{Vi}) was evaluated, using Equation (3):

$$\beta_{Vi} = \frac{V_i - V_0}{V_0} \times 100 (\%) \quad (3)$$

where: V_i —volume of the moist specimen at the defined time of soaking (mm³) and V_0 —volume of the oven-dry specimen (mm³).

2.7. Impact Bending Strength and Brinell Hardness

Impact bending strength of specimens in tangential direction (I) was determined according to the Standard ISO 3348 [32], using Equation (4):

$$I = \frac{W}{b \times h} (J \cdot cm^{-2}) \quad (4)$$

where: W —work done for cutting the specimen (J) and b and h —specimen cross section dimensions (cm).

Brinell hardness of specimens in radial direction (H_B) was evaluated according to the Standard EN 1534 [33] using a steel ball with a diameter of 11.284 mm impressed into the wood surface with a force of 500 N. It was calculated by Equation (5):

$$H_B = \frac{F}{S} = \frac{2 \times F}{\pi \times D \times (D - \sqrt{D^2 - d^2})} (MPa) \quad (5)$$

where: F —force on the ball (N), D —ball diameter (mm) and D —diameter of the impressed area (mm).

3. Results and Discussion

3.1. The Rot Resistance

All paraffin-thermal modifications of beech wood specimens resulted in an increase in their rot resistance (Table 1). The highest weight losses (Δm) caused by wood-decaying fungi were observed in the case of the reference beech specimens (22.14% with *Poria placenta* and 29.65% with *Trametes versicolor*). On the contrary, the lowest weight losses <1% were observed in the specimens modified

with the most severe modification regimes, i.e., at 210 °C for 3 h or 4 h. The modified specimens were usually more intensively attacked by the white-rot fungus *T. versicolor* (Δm from 0.15% to 14.8%) than by the brown-rot fungus *P. placenta* (Δm from 0.35% to 6.34%). However, in the case of their exposure to the most severe regimes (210 °C/3 or 4 h) the result obtained was opposite. This disproportion arose probably due to a greater inhibitory effect of specific carbonized wood components created with prolonged exposure to 210 °C on the growth and enzymatic activities of *T. versicolor*.

Table 1. Weight losses (Δm) of the reference and modified beech specimens after action of the wood-decaying fungi *Poria placenta* and *Trametes versicolor*.

Paraffin-Thermal Modification	<i>P. placenta</i> Δm (%)	<i>T. versicolor</i> Δm (%)
Reference	22.14 (4.50)	29.65 (6.53)
190 °C/1 h	6.34 (2.91) a	14.80 (6.19) a
190 °C/2 h	5.32 (2.17) a	10.05 (3.86) a
190 °C/3 h	5.33 (2.04) a	9.68 (3.70) a
190 °C/4 h	3.76 (1.66) a	7.83 (3.02) a
210 °C/1 h	5.25 (1.95) a	7.74 (2.98) a
210 °C/2 h	2.67 (1.07) a	4.87 (1.93) a
210 °C/3 h	0.92 (0.42) a	0.25 (0.19) a
210 °C/4 h	0.35 (0.28) a	0.15 (0.11) a

Note: mean values are from four replicates, and from 16 reference replicates. Standard deviations are in italics and parantheses. The Duncan test, with significance levels a = 99.9%, b = 99%, c = 95% and d < 95%, was performed in relation to reference specimens—at which differences always occurred at the 99.9% significance level (a).

Lesar and Humar [34] found out that wood attacked with wood-decaying fungi could degrade slower when impregnation with waxes is applied. The wax-barrier located in the cell lumens of wood slows down the diffusion, both of fungal enzymes and products resulting from the cell wall degradation, between hyphae of wood-decaying fungi and wood structural components. Specific changes in the molecular structure of wood, causing an increase in its resistance to decay, occur as a result of its parallel wax and thermal modification. The fungal growth inhibition is here also caused due to polysaccharide dihydroxylation and resulting in a lower moisture content of wood [35]. Boonstra et al. [36] mentioned that the thermal modification of wood could result in chemical transformation of components like minerals, vitamins and lower molecular weight carbohydrates necessary for the activity of wood-decaying fungi. At the higher temperatures of 210 °C, hemicelluloses degrade to substances with lower hygroscopicity and higher toxicity to fungi, e.g., like furfural polymers [37,38]. According to Lacić et al. [39], an increase in the rot resistance of alder wood, markedly to the brown-rot fungus *P. placenta* and less significantly to the white-rot fungus *T. versicolor*, resulted from its thermal modification at the temperatures of 180 °C and 200 °C for 6 h and 10 h in proportion to an increase in temperature and time. Similarly, several researchers found out that the rot resistance of spruce, pine and other wood species to wood-decaying fungi *Coniophora puteana* and *T. versicolor* is increased by their thermal modification in atmosphere [40] or in plant oils [14,41]. For example, Rapp and Sailer [14] determined that the rot resistance of thermally modified spruce wood and sapwood of pine to *C. puteana* increased at the plant oil temperature ranging from 190 °C to 220 °C—since the weight losses of wood during the decay processes decreased from 40% to 5.5% in the case of spruce wood or from 48% to 11% in the case of pine sapwood. Yilgör and Kartal [15] found out that the rot resistance of the thermally modified sugi (*Cryptomeria japonica* D.) sapwood, exposed to a temperature of 180 °C for 2 and 4 h or to a temperature of 220 °C for 2 h, increased significantly against the white-rot fungus *T. versicolor*—since its weight losses decreased evidently from 41.4% to 4.1% in dependence to an increase in the temperature and time. According to Kartal [42], thermal modification of sugi sapwood at a temperature of 180 °C for 2 and 4 h did not result in an increase in its rot resistance to the brown-rot fungus *Fomitopsis palustris*, but there was a slight increase in its resistance to the white-rot fungus *T. versicolor*.

3.2. The Mold Resistance

The growth intensities of the mold *Aspergillus niger* on the surface of beech wood specimens subjected to different paraffin-thermal modifications were markedly reduced only at the beginning of testing, after the 7th and 14th day (Table 2). Only beech specimens modified for the longest time, for 4 h at the temperatures of 190 °C or 210 °C, showed lower growth intensity of this mold (GIM ≤ 2) on the final 21st day of testing (Table 2).

Table 2. Growth intensities of the mold *Aspergillus niger* (GIM from 0 to 4) on the top surfaces of beech wood specimens subjected to different paraffin-thermal modifications.

Paraffin-Thermal Modification	<i>A. niger</i> GIM (0–4)	<i>A. niger</i> GIM (0–4)	<i>A. niger</i> GIM (0–4)
	7th day	14th day	21st day
Reference	3	3	4
190 °C/1 h	1	2	2.75
190 °C/2 h	1	2	3
190 °C/3 h	0.5	1.5	2.5
190 °C/4 h	0.25	1	2
210 °C/1 h	1	1.75	3
210 °C/2 h	1	2.25	2.5
210 °C/3 h	0	1.5	2.25
210 °C/4 h	0	1	1.25

Note: mean values are from four replicates, and from 16 reference replicates..

Results of the experiment can be compared to the results obtained by [17] who searched mold resistance of beech and pine woods thermally modified by the oil heat treatment (OHT) process in technology in rapeseed oil—when both wood species showed markedly increased resistance to the mold *A. niger* only in the case of modification performed at the highest temperature of 220 °C for 3 h or 6 h. Similarly, Yılmaz and Kartal [15] found out that the resistance of sugi wood, modified at a temperature of 180 °C for 2 and 4 h and at a temperature of 220 °C for 2 h, to the molds *Rhizopus javanicus* and *Trichoderma virens* increased slightly, whereby to the mold *A. niger* increased only negligibly. Impregnation of beech and spruce woods with various wax emulsions had no significant impact on an increase in the resistance of mentioned wood species to molds [34].

3.3. The Soaking and Swelling Resistance

Paraffin is a hydrophobic substance. In the impregnated wood it is located in the cell lumens and on the S₃ layer of cell walls, due to what it reduces its soaking and swelling [43]. However, paraffin does not penetrate the wood cell walls, which allows water vapor diffusion in its structure, and thus the effect of paraffin on improving the dimensional stability of wood is only temporary [26]. Lesar and Humar [34] mentioned the effect of waxes in spruce wood on a decrease in the moisture absorption and soaking kinetics of modified wood.

Similar inhibition effects of paraffin in wood against its soaking and swelling in distilled water were investigated and founded in this experiment (Table 3, Figures 4 and 5). The alone paraffin reduced the capacity of water penetration into wood during the soaking test (Figure 4). Paraffin up to 8 h evidently suppressed kinetics of wood swelling, however, after 24 h its anti-swelling effect was already smaller (Table 3, Figure 5).

Table 3. Soaking and volume swelling in distilled water of beech wood specimens subjected to different paraffin-thermal modifications—results after 24 h and 336 h.

Paraffin-Thermal Modification	Soaking— S_i (%)		Swelling— β_{vi} (%)	
	24 h	336 h	24 h	336 h
Reference	74.34 (10.82)	96.92 (12.52)	19.43 (3.46)	20.55 (3.83)

Paraffin only	27.67 (0.78) a	78.68 (1.45) b	16.56 (3.19) c	19.19 (1.16) d
190 °C/1 h	38.15 (4.67) a	66.46 (2.88) a	14.46 (0.99) b	14.67 (1.20) a
190 °C/2 h	39.49 (2.90) a	64.46 (2.37) a	14.68 (0.59) b	15.04 (0.82) a
190 °C/3 h	34.03 (3.41) a	63.26 (2.16) a	13.58 (0.71) a	14.25 (0.81) a
190 °C/4 h	31.24 (3.18) a	65.50 (1.46) a	12.21 (0.98) a	12.81 (1.08) a
210 °C/1 h	36.06 (4.46) a	66.13 (1.38) a	12.36 (0.61) a	12.16 (1.04) a
210 °C/2 h	31.95 (3.55) a	67.61 (1.33) a	10.14 (0.96) a	10.86 (0.82) a
210 °C/3 h	22.75 (1.08) a	67.22 (1.79) a	7.81 (0.45) a	8.37 (0.24) a
210 °C/4 h	20.26 (2.29) a	62.20 (1.62) a	6.99 (0.53) a	7.62 (0.52) a

Note: mean values are from six replicates. Standard deviations are in italics and parantheses. The Duncan test, with significance levels a = 99.9%, b = 99%, c = 95% and d < 95%, was performed in relation to reference specimens—at which differences usually occurred at the 99.9% significance level (a), or at swelling also at lower significance levels, the 99% (b) and 95% (c), respectively none for specimens modified only with paraffin (d)

In accordance with several research studies [44–46] the fact that swelling of wood was reduced especially due to its thermal modification while the role of paraffin was only to slow down kinetics of swelling was confirmed (Table 3, Figure 5). Thermal modification of wood results in changes in its molecular structure, i.e., the polysaccharides (especially hemicelluloses) depolymerized, the microcrystalline cellulose portion increased, the lignin linkage occurred and therefore, the presence of free hydroxyl groups in wood decreased [47].

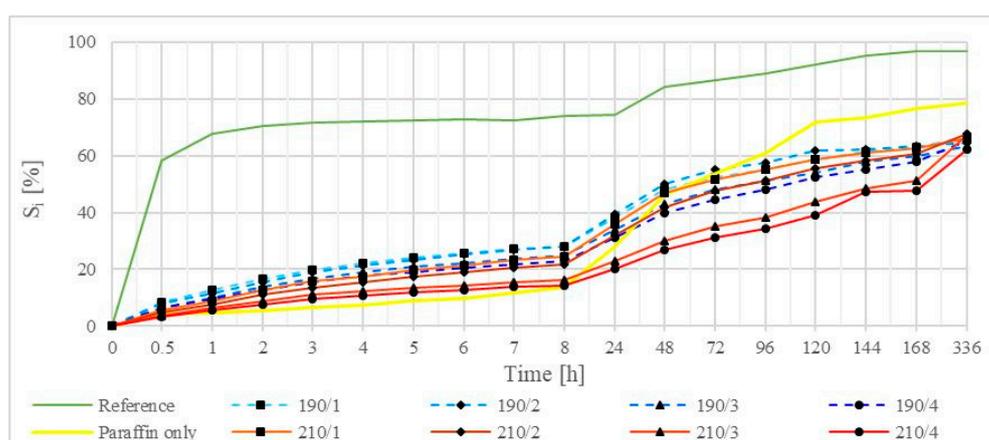


Figure 4. Soaking kinetics of reference and paraffin-thermally modified beech wood specimens.

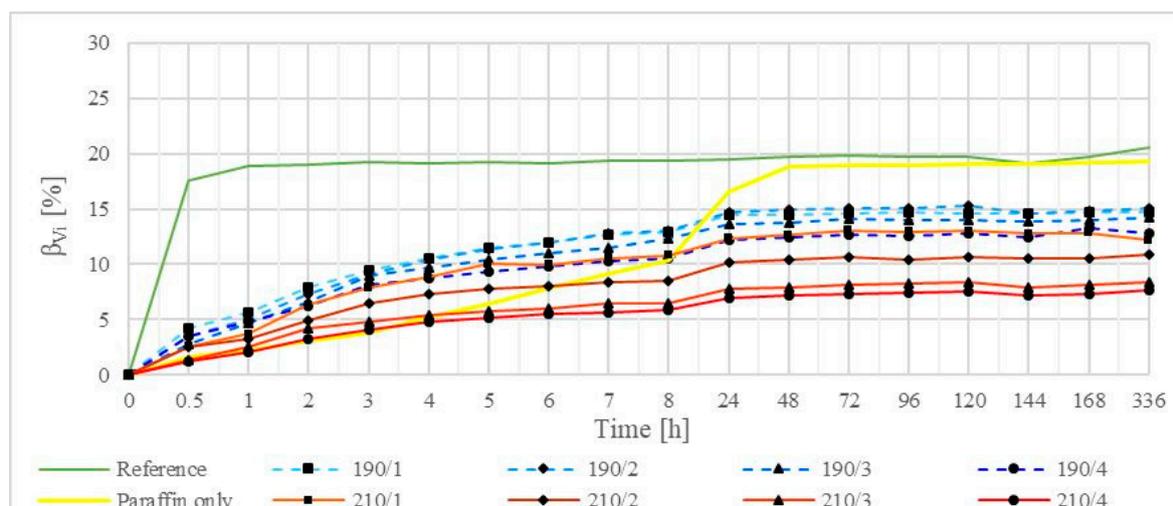


Figure 5. Volume swelling kinetics of reference and paraffin-thermally modified beech wood specimens.

The values of soaking and swelling of paraffin-thermally modified beech wood were in all cases lower in comparison to the reference beech wood specimens (Table 3, Figures 4 and 5). The swelling of beech wood reduced proportionally to an increase in temperature and time of modification (Table 3, Figure 5). Significantly reduced swelling of beech wood, by approximately 60%, was observed in the case of specimens modified under the regimes at higher temperature of 210 °C for 3 h and 4 h. However, significantly reduced soaking, by approximately 30%, already occurred when modifying the wood under the mildest regime at a temperature of 190 °C for 1 h, especially due to a high presence of paraffin in cell lumens (Table 3, Figure 4).

Similarly by Reinprecht and Vidholdová [17], the soaking and swelling of beech and spruce woods modified by the OHT process in rapeseed oil were reduced especially in the case of the highest temperature of 220 °C acting for the longest time of 6 h. Bal [48] determined physical properties, including volume swelling, of beech thermowood modified in the hot oil medium or hot air at the temperatures of 160 °C, 190 °C and 220 °C for 2 h. In accordance with our experiment, the volume swelling decreased in the case of the most severe modification regime from 17.6% to 4.2%—i.e., in percentage it reduced proportionally to higher temperature and prolonged time of thermal modification from about 8.5% up to 76%. The swelling of beech wood thermally modified in hot oil was reduced more in comparison to the modification process performed in hot air.

In general, the fact that the effect of thermal modification of wood in hot oils or waxes on reducing the swelling is more significant than the effect of thermal modification by hot air can be stated. It can be due to the presence of hydrophobic media located in cell lumens also after thermal modification, therefore, the barrier reducing the process of water absorption by cell walls is made [16,34,49,50]. The correlation between the weight loss of wood during the process of thermal modification and soaking and swelling was mentioned in several previous research works [51–53]. It is observed mainly in the case of wood modification at higher temperatures when an increase in hydrophobicity is affected more by degrading and linking its structural components.

3.4. The Impact Bending Strength and Brinell Hardness

Lots of researchers found out that mechanical properties of wood like compressive strength [22] bending strength [21] and hardness [21,22] can be improved by impregnating the wood with waxes. Mechanical properties of wood like hardness [17,54], bending strength [54], compressive strength [54–56] and modulus of elasticity [57] were improved also under milder conditions of its thermal modification. An increase in the compressive strength of thermowood can be explained with a relative increase in the lignin content and its condensation confirmed by the near infrared spectroscopy (NIR) [55]. It is supposed that an increase in the modulus of elasticity of thermowood

relates to forming new chemical bonds with higher bond energy in comparison to the energy of absent hydrogen bonds [57]. However, the mechanical properties get worse when modified temperatures are higher, usually above 220 °C, and the time of modification is longer [10,17,54,58–61]. It is especially due to significant thermal degradation of hemicelluloses situated between cellulose microfibrils in wood cell walls and also due to organic acids resulting from the hemicellulose decomposition catalyzing the cleavage of lignin–carbohydrate complex of wood [62]. Mechanical properties of commercial thermowood get worse by 10%–30% and such wood is not recommended to be used in load-bearing structural elements [63].

The impact bending strength of beech wood decreased slightly about 20.63% due to the presence of paraffin, however, more rapidly after paraffin-thermal modifications in the range from 17.84% to 48.33%—proportionally to an increase in temperature and time of modification (Table 4). The impact bending strength of poplar wood heated at a temperature of 210 °C for 3 h decreased even by about 61% [64]. The fact that this mechanical property decreases significantly at higher temperatures especially in the case of hardwoods is generally known. It is owing to pentosans decomposition and loss of their elastic-mechanical function in cell walls. Beech and other hardwoods contain 2 or 2.5 times more of pentosans in comparison to coniferous wood [65].

Table 4. Impact bending strength and Brinell hardness of beech specimens subjected to different paraffin-thermal modifications.

Paraffin-Thermal Modification	Impact Bending Strength <i>I</i> (J.cm ⁻²)	Brinell Hardness <i>H_B</i> (MPa)
Reference	5.38 (0.83)	31.56 (5.29)
Paraffin only	4.27 (0.40) b	32.22 (4.86) d
190 °C/1 h	3.76 (0.65) a	30.81 (5.02) d
190 °C/2 h	4.42 (0.47) c	29.09 (1.94) d
190 °C/3 h	3.87 (0.23) a	25.46 (4.96) c
190 °C/4 h	3.36 (0.77) a	27.86 (3.47) d
210 °C/1 h	3.90 (0.31) a	18.87 (1.88) a
210 °C/2 h	3.66 (0.31) a	18.46 (0.94) a
210 °C/3 h	3.40 (0.22) a	13.15 (0.70) a
210 °C/4 h	2.78 (0.55) a	11.38 (1.37) a

Note: mean values are from six replicates. Standard deviations are in italics and parantheses. The Duncan test, with significance levels a = 99.9%, b = 99%, c = 95% and d < 95%, was performed in relation to reference specimens—at which mechanical properties of specimens modified at 210 °C always decreased on the 99.9% significance level (a).

The Brinell hardness of paraffin-thermally modified beech wood decreased in the range from 2.38% to 63.94%, especially at a higher temperature of 210 °C. However, harness was not affected by alone paraffin (Table 4). Significant decrease in hardness was investigated especially in the case of specimens modified at 210 °C. Reinprecht and Vidholdová [17] determined a decrease in the Brinell hardness by 1.5%–33% when modifying beech wood in rapeseed oil at a temperature of 180 °C and 220 °C for 3 h to 6 h. Bakar et al. [63] investigated a decrease in hardness of oak wood by 33.3% resulting from thermal modification at a temperature of 190 °C for 8 h. Borůvka et al. [66] determined different changes in the Brinell hardness of thermally modified beech and birch woods (210 °C/3 h)—the hardness of beech wood decreased by 37% and the hardness of birch wood increased by 9%. An increase in hardness of birch wood was explained due to a higher content of mannans in hemicelluloses. By Bonstra et al. [36], the finding for pine and spruce woods that the Brinell hardness parallel to grains increased by 48% or perpendicular to grains by 5%—as a result of their primary hydrothermal modification and subsequent thermal modification—can be considered interesting.

4. Conclusions

- Paraffin-thermal modification resulted in a significant increase in the rot resistance of beech

- wood to decaying fungi—the brown-rot fungus *Poria placenta* by 71.4%–98.4% and the white-rot fungus *Trametes versicolor* by 50.1%–99.5%. The lowest weight loss, less than 1%, was observed in the case of beech wood specimens modified in paraffin at a temperature of 210 °C for 3 h or 4 h.
- The mold resistance of paraffin-thermally modified beech wood to the microscopic fungus *Aspergillus niger* increased significantly in the first days of testing. However, on the final 21st day of the mold test, the growth intensity of *A. niger* reduced only in the case of specimens modified under the most severe modification regimes.
 - The soaking and volume swelling of beech wood reduced markedly as a result of paraffin-thermal modification—the soaking was reduced in all cases by more than 30% and the volume swelling was reduced by 26.8%–62.9%. The specimens of beech wood modified at a temperature of 210 °C for 3 h or 4 h were the most resistant to swelling. On the contrary, soaking was not affected by the temperature and the time of modification.
 - Mechanical properties of beech wood got worse as a result of an increase in temperature and time of modification. There was a decrease in the impact bending strength in the range from 17.8% to 48.3% and in the Brinell hardness in the range from 2.4% to 63.9%.
 - Generally, beech wood modified with hot paraffin showed significantly better resistance to wood-decaying fungi, slightly better resistance to mold growth, and reduced soaking and swelling. Wood modified this way can be used as a material for making products especially in the demanding interior projects, e.g., sauna, bathroom, kitchen paneling, as well as in exterior projects, e.g., facade or swimming pool panels. However, due to lower values of the impact bending strength and Brinell hardness, the wood modified this way is not convenient for load-bearing structural elements and in projects where good mechanical properties are necessary.

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