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The Biological Durability of Thermally- and Chemically-Modified Black Pine and Poplar Wood Against Basidiomycetes and Mold Action

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Received: 18 November 2019; Accepted: 3 December 2019; Published: 5 December 2019

Abstract: Wood of black pine and poplar species were subjected to thermal modification under variant conditions, while subsequently, a number of the thermally-modified black pine specimens were subjected to surface modification with organosilane solutions, and the biological resistances of the different materials were examined using laboratory agar block tests against the action of basidiomycetes and microfungi. Thermally-modified pine specimens were exposed to the brown rot fungi *Coniophora puteana* and *Oligoporus placenta*, whereas poplar wood was exposed to the white rot fungus *Trametes versicolor* and *O. placenta*. Regarding the biological durability of thermally-chemically-treated pine wood with organosilanes, it was tested against the action of *C. puteana.* Additionally, both of the thermally-treated wood species, as well as thermally-chemically-treated pine wood were exposed to a microfungi mixture, so that the wood treatments efficacy would be evaluated through a visual assessment of fungal growth on the specimen's surface The thermal treatments seem to increase the biological resistance of black pine against *C. puteana* by 9.65–36.73% compared to unmodified wood. The most significant increase in biological durability among all the thermally-treated wood categories was recorded by *O. placenta*, with 28.75–68.46% lower mass losses in treated pine specimens and 31.98–64.72% in thermally-treated poplar, respectively, compared to unmodified wood. The resistance of treated poplar against *T. versicolor* was also found increased (13.25–46.08%), compared to control. Thermal modification affected positively the biological resistance of both species, though it did not manage to protect effectively pine and poplar wood from the microfungi action. The combination of thermal and organosilanes treatment revealed a significant improvement of the durability of pine wood compared to? control (45.68–87.83% lower mass losses against *C. puteana*), as well as against the microfungi action, with the presence of benzin to have a positive effect on the silanes solutions performance and protective action.

Keywords: basidiomycetes; heat; molds; pine wood; poplar wood; silanes; thermal treatment

1. Introduction

The resistance of wood to rot is often considered to be synonymous with its duration. The action of various micro-organisms may cause damages and deterioration in the appearance, structure and chemical composition of wood. Several methods have been proposed so far for improving the natural durability of wood [1]. Apart from chemical protection measures, one of the most effective ways to prevent or limit the action of microorganisms in wood is to keep the moisture content low enough or to prevent at least one of the necessary growth requirements of the microorganisms to be fulfilled, such as the presence of oxygen in wood, proper pH (3–8), appropriate temperature (15 °C–40 °C), absence of toxic extracts, presence of other growth factors such as vitamins, nitrogen etc. [2].

Thermal modification consists of a non-biocidal, environmentally friendly wood protection method to enhance the behavior of wood and some characteristics critical for its service life expectancy and its utilization perspectives. Heat induces changes to the chemical constituents of wood, and therefore, to the chemical, physical and mechanical properties of wood, as well. Despite the fact that thermal treatment decreases the density and most of the times the mechanical strength of wood, since it increases its brittleness, it seems to limit the hygroscopic nature and enhance the natural durability of wood, providing the chance, (especially to species characterized by low water resistance, dimensional stability and susceptibility to bio-degradation factors), to be adequately utilized, participating in a much wider range of applications [3–6].

Several researches have been implemented to deal with the biological resistance of thermally-modified wood, the most significant of which are summarized hereupon. Li Shi et al. [7] reported that thermally-modified yellow-poplar and jack pine (210 °C for 15 min) were found to be more resistant to the brown rot fungus *Gloeophyllum trabeum* than the unmodified wood; while referring to aspen and Scots pine, the resistance was improved after the thermal modification, but it remained susceptible to this brown-rot fungus decay. Mburu et al. [8] modified the heartwood of silky oak (250 °C for 7 h) and observed that durability against fungi and termites was greatly improved after treatment, highlighting a good correlation between decay resistance and mass loss due to thermal treatment. Vetter De et al. [9] exposed many species, thermally-modified under various conditions in mycological tests of the fungi *C. puteana, O. placenta* and *T. versicolor*. Heat-modified *Picea abies* recorded a reduced resistance to *O. placenta* action with mass losses close to the control level, while the action of *C. puteana* was inhibited by heat treatment with mass losses less than 3%. Mazela et al. [10] examined the resistance of thermally-modified (160 °C–220 °C for 6 h and 24 h) wood of Scots pine against *C. puteana, G. trabeum, O. placenta* and *T. versicolor*, concluding that the brown rot fungi recorded a more intense action (mass loss of 23–46%) compared to white-rot fungi. *T. versicolor* did not prefer coniferous species (low loss of 15.4%), while *C. puteana* caused a mass loss of 39.4%, *G. trabeum* 23.5% and *O. placenta* a loss of 45.8%, respectively. Mohareb et al. [11] examined the biological durability of *Pinus patula* species after its thermal treatment using different treatment intensities, and concluded that the elemental composition of wood could be used as a valuable marker to predict treatment intensity and decay durability. Since the results of the studies published in the literature so far reveal different tendencies, the kind and range of the thermal treatment impact upon the biological resistance of wood against basidiomycetes seem not to have been thoroughly investigated and elucidated so far.

Organosilicon compounds have been applied by researchers in recent years to modify solid wood to increase hydrophobicity, durability or water resistance and dimensional stability, to prevent leaching of active ingredients or to promote adhesion or to improve fire resistance, etc. [12–15]. Although numerous studies have been conducted on silane modification of solid wood referring to its hygroscopic properties and dimensional stability, there is scant research on the efficacy and influencing mechanism of silanes modification on the biological durability of wood. Additionally, aiming to improve the biological durability of wood, a combination of thermal treatment and organosilanes treatment has not been proposed or investigated so far, according to the bibliography.

Specifically, Donath et al. [13] used the coupling agent γ-methacryloxypropyltrimethoxysilane (TEOS), and organo functional alkoxysilanes and found good incorporation into the cell wall, when conditioned wood was impregnated with alcoholic solutions of the two silanes methyltriethoxysilane and propyltriethoxysilane. Durability of the treated wood towards the white rot fungus *T. versicolor* was increased considerably, but especially when the silane penetrated and bulked the cell wall. In a soil block test, decay was delayed, but not prevented. Hill et al. [16] treated black pine sapwood with the two coupling agents γ-methacryloxypropyltrimethoxysilane and vinyltrimethoxysilane and found incorporation of the silicon material into the cell wall, and concerning the fungal decay tests, only little increase of resistance to *C. puteana* was recorded. Incubation with *T. versicolor* and *Phanerochaete crysosporium* displayed decay resistance of the treated wood above weight percent gain (WPG) of 40%

for *T. versicolor* and around 40–50% for *Phanerochaete crysosporium* [16]. Higher decay resistance was found, when amino-functional silanes were applied.

Donath et al. [13] treated wood with an amino-functional oligomeric silane system and found complete decay resistance of Scots pine sapwood to *C. puteana* (16% WPG) even after prolonged incubation (18 weeks). However, European beech wood treated with the same silane system (11% WPG), revealed considerable mass loss after incubation with *T. versicolor*. Wood treated with silicon compounds without biologically-active substance indicated a rather unsatisfactory resistance against wood decay fungi [12,15].

Microfungi develop mainly upon the surface of wood and the presence of a mold colony may make wood more vulnerable to the growth of a fungal colony, as well [17]. Boonstra et al. [2] reported in their research work that thermal treatment did not manage to inhibit the growth of mold in the surface of the specimens, while Kocaefe et al. [18], who modified Jack pine and white poplar wood thermally, recorded an improvement in wood resistance to mold growth, although this improvement did not correspond to statistically significant differences. Analogous results have been found by Gobakken and Westin [18] who observed a small resistance improvement, but very low compared to other treatments and Fojutowski et al. [19] who examined thermally-treated black poplar and black alder wood.

The aim of this research is to examine the biological resistance of black pine (*Pinus nigra* L.) and poplar (*Populus* sp.) wood after short-term thermal modification for three different durations at two temperature levels, as well as, for the first time, the combination of the described thermal modification with a subsequent chemical surface modification with water-borne and benzin-borne organosilane systems of different ratios on black pine wood, against the action of some of the common European basidiomycetes species and a mixture of commonly found microfungi (molds) species. Poplar has been chosen as a species of low quality, physical properties and natural resistance, and the black pine species was chosen, since especially its sapwood is considered to be non-resistant to wood-destroying fungi attacks, and both species seem to need enhancement e.g., [1]. Additionally, the specific species are of great importance for the Mediterranean, as well as the whole Europe area, concerning availability, timber and wood-products trade, etc., and the thermal and chemical treatments could offer them a chance to compete for specific applications with species of higher cost and value.

2. Materials and Methods

Boards of black pine (*Pinus nigra* L.) and poplar (*Populus* sp.) wood of Greek origin (poplar wood was obtained from the Drama region in North Greece and black pine from the Kalampaka region in the central part of Greece) were placed for about eight months into an air-conditioned room at a temperature of 20 ± 2 °C and 60% ± 5% relative humidity, and left there to dry naturally until there existed a constant weight recording an equilibrium moisture content (EMC) of 11.44% for pine and 10.50% for poplar wood (ISO 13061-1) [20]. The mean density (mass/volume, measured with moisture content at the reported levels) of the pine was 0.662 g/cm^3 (presenting dense structure with thin annual rings) and 0.385 g/cm^3 of poplar (ISO 13061-2) [21]. The dimensions of the boards prior to the treatment were 35 mm thick × 70 mm wide × 400 mm in length, with their length to be in a direction parallel to the grain, while they consisted mainly from the part of sapwood, and the sampling method was based on the methodology of ISO 3129 [22].

2.1. Thermal Treatments

The treatment of the boards was carried out in a laboratory drying chamber (800 mm × 500 mm × 600 mm). The treatments were carried out at 180 °C and 200 °C under atmospheric pressure in the presence of air. The moisture content of the boards was 11.44% and 10.5% for black pine and poplar wood, respectively, when placed in the chamber, which was preheated to the final temperature. In each treatment, 10 identical non-sanded boards were placed into the chamber in specific places of equal space from the walls of the chamber and from one another, in order to ensure the uninterrupted movement of the air between the boards. The treatment durations of 3, 5 and 7 h (shorter than those

durations industrially used) were applied, counting 15 min more for the recovery of the temperature in the chamber.

The specific durations were selected as they differentiate from the existing literature of thermal treatment processes, providing new data. After thermal treatment, the boards were placed into large desiccators to return gradually to ambient conditions, and stacked in an air-conditioned room at constant conditions (60% ± 5%, 20 ± 2 °C). The mass loss (ML) of the specimens induced by the process of thermal treatment (thermodegradation) was determined according to the following Equation (1):

$$ML = [(M_0 - M_1)/M_1] \times 100 \quad (1)$$

where:

ML: Mass loss (%)
M_0: Initial oven-dry mass of the specimen before thermal treatment (g)
M_1: Oven-dry mass of the same specimen after thermal treatment (g)

The surfaces of the prepared samples were sanded using 80 and 220 grit sandpaper. Only defect-free material and only sapwood blocks (30 mm × 20 mm × 8 mm) of wood were selected to be used in decay tests, which were prepared from all the mass of each of the prepared treated and untreated boards of the species. The present study investigates only the biological durability of the modified materials against basidiomycetes and mold, but since it constitutes a part of an experimental work, other critical properties of the materials, such as their physical (EMC, density, color etc.), hygroscopic (tangential and radial swelling, adsorption) and mechanical properties (static bending strength, modulus of elasticity, impact bending strength, hardness, compression strength, surface roughness, etc.) have already been investigated [23–26].

2.2. Chemical Treatment

Some of the thermally-modified black pine wood specimens in dimensions of 30 mm × 20 mm × 5 mm and in variant EMC and density levels, according to the conditions of thermal treatment they had been exposed to (Table 1), were subjected to an additional chemical surface treatment with the hydrophobic agent of organosilanes, in order to form a thin layer of the solution in the surface of wood, that could potentially improve even more the biological durability, except for other properties associated to its hygroscopic nature.

Table 1. Mean values of equilibrium moisture content (EMC) and density of unmodified and thermally-modified pine and poplar wood after four weeks of conditioning.

Treatment	EMC (%)		Density (g/cm^3)	
	Pine	Poplar	Pine	Poplar
Control	11.448 (0.172) [1]	10.506 (0.521)	0.662 (0.015)	0.385 (0.002)
180 °C—3 h	9.075 (0.622)	8.535 (0.377)	0.657 (0.022)	0.381 (0.006)
180 °C—5 h	8.875 (0.598)	7.972 (0.500)	0.653 (0.026)	0.356 (0.007)
180 °C—7 h	8.441 (0.963)	7.520 (0.871)	0.645 (0.021)	0.346 (0.007)
200 °C—3 h	8.026 (0.347)	6.181 (0.654)	0.600 (0.021)	0.336 (0.005)
200 °C—5 h	7.531 (0.826)	5.691 (0.246)	0.590 (0.037)	0.333 (0.002)
200 °C—7 h	7.049 (0.412)	5.337 (0.402)	0.528 (0.021)	0.291 (0.005)

[1] Standard deviation values inside the parentheses.

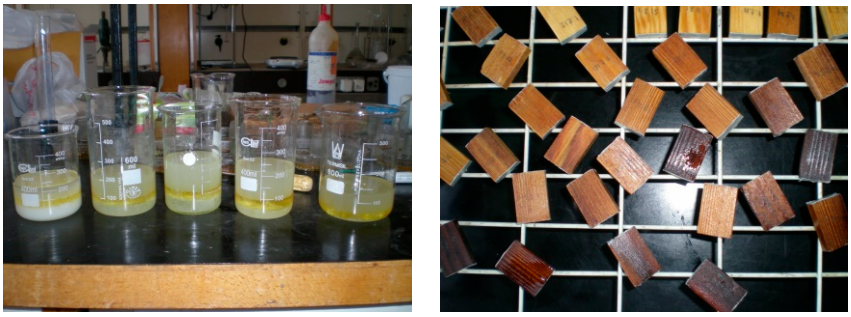
Concerning the EMC values of the thermally-treated wood, statistically significant differences were recorded between the EMC value of untreated wood and the respective values of all the different

categories of thermally-treated wood, which applied to both of the wood species, revealing the impact of heat upon the hygroscopicity of wood. Referring to treated black pine wood, statistically significant differences were not recorded, except for the following cases: the EMC value of the mildest treatment (180 °C) differed significantly from the respective values of the specimens treated at 200 °C, regardless of the duration. The EMC values of the specimens treated at 180 °C—5 h, 180 °C—7 h and 200 °C—3 h were found to differ significantly only from the most intensive treatment (200 °C—7 h).

Referring to treated poplar wood, only the following cases appeared to have statistically significant differences: The EMC value of the mildest treatment (180 °C) differed significantly from the respective values of the different categories of specimens treated at 200 °C, as well as the EMC values of the specimens treated at 180 °C—5 h. The value of specimens treated at 180 °C—7 h differed significantly from the respective values of the two most intensive treatments (200 °C—5 h and 200 °C—7 h).

Concerning the density values of the materials, the following statistically significant differences were recorded. Referring to the species of pine wood, the density value of the untreated wood, as well as the treatments of 180 °C, were found to differ significantly from all the respective values of the specimens treated at 200 °C, regardless of the duration. The value of the specimens treated at the most intensive treatment (200 °C—7 h) was found to differ significantly from all the other categories of thermally-treated wood, as well as the untreated wood. Referring to the species of poplar wood, statistically significant differences were recorded between the density value of untreated wood and the respective values of all the different categories of thermally-treated specimens. The density value of specimens treated at the mildest treatment (180 °C—3 h) differed significantly from all the values of the poplar specimens. The density value of specimens treated at 180 °C—5 h differed significantly also from the respective values of all the poplar specimens treated at 200 °C, and the density value of specimens treated at 180 °C—7 h differs significantly also from the values of the specimens subjected to the two most intensive treatments (200 °C—5 h and 200 °C—7 h). The value of the specimens treated at the most intensive treatment (200 °C—7 h) was found to differ significantly from all the other categories of thermally-treated wood, as well as the untreated wood.

Prior to the surface modification, the end-grains of the pine samples were sealed with a single-component polyurethane adhesive in order to prevent penetration of the agents along the grain [27], a process which was commonly followed in the preparation of all the specimens (thermally-treated, thermally-chemically-treated), in order to provide comparable results. Three different organosilanes solutions were used, in which silanes were included as the active substance (XIAMETER OFS-6020 SILANE, San Francisco, California, USA) and Alkyd resin (FTALAK S-6575; Plastbud Sp.z.o.o., Pustków, Poland) of 75% solids content, based on different ratios, while distilled water or benzin were used as a solvent. Specifically, in the three prepared solutions, silanes content corresponded to 5%, resin to 22% and the remaining 73% was the solvent in three different ratios of benzin to distilled water, 50:50 (T-C 1), 70:30 (T-C 2) and 100:0 (T-C 3), respectively. Benzin could not be considered as an environmentally friendly substance, but it was chosen because of its low cost, high availability, satisfying performance and examined the different ratios with water for comparative reasons. A stirring machine was used to homogenize the ingredients (YellowLine DI25 basic; IKA Werke GmbH & Co, Staufen im Breisgau, Germany). Each pine specimen was weighted, immersed in solution of 100 mL for 120 sec. and then left to be drained, weighed again, and finally left to be dried for at least one week in a conditioned room (20 ± 2 °C, 60 ± 5% relative humidity), before the decay tests (Figure 1). For each thermally-treated material category, 16–18 specimens were chemically-treated per each of the three different solutions (T-C 1, T-C 2, T-C 3). For each category of T-C material, approximately 10 specimens were used for the determination of EMC and density, while the rest of the 6–8 specimens were used for each of the decay tests. The weight percent gain (WPG) of the modified pine wood specimens was found to range between 8–15%, with the solutions of T-C 3 to present the highest values of WPG. The EMC and density values of all the different categories of chemically-treated pine specimens were examined.



(**a**) (**b**)

Figure 1. (**a**) Organosilanes formulations, (**b**) wood specimens left to drain after surface modification

2.3. Mycological Tests

2.3.1. Basidiomycetes

The methodology of the basidiomycetes decay tests was based on the EN 113 standard processes [28]. According to the mycological test process, 50mL of 'medium' (2000 mL water, 40 g agar, 100 g malt) was placed in each Kollev flask, which were closed and placed in the autoclave for sterilization at 121 °C for 60 min.

During the inoculation process, small, round samples were taken from precultures grown on malt agar in Petri dishes, where there were previously prepared freshly grown monoculture fungi colonies, and they were placed in the center of each Kolle flask. The flasks were placed in the incubation room (25 °C and relative humidity of 70%). After about two weeks, that the fungal mycelia appeared to cover the entire surface of the flasks, the wood specimens were aseptically added inside.

Wood samples had been previously dried (103 °C for 24 h), placed into glass desiccators for 30 min, and weighed accurately to record their initial dry weight. Subsequently, they were sterilized in the autoclave (121 °C, 60 min), before being inserted in the flasks. For each category of wood, at least six Kolle flasks were used, as well as a correction value flask. This flask contained only 50 mL of medium and 2 mL of phenol (as a protective substance against fungi action) without colony fungus, as well as two specimens of each modified specimens category. This is so that the potential weight loss of the specimens, (due to their coexistence with the medium), could be subtracted from the final mass loss results, so that corrected data calculated from the dry mass before and after the test, would be provided [29].

Therefore, eight specimens were used for each category of modified wood, and 36 control specimens for each type of wood (poplar or pine) and for each fungus species tested. Pine wood specimens were exposed to the brown-rot fungi *Coniophora puteana* (Schumach) P. Karst and *Oligoporus placenta* (Fr.) Gilb. & Ryvarden, while poplar specimens to *Trametes versicolor* (white rot) and *Oligoporus placenta* (Fr.) Gilb. & Ryvarden. *C. puteana* was chosen since it strongly decays softwood species, especially pine wood, *T. versicolor* decays hardwood species such as poplar to a large extent, while *O. placenta* is a major threat to several species, especially softwoods. Regarding the decay tests of thermally- and chemically-treated pine wood with organosilanes, the specimens were tested against the action of *C. puteana*.

After the addition of the wooden specimens inside the flasks, they were placed again in the incubation room where they remained exposed to fungal activity for a 4-month period.

Subsequently, the specimens were removed from the flasks, their surface was cleaned from the adhering mycelium and weighed to the nearest thousandth of a gram to calculate their moisture content. Oven-drying of all the specimens followed (103 °C for 24 h) and reweighting, to calculate the

dry weight at the end of the decay test. The mass loss due to fungal attack was determined based on the dry weight before and after the decay test by the following equation 2:

$$ML = \left(\frac{W - W_1}{W}\right) \times 100 \quad (2)$$

where W: the dry weight of the specimens before the decay test, W_1: the dry weight of the specimens after the decay test.

2.3.2. Microfungi

The medium used to cultivate microfungi was prepared using water, agar, malt and salt in a specific ratio (1000 mL water, 20 g agar, 30 g malt, 4 g mixture of salt (CZAPEK DOX: $NaNO_3$ 2 g, KH_2PO_4 0.7 g, K_2HPO_4 0.3 g, KCl 0.5 g, $MgSOi_7H_2O$ 0.5 g) and was introduced into the autoclave for sterilization, with all the wood specimens and necessary tools. 50 mL of medium was placed into each of the plastic containers (110 mm × 110 mm) used for the test. The microfungi inoculation chamber had already been sterilized with alcohol and UV radiation. Five specimens were used per each modified wood category, and one modified specimen was placed in each container together with one control specimen.

The dimensions of wood specimens were: 8 mm in thickness × 20 mm in width × 30 mm in length. A spore suspension was prepared by mixing three common cultures of wood-attacking microfungi, *Aspergillus niger* var. niger, *Trichoderma viride* Pers. ex Fries and *Penicillium cyclopium* Westling. Microfungi were inoculated through spreading the spores onto the agar medium surface of the containers, as well as the specimens. After the inoculation, all the containers were placed into an incubator for 21 days at 28 ± 2 °C with relative humidity of 75% ± 5%. The evaluation of wood treatment efficacy was performed after 7, 14 and 21 days by means of visual monitoring of fungal growth on the wood surface in accordance with the scale set out in Table 2, according to ASTM D 5590-17 [30].

Table 2. Rating system for fungal growth [30].

Index Rating System	
0z	no growth of fungi on the specimen, inhibition zone on the medium
0	no growth of fungi on the specimen
1	less than 10% of the specimen area covered by fungi
2	less than 30% of the specimen area covered by fungi
3	less than 60% of the specimen area covered by fungi
4	specimen totally overgrown by fungi

2.4. Statistical Analysis

SPSS Statistics PASW 18 statistical package was used for statistical analysis and processing of the results. The Least Significant Difference two way Analysis of Variance (LSD-Two-way ANOVA) method was also used in the thermal treatment results, which examines the effect of two different independent variables (temperature and duration), but also the effect of any interaction between these two factors upon the dependent variable of the biological durability of wood.

3. Results and Discussion

According to the results, thermal treatment of black pine wood under the abovementioned conditions induced mass losses in the range of 10.63–15.25% of which a 11.44% refers to moisture content lost, whereas thermally-treated poplar wood recorded mass losses of 11.24–18.88%, of which 10.50% corresponds to moisture, generated by the thermo-degradation during the process (Table 3). The wood of black pine contains a significant amount of resin, and the mass loss could be partly

attributed also to the evaporation of the resin during the thermal treatment, as well as other volatile compounds and unstable components.

Table 3. Mean mass loss values of black pine and poplar wood specimens due to the heat treatment thermodegradation process.

Species	Mass Loss (%)					
	180 °C—3 h	180 °C—5 h	180 °C—7 h	200 °C—3 h	200 °C—5 h	200 °C—7 h
Pine	10.629 (0.270) [1]	11.262 (0.507)	11.444 (0.572)	12.854 (1.035)	13.984 (1.172)	15.248 (1.516)
Poplar	11.237 (2.512)	11.601 (0.645)	11.935 (0.975)	13.461 (2.192)	16.409 (1.974)	18.884 (2.642)

[1] Standard deviation values in parentheses.

3.1. Basidiomycetes

3.1.1. Thermal Treated Black Pine

The results of the biological resistance tests revealed that the thermal treatment improved, in every case, the biological resistance of the black pine wood specimens against the decay action of *Coniophora puteana* and *Oligoporus placenta* (Figure 2), and this improvement seems to be analogous of the treatment intensity.

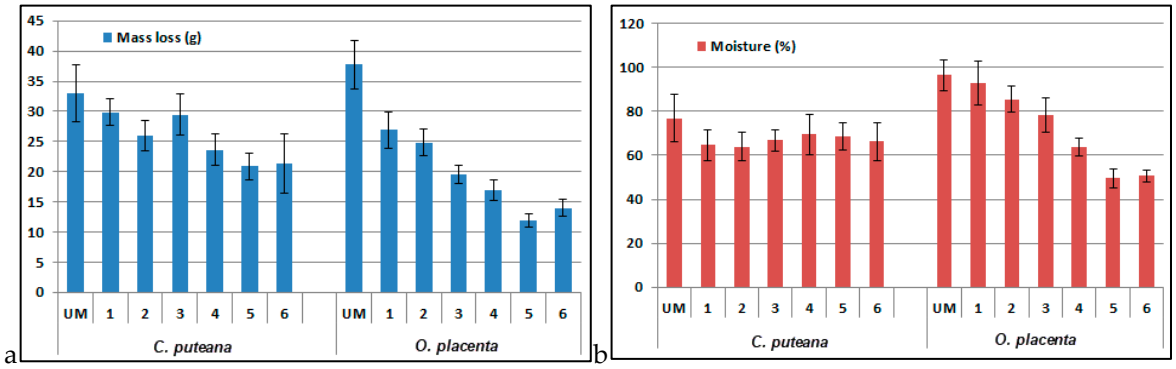


Figure 2. Mean mass loss (**a**) and moisture content rates (**b**) recorded by unmodified (UM) and heat-modified (1: 180 °C—3 h, 2: 180 °C—5 h, 3: 180 °C—7 h, 4: 200 °C—3 h, 5: 200 °C—5 h, 6: 200 °C—7 h) black pine specimens after their exposure to *C. puteana* and *O. placenta.*

Specifically, referring to *C. puteana* test results, the treatments of 200 °C appeared to reduce even more the mass loss rates caused by fungal action and deterioration, compared to treatments of 180 °C. Regardless of the treatment temperature, the treatment duration of 5 h resulted, in each case, in higher resistance of specimens to fungal action, compared to treatment duration of 3 or 7 h. This may indicate that a 3-h duration is not enough to achieve the greatest possible improvement in durability, while the 7-h duration exceeds the point of maximum improvement, and the wood may have suffered enormous mass loss and probably both the critical wood component de-polymerization due to thermal treatment and the density decrease leave, once again, the wood quite vulnerable to fungal biodegradation. The treatments of 180 °C and durations of 3, 5 and 7 h reduced the mean mass loss percentage, compared to unmodified wood, by 9.65%, 21.53% and 10.77%, while the treatments of 200 °C (3, 5 and 7 h) reduced the loss by 28.39%, 36.73% and 35.37%, respectively.

The statistical analysis revealed that the mass loss percentage values of unmodified wood, due to *C. putena* action, statistically differed significantly only from the respective values of the 200 °C treatments. The mass loss of specimens treated at the mildest treatment (180 °C—3 h) as well as the treatment 180 °C—7 h of also differed significantly only from the values of the three 200 °C treatments.

The mass loss of specimens treated at the treatment of 180 °C—5 h differed significantly only from the value of the specimens treated at 200 °C—5 h.

Statistical analysis of Two Way ANOVA showed that the effect of treatment temperature was found statistically significant and influenced its variability by 96.6%, while the treatment duration also presented a statistically significant effect on the mass loss, affecting its variability by 83.5%. The interaction between temperature and duration was significant as well, and affected the mass loss variability by 53.6%. The largest effect of temperature was observed in the 7—h treatments, which corresponded to statistically significant differences.

The moisture content of the thermally-modified pine specimens after the mycological test was found to be, in each case, lower than the respective value of the control specimens. In general, the higher the moisture content value of the specimen found after the mycological test, the more intense the decay by the fungus seems to be, and therefore, the mass loss rate is usually analogous to the moisture content rate of the decayed specimen.

However, treatments of 200 °C showed high moisture content in the specimens after the biological resistance test, which could be translated as an extensive presence of *C. puteana*, but which does not correspond to the continuity of its intense destructive action, since *C. puteana* prefers, as a brown-rot fungus, to degrade holocellulose, e.g., [10], and a significant part of the essential nutrients for this fungi (hemicelluloses, extracts) have been degraded and evaporated, and some by-products thereof have been re-polymerized in new structures not recognizable by the fungal enzymes. This improvement of the thermally-modified wood resistance against fungi action could be possibly attributed to the increased hydrophobicity it acquires after treatment (lower moisture content, EMC), the decomposition of hemicelluloses and amorphous areas of cellulose, which constitute nutrients for fungi especially in the early stages of rot, as well as the production of biocidal extractives during the treatment, which could act as fungicides, e.g., [31,32]. Furthermore, in thermally-modified wood, the enzymes involved in fungal degradation have difficulties to identify the modified polymeric components of wood, and to penetrate in the cell walls due to the decrease in porosity [1].

The results of treated black pine wood resistance against the action of *O. placenta* also seem to be encouraging, since all treatments have greatly improved the bio-resistance of wood, and as shown, this improvement is in line with the intensity of the treatment. As the temperature and duration of treatment increase, lower mean mass loss percentages are being recorded. The only exception is the most intensive treatment (200 °C—7 h), which recorded a slightly higher mass loss compared to the previous treatment of the immediately lighter intensity (200 °C—5 h), possibly attributed to the high mass loss and loss of chemical components carried out during the thermal treatment, critical for the resistance of wood. Specifically, treatments of 180 °C and durations of 3, 5 and 7 h reduced the mass loss compared to the unmodified wood by 28.75%, 34.18% and 48.09% respectively, while the treatments of 200 °C (3, 5 and 7 h) reduced the loss by 55.11%, 68.46% and 62.9%, respectively.

The mean mass loss value recorded by the unmodified pine wood statistically differed significantly from all the respective treated wood categories, revealing the resistance improvement of the materials, which is found higher than that of the same wood species against the fungus *C. puteana*. The mass loss of specimens treated at the mildest treatment (180 °C—3 h) presented similar values to the value of the specimens of next treatment (180 °C—5 h) and both were found to differ significantly from the respective values of all the other treatments. The mass loss of specimens treated at 180 °C—7 h presented similar values to the specimens of the treatment 200 °C—3 h and both were found to differ significantly from the respective values of all the other treatments. Finally, the value of the specimens treated at 200 °C—5 h presented the lowest mass loss value, which differed significantly from the values of all the other categories.

Two-Way ANOVA showed that the effect of temperature on mass loss rate was statistically significant, and influenced its variability by 86.6%, whereas the duration factor did that by 61.4%. The interaction between temperature and duration was also statistically significant, affecting the loss

variability by 44.1%. The greatest effect of temperature was observed in 5 h treatments, recording a statistically significant difference.

Finally, the moisture content of the specimens after the mycological test decreased in each case compared to control sample, and its trend was found similar to that of the mass loss. Referring to pine wood, one of the phenolic components arising during thermal treatment (vanillin) may hinder and slow the growth of fungi by inhibiting the production of their enzymes, and it could also be partially responsible for the antifungal activity of pine against *O. placenta* [2]. According to the results of the current research, both fungi species *C. puteana* and *O. placenta* have been proven to be very active and aggressive to black pine wood, with *O. placenta* to cause extended decay to unmodified wood, but the lowest decay in thermally-treated samples.

Mazela et al. [10], who examined the resistance of thermally-treated (160 °C–220 °C, 6 h–24 h) Scots pine, recorded also higher mass losses caused by *C. puteana* (39.4%) and *O. placenta* (45.8%) action, with the thermal treatment of the highest intensity to result in the highest levels of biological resistance recorded.

Tremblay [33] presented an improvement of the biological resistance of *Pinus banksiana* wood after thermal treatment, while Chaouch et al. [34], who subjected Scots pine wood to thermal treatment, did not record differences in resistance levels between modified and unmodified wood to *O. placenta* action. Kortelainen and Viitanen [35] recorded resistance improvement of thermally-modified Scots pine and Norway spruce wood (especially of heartwood) only in the most intense treatment (230 °C) used.

3.1.2. Thermally-Chemically-Treated Black Pine

According to the results (Table 4), all the categories of the specimens that had been subjected to thermal in combination with surface treatment with silanes solutions recorded significantly lower EMC values compared to the control, as well as compared to all the respective values of specimens that had been only thermally treated. This suggests that silanes treatment could limit even more the hygroscopicity of wood, compared to thermal treatment under specific conditions, probably because silane molecules are capable of filling the large pores of wood cell cavities and reacting with the hydroxyl groups. Therefore, the long chains of the silane manage to hinder the degree of moisture uptake [36], improving the dimensional stability and surface hydrophobicity of silane-modified wood. Additionally, by increasing the participation of benzin in the organosilane solutions against the participation of water as a solvent, the EMC seems to be even lower, which could be possibly attributed to better performance and the slightly higher absorption of the silane solution in the mass of wood during the surface modification. This perspective could be supported also by the fact that the density values of pine wood were found almost in all cases higher in the solutions with higher participation of benzin as a solvent (T-C 3).

Table 4. Mean values of equilibrium moisture content (EMC) and density levels of unmodified and thermally-chemically (T-C) modified black pine after two weeks of conditioning.

Thermally and Chemically (T-C) Treatments	EMC (%)			Density (g/cm^3)		
	T-C 1	T-C 2	T-C 3	T-C 1	T-C 2	T-C 3
Control	11.45 (0.172) [1]	11.45 (0.172)	11.45 (0.172)	0.662 (0.015)	0.662 (0.015)	0.662 (0.015)
180 °C-3 h	7.194 (0.622)	7.007 (0.541)	7.082 (0.672)	0.665 (0.142)	0.664 (0.115)	0.666 (0.070)
180 °C-5 h	6.433 (0.598)	6.390 (0.738)	6.256 (0.650)	0.667 (0.086)	0.668 (0.042)	0.665 (0.053)
180 °C-7 h	6.003 (0.963)	6.120 (0.570)	6.045 (0.783)	0.656 (0.021)	0.660 (0.120)	0.662 (0.080)
200 °C-3 h	5.724 (0.347)	5.604 (0.732)	5.340 (0.413)	0.624 (0.076)	0.641 (0.063)	0.658 (0.035)
200 °C-5 h	5.231 (0.826)	5.015 (0.280)	4.694 (0.520)	0.601 (0.037)	0.623 (0.048)	0.642 (0.058)
200 °C-7 h	4.845 (0.412)	4.630 (0.687)	4.320 (0.580)	0.557 (0.021)	0.575 (0.084)	0.587 (0.043)

[1] Standard deviation values inside the parentheses.

According to the statistical analysis, statistically significant differences were recorded between the EMC value of untreated wood and the respective values of all the different categories of thermally-chemically-treated wood, which applied to all the different categories of thermally-chemically-treated wood (T-C 1, T-C 2, T-C 3), revealing the great impact of the combination of heat and organosilanes on the hygroscopic nature of wood. Referring to the treated black pine wood, in the cases of T-C 1- and T-C 3-treated specimens, the EMC value of the specimens of the mildest thermal treatment (180 °C—3 h) differed significantly from the respective values of all the categories of specimens thermally-treated at 200 °C, the value of the specimens treated at 180 °C—5 h differed significantly from the respective values of the most intensively thermally-treated specimens at 200 °C—5 h and 200 °C—7 h. There was also recorded a statistically significant difference between the EMC values of the specimens treated at 200 °C—3 h and 200 °C—7 h. In the case of T-C 2-treated specimens, the EMC value of the specimens of the mildest thermal treatment (180 °C—3 h) differed significantly from the respective values of all the categories of specimens thermally-treated at 200 °C, while the value of the specimens treated at 180 °C—5 h differed significantly from the respective values of the most intensively thermally-treated specimens at 200 °C—5 h and 200 °C—7 h.

Generally, the density of thermally-chemically-treated pine wood was found slightly higher in most cases compared to the respective values of specimens treated just thermally. Referring to the statistical analysis of the density values of black pine wood specimens after their thermal and organosilanes treatment, in the case of T-C 1, the value of untreated wood was found to differ significantly only from the respective value of specimens treated at the two most intensive treatments (200 °C—5 h and 200 °C—7 h), and another statistically significant difference was recorded between the value of specimens treated at 180 °C—5 h and the most intensive one (200 °C—7 h). In the case of T-C 2, statistically significant differences were not recorded between the density values, since the values of standard deviation (SD) were found to be higher than the respective values of thermally-treated material. This could be possibly attributed to the fact that the density of these thermally-chemically-treated specimens are strongly influenced, not only by the thermodegradation process during the thermal treatment that decreases the density, but also by the penetration and absorption percentage of the organosilanes solution in the mass of wood. In the case of T-C 3, the only statistically significant difference was recorded between the density value of the untreated wood and the respective value of the specimens subjected to the most intense treatment (200 °C—7 h).

According to the decay tests results (Figure 3), the combination of thermal treatment with silanes solutions treatment improved significantly the biological durability of wood, recording mass losses, caused by the action of fungi, much lower than those of the unmodified wood, as well as lower than the respective mass loss values of thermally-treated wood specimens categories. This improvement of biological resistance of black pine specimens seems to be also in this case of treatments combination analogous of the thermal treatment intensity.

The presence of benzin in silane solutions used in this research work seems to increase the protective effect of the surface modification process on the biological durability of wood. This improved action of silanes solutions in the case of higher benzin participation can be attributed to the hypothesis that benzin contributes to a higher dispersion/mixing of the solution or to a deeper penetration of the solution in wood mass and reaction with its chemical components, and as a result, improved protection by the action of fungi. Specifically, the treatment of T-C 1 resulted in 45.68–79.74% lower mass losses compared to unmodified pine wood, while the treatments of T-C 2 and T-C 3 caused 54.76–83% and 70.21–87.83% lower mass losses, respectively against the action of *C. puteana*.

The statistical analysis of the mass loss values of thermally- and chemically-treated black pine wood revealed that in each case of T-C treatment there were statistically significant differences between the mass loss values of untreated wood and the respective values of all the thermally-chemically-treated wood categories, revealing the positive impact of the methods combination on the biological durability of wood. In the case of T-C 1, the mean mass loss value of the mildest thermal treatment (180 °C—3 h) was found to differ significantly from all the other categories of treated wood, except for the one of 180

°C—5 h. The value of the specimens treated at 180 °C—5 h differed significantly from all the respective values recorded by the specimens of the more intensive thermal treatments. The value of the specimens treated at 180 °C—7 h differed significantly from the respective values of all the other categories of treated or untreated wood.

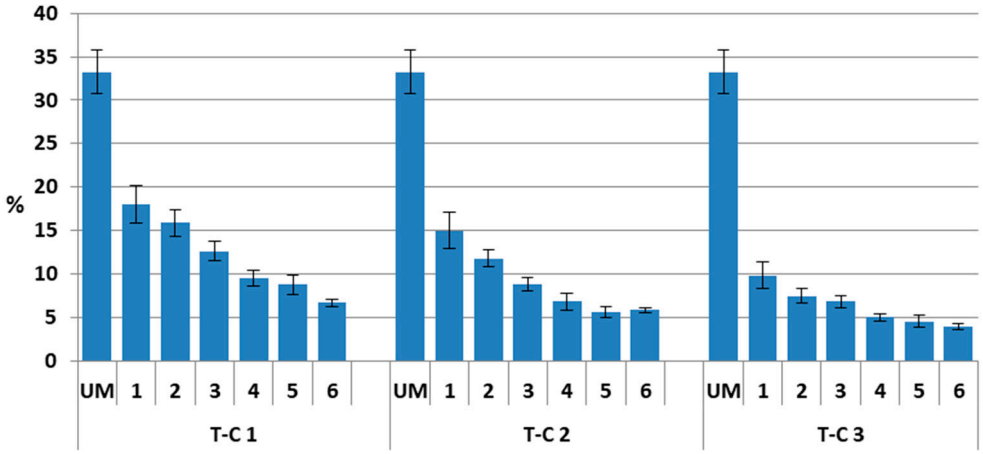


Figure 3. Mean mass loss rates recorded by unmodified (UM) and heat-modified (1: 180 °C—3 h, 2: 180 °C—5 h, 3: 180 °C—7 h, 4: 200 °C—3 h, 5: 200 °C—5 h, 6: 200 °C—7 h) black pine specimens that have been subjected also to chemical modification with organosilanes (T-C 1, T-C 2, T-C 3), after their exposure to *C. puteana*.

Statistically significant differences were presented between the value of the specimens treated at 200 °C—3 h and the respective values of all the other categories of treated or untreated wood, except for the specimens of the treatment 200 °C—5 h. The value of the most intensively treated (200 °C—7 h) specimens differed significantly from all the rest of the categories of specimens. In the case of T-C 2, all the mean mass loss values of different specimens categories differed significantly from one another, except for the three treatments of 200 °C that presented insignificant differences between one another. In the case of T-C 3, the mean mass loss value of the mildest thermal treatment (180 °C—3 h) was found to differ significantly from all the other categories of treated wood. The value of the specimens treated at 180 °C—5 h differs significantly from all the respective values recorded by the specimens of all the treatments, except for the one of 180 °C—7 h. Additionally, the mass loss values recorded by the three specimens categories of 200 °C were revealed to be similar to one another, but differed significantly from all the respective values of the other specimens categories.

3.1.3. Thermally-Treated Poplar

According to the mycological test results of poplar wood against the action of *T. versicolor* and *O. placenta* (Figure 4), the percentage of mean mass loss was found to be, in each case, much lower in the heat-modified poplar specimens than the unmodified wood, which demonstrates an improvement of the biological resistance in thermally-modified wood. Alhough, *T. versicolor*, as well as *O. placenta*, has been proven to be quite active and aggressive against untreated poplar wood species, causing high mass losses.

Referring to the test of *T. versicolor*, the treatments of 200 °C seem to reduce mass loss to a greater extent compared to those of 180 °C. Referring to treatments of 180 °C, the 3 h-duration resulted in a great improvement of resistance, while durations over 3 h (5 or 7 h) contributed to a slight increase in mass loss. This not statistically significant increase may indicate that duration over 3 h at 180 °C contributes to the formation of some components or the loss of some others, which leave the wood vulnerable again to the attack of the specific fungus. Specifically, the treatments of 180 °C and duration of 3, 5 and 7 h reduced the mass loss compared to the control by 34.63%, 30.84% and 26.36%, respectively, while the treatments of 200 °C (3, 5 and 7 h) reduced the loss by 41.02%, 37.29% and 36.11%, respectively.

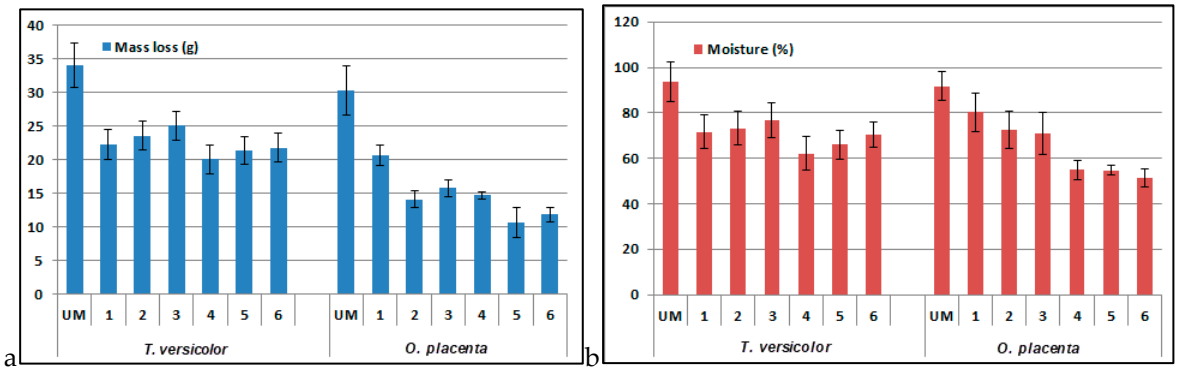


Figure 4. Mean mass loss rates (**a**) and moisture content (**b**) recorded by unmodified (UM) and heat-modified (1: 180 °C—3 h, 2: 180 °C—5 h, 3: 180 °C—7 h, 4: 200 °C—3 h, 5: 200 °C—5 h, 6: 200 °C—7 h) poplar specimens after their exposure to *T. versicolor* and *O. placenta.*

The statistical analysis revealed that the mean mass loss value of unmodified wood statistically differed significantly from the respective values of all the other treatment categories. Between the mass loss values of the thermally-treated poplar of different categories, statistically significant differences were not recorded, except for the case of the specimens treated at 180 °C—7 h that differed significantly from the respective value of the specimens treated at 200 °C—3 h.

The Two-Way ANOVA reported that the effect of temperature appeared to be statistically significant, affecting the variability of resistance by 62.1%, and the duration by 42%. The interaction between temperature–duration was also found statistically significant, affecting the resistance variability by 30%. The greatest effect of temperature was observed in 7-h treatments (statistically significant).

Similarly to the case of pine wood, the moisture content of the modified poplar specimens, after their mycological test process, was found to be in each case lower than the control sample level, presenting a course analogous to that of the mass loss rate.

In the case of testing the resistance of poplar against the *O. placenta* fungus, the results are even more encouraging, since all treatments have increased the bio-resistance of wood. The treatments of 200 °C seem to reduce mass loss to a greater extent, compared to those of 180 °C. Irrespectively of the treatment temperature, the duration of 5 h has caused a greater reduction in the mass loss rate, hence a greater resistance to attack, compared to treatment of 3 or 7 h, indicating probably that the treatment duration of 7 h exceeds the point of maximum improvement and the wood has undergone quite intense mass losses during the treatment, which once again leave it vulnerable to fungal activity. Specifically, the treatments of 180 °C and durations of 3, 5 and 7 h reduced the mass loss percentage compared to unmodified wood by 31.98%, 53.41% and 47.94%, respectively, while the treatments of 200 °C (3, 5 and 7 h), reduced the loss by 51.46%, 64.72% and 60.9%, respectively. Finally, after the mycological test the moisture content of the specimens decreased in each case compared to that of our control, and demonstrated a similar course to that of the mass loss rate. The research results are in line with the claim of Boonstra et al. [2], that the hemicellulose reduction due to treatment favors more the biological resistance of modified wood decayed by brown rot, compared to the white rot. Boonstra et al. [2] have reported that the action of *O. placenta* and *T. versicolor* continues to cause high mass losses in thermally-treated wood, until thermal degradation during treatment becomes so intense to ensure the branching of lignin, whereas the fungus *C. puteana* was inhibited by thermal modification, causing lower mass loss rates. Mazela et al. [37] recorded also an improvement in resistance of thermally-treated poplar wood to all the fungi species tested, with the aggressive fungus *O. placenta* to mark a mass loss of 18.5%.

The mean mass loss rate of the control specimens was found to statistically differ significantly from all the treated wood categories, revealing the improvement of the biological resistance against this fungus species. The mass loss of specimens treated at the mildest treatment (180 °C—3 h) differed significantly from the respective values of all the other treatments. Additionally, among the rest of the

mass loss values of the thermally-treated poplar, statistically significant differences were not recorded, except for the case of the respective values of the specimens of the most intensive treatments (200 °C—5 h and 200 °C—7 h).

Two Way ANOVA revealed that the effect of temperature was statistically significant, influencing the variability of the resistance by 75.8%. An equally important factor was the treatment duration, affecting its variability by 76%, while the interaction between temperature against duration was weak. The most remarkable effect of temperature was observed in the treatment duration of 3 h.

3.2. Microfungi

3.2.1. Thermally-Treated Black Pine and Poplar

Results of the microfungi growth test on the surface of thermally-modified and -unmodified specimens (Figure 5) revealed that thermal modification does not effectively protect pine and poplar wood from microfungi growth, since the samples were found totally overgrown in the measurement of the seventh day, probably attributed to the free sugars coming from the hemicellulose decomposition during thermal treatment [2]. Nevertheless, the treatments recorded a delay of small extent in the attack and growth of microfungi on the wood surface. The surface of the unmodified specimens, from the first visual assessment implemented in the fourth day, was almost entirely covered by mold, while the thermally-modified samples were covered to a lower extent (Figure 6). This retardation tendency of the microfungi development is evident in both of the wood species tested.

As the intensity of treatment (temperature and duration) increases, the degree of mold growth (coverage) in poplar and pine specimens is found to decrease, compared to the unmodified wood, only until the fourth day. In this resistance improvement course, which is analogous to treatment intensity course, exceptions include the two more intensive treatments (200 °C—5 and 7 h) in both wood species, the specimens of which presented a small increase of surface coverage by mold, compared to the lighter treatments; nevertheless, these percentages do not approach the respective values of unmodified wood.

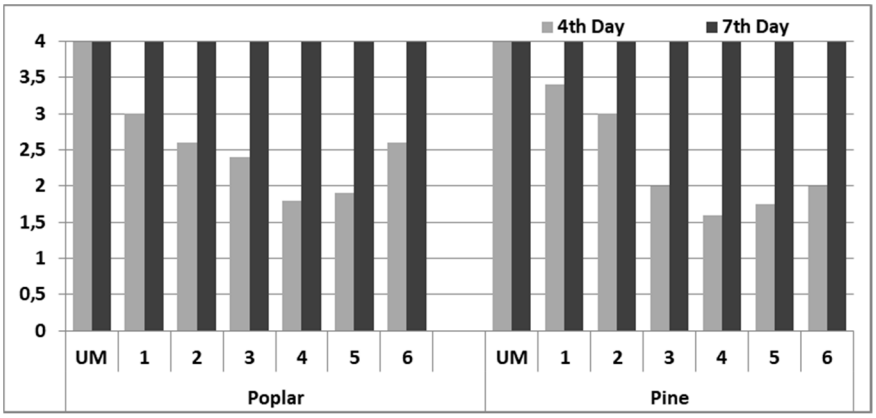


Figure 5. Microfungi growth degree evaluation according to the fungal growth rating system (Table 2) on the surface of unmodified (UM) and thermally-modified (1: 180 °C—3 h, 2: 180 °C—5 h, 3: 180 °C—7 h, 4: 200 °C—3 h, 5: 200 °C—5 h, 6: 200 °C—7 h) poplar and black pine wood.

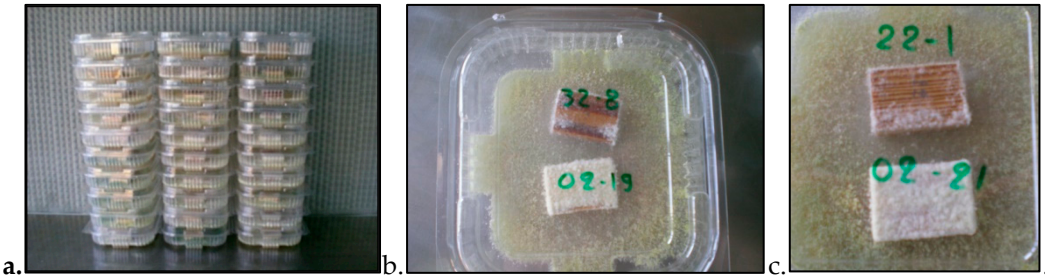


Figure 6. (a) Plastic containers, **(b)** mold growth on the surface of a thermally-modified pine sample at 180 °C-7 h (on the top) and the control specimen (on the bottom) recorded in the 4th day of exposure, **(c)** the respective mold growth on the surface of a thermally-modified pine sample at 180 °C–5 h (top) and the control specimen (bottom) (4th day of exposure)

3.2.2. Thermally-Chemically-Treated Black Pine

The combination of thermal treatment and surface modification process seems to increase in great extent the resistance of black pine wood against the action of microfungi (Figure 7). The unmodified wood was found fully covered with mold from the first visual assessment in the fourth day of exposure, while the thermally-chemically-modified pine wood was in a very small extent covered only in the last measurements in the 14th and 21st days of exposure. As the intensity of thermal treatment increases, the growth of mold is lower, except for the most intensive treatment, which reveals the protective effect of thermal treatment on wood. The results of these treatments combination could be considered as an evidence of an adequately protective technique against the action of microfungi.

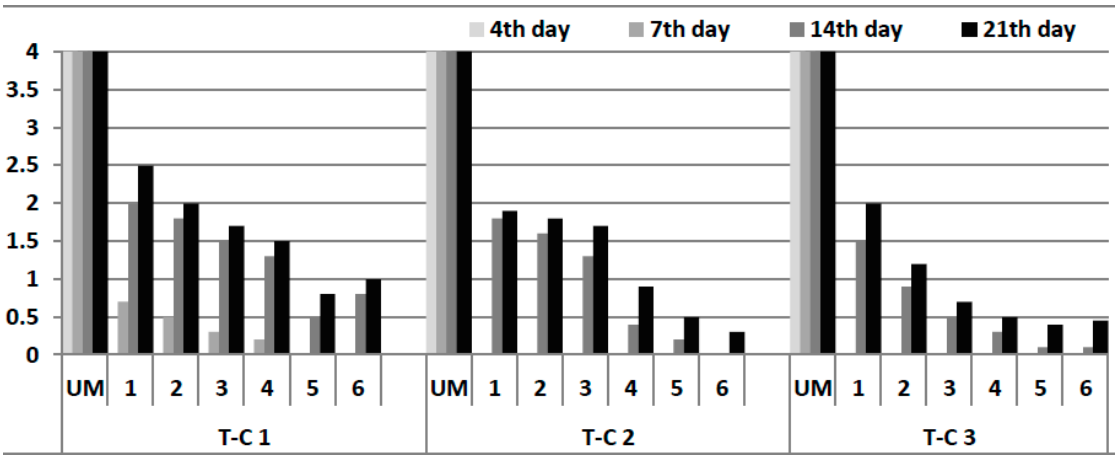


Figure 7. Microfungi growth degree evaluation according to fungal growth rating system (Table 2) on the surface of unmodified (UM) and thermally (1: 180 °C—3 h, 2: 180 °C—5 h, 3: 180 °C—7 h, 4: 200 °C—3 h, 5: 200 °C—5 h, 6: 200 °C—7 h) and silanes modified black pine wood.

4. Conclusions

According to the findings, short-term thermal treatments (even in the presence of air, performed in simple drying laboratory equipment) could enhance the biological resistance of wood, and therefore expand its service life.

Thermally-treated black pine wood presented 9.65–36.73% lower mass loss caused by *C. puteana* compared to the unmodified wood. As the intensity of thermal treatment increases, black pine presents a higher resistance against the *O. placenta* fungus and the mass loss of treated wood was found 28.75–68.46% less than that of the unmodified wood. Both fungi species, *C. puteana* and *O. placenta*, have been proven to be very active and aggressive to black pine wood, with *O. placenta* to cause

extended decay to unmodified wood, but the lowest decay action in thermally-treated samples of this research.

Thermally-treated poplar displayed a significant decrease in mass losses (26.36–41.02%) caused by the action of *T. versicolor* compared to control. All thermal treatments improved the biological resistance of poplar wood against the fungus of *O. placenta*, presenting a mass loss reduction of 31.98–64.72%, compared to our control. The treatment duration of 5 h (middle intensity) revealed the highest biological resistance values for almost all fungi and both wood species tested, which suggests that the 3-h duration was not adequate to achieve the desirable chemical reactions in wood mass, necessary to improve durability at the highest possible level, while the 7-h treatment duration seemed to be long enough to induce great weight losses (poplar: 18.88%, black pine: 15.25%), leaving wood once again susceptible to the catastrophic action of basidiomycetes.

The variability of biological resistance improvement referring to thermal treatments was found to be highly influenced by the factor of treatment temperature, to a lower extent by the treatment duration, and even less by the interaction between the temperature-duration factors.

The combination of thermal treatment with silanes components treatment improved significantly the biological durability of black pine wood, recording mass losses, caused by the action of fungi, much lower than those of the unmodified wood, as well as lower than the respective mass loss values of thermally-treated wood specimens, with this biological resistance improvement to be analogous to the thermal treatment intensity. T-C 1, T-C 2 and T-C 3 resulted in 45.68–79.74%, 54.76–83% and 70.21–87.83% lower mass losses, respectively, compared to unmodified wood against the action of *C. puteana*. The presence of benzin in silane solutions increased the protective effect of the surface modification process and the biological durability of wood, probably attributed to the fact that benzin contributed to a higher dispersion of the solution or a deeper penetration of the solution in wood mass (WPG approximately 15%).

Thermal modification did not manage to effectively protect pine and poplar wood from microfungi growth, but it only contributed to a retardation of the attack and growth process, confirming the tendency and results of previous studies, examining the durability of other thermally-treated species. On the contrary, the combination of thermal treatment and surface modification process increased in great extent the resistance of black pine wood against the action of microfungi, and can be considered as an adequately protective technique against the mold action.

Generally, the biological strength of thermally-treated pine and poplar wood against basidiomycetes was found to be enhanced to a small extent, and they should not be exposed directly above ground without the application of additional protective techniques, whereas the treatment with silane components enhanced significantly the resistance against basidiomycetes and mold action, and could be suitable for numeral interior, under shelter or even exterior applications. Additional research should be carried out on this direction of thermal and silanes treatment methods combination, in order to achieve even more enhanced durability by optimizing the treatments conditions and process through the simultaneous testing of the physical, chemical and mechanical properties of the studied wood species.

Funding: This research received no external funding.

Acknowledgments: The author warmly thanks the team of Institute of Chemical Wood Technology (Faculty of Wood Technology) in Poznan University of Life Sciences, for the provision of decay tests equipment.

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

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