Tree Species-based Differences *vs.* Decay Performance and Mechanical Properties Following Chemical and Thermal Treatments

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Many thermal and chemical treatments are known to inhibit wood decay despite the wood grade processed, but their impact, *e.g.*, chemicals' leaching and decay resistance, may not be similar. The aim of this study was to test whether some model treatments retain their performance in different wood species. Additionally, the effects of thermal modification and linseed oil-based varnish treatments as means to mitigate water-soluble chemicals leaching were assessed. The mass loss caused by *Trametes versicolor* was measured after a 12-week exposure to analyze whether the different treatment approaches prevented the fungal decay after a standard leaching test. The mechanical properties before and after exposure were tested independently to determine whether the mechanical properties of different wood species were affected by the tested treatments and wood decay. The responses of the tested wood species were found to vary by treatments, but thermal and chemical fixation methods for water-soluble tannins were beneficial in all cases considering the mass loss and the degradation of modulus of rupture and modulus of elasticity of treated wood. Varnish was overall the most effective treatment against decay, but the results emphasize the need for testing potential preservation methods and chemicals on several species.

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INTRODUCTION

The construction sector is continuously expanding its material portfolio of sustainable material resources, and the carbon storage of engineered or massive wood materials is one of the venues of rapid expansion. In Europe, hardwoods are mainly used for furniture and design elements and to some degree for cladding, decking, and paneling, while they are less common than softwoods in outdoor applications or structural load-bearing materials. The cost, availably, and quality of wood are considered essential, often not in this order, and there is a growing interest in many abundant yet not actively refined tree species in Europe, such as eucalypt, aspen, birch, oak, and walnut.

One of the challenges of wood buildings is that natural materials are vulnerable to decay. This natural process is caused by different biotic and abiotic factors, but fungi are considered the principal cause (Broda 2018). To slow down this natural decay process,

wood is treated with chemical preservatives or other wood modifiers (Sandberg *et al.* 2017). The type and amount of preservative required depends on the wood species properties, such as density and porosity, and the intended end-use of the wood (Ding *et al.* 2009). Several preservation methods also have negative effects on the environment, such as the chromated copper arsenate (Liu *et al.* 2018) and on humans, such as creosotes (Hiemstra *et al.* 2007), which are still used due to the lack of effective substitutes on the market (Humar 2017). Bio-based antifungals such as mistletoe (Yildiz *et al.* 2020), monoterpenes (Zhang *et al.* 2016), propolis extracts (Woźniak *et al.* 2020), coconut shell pyrolytic oil distillate (Shiny *et al.* 2017), and wood pyrolysis distillates (Barbero-López *et al.* 2019) are known to be effective as wood-decaying fungi inhibitors, although their toxicity can also be as high, even higher than of the traditional preservatives (Barbero-Lopez *et al.* 2021).

The main drawback of bio-based wood preservatives is the high solubility of antifungals in water, which makes them leach out from wood as the wood is wetted, as happens with caffeine (Kwaśniewska-Sip *et al.* 2019). Tannins, as one alternative, have been considered a potential wood preservative for many years (Laks and McKaig 1988; Anttila *et al.* 2013), although they are scarcely used due to their high leachability from wood. As an example, Barbero-Lopez *et al.* (2021) found in an *in vitro* decay test that unleached tannin-treated wood specimens performed very well when exposed to decay fungi, but the performance of leached tannin-treated specimens was even worse than that of the control specimens. Some studies have also focused on fixing tannins to wood with success, further promoting their use (Thevenon *et al.* 2009; Tondi *et al.* 2012, 2015). Nevertheless, these methods are not applied on a commercial scale, which shows that new, alternative methods are still needed. Finding methods to fix natural preservatives to wood would provide the wood industry the possibility of substituting the present synthetic preservatives with natural ones.

Many investigations have aimed to fix antifungal natural extractives in wood, with successful results. Kwaśniewska-Sip *et al.* (2019) fixed caffeine in wood with a thermal modification after impregnating the caffeine in wood, resulting in a caffeine-leaching reduction from the wood specimens. Oil treatments are effective for fixing some industrial wood preservatives impregnated in wood, such as copper azoles (Can and Sivrikaya 2017). However, these methods have not yet been tested for fixing tannins to wood, although their leaching is one of the main reasons for not using them as wood preservatives.

The suitability of different grades of wood and the performance of different modification and preservation strategies have mostly been reported using only European beech and Scots pine wood, as required in standard decay test EN113 (CEN 1997), so it remains unclear whether the results can be generalized across the plethora of possible timber grades. The aim of this study is to test how tannins should be fixed into different wood species using two different methods: thermal modification and linseed oil-based varnish treatment. More importantly, the previously successful method was evaluated alone and in combinations to treat different hardwood species, namely the silver birch, European aspen, and European blue-gum eucalyptus.

EXPERIMENTAL

Wood Specimens and Their Treatments

Silver birch (*Betula pendula* Roth), European aspen (*Populus tremula* L.), and European blue-gum eucalyptus (*Eucalyptus globulus* Labill.) were used in this experiment. European Beech (*Fagus sylvatica* L.) and Scots pine (*Pinus sylvestris* L.) were included as controls in the experiment, as indicated in the EN113 (CEN 2021) and several published studies. The specimen dimensions were 40 × 10 × 5 mm^3. The longitudinal faces were parallel to the grain direction.

The treatments applied were tannin impregnation, linseed oil-based varnish treatment, thermal modification, tannin impregnation with subsequent linseed oil-based varnish treatment, and tannin impregnation with subsequent thermal modification. Untreated specimens of each wood species were used as controls. The number of replicates per treatment for each species was between 31 and 37.

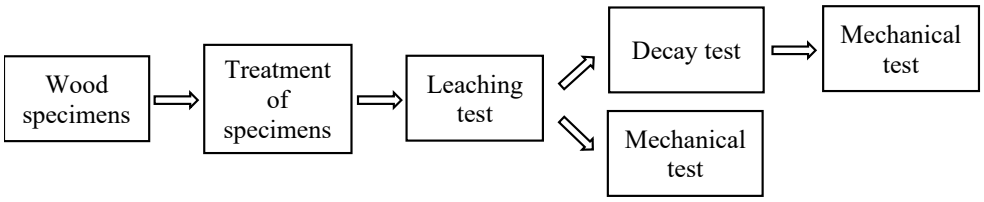

Fig. 1. Flowchart of the methodology used in this experiment

Table 1. Summary of Wood Treatment Combinations

Treatment no.	1st step	2nd step
1	Tannin	-
2	Thermal	-
3	Varnish	-
4	Tannin	Thermal
5	Tannin	Varnish

Tannin Impregnation

For treatments 1, 4, and 5, the specimens were treated with the commercial tannin-rich bark extract Colatan GT10 (Haarla Ltd, Tampere, Finland), obtained from *Schinopsis lorentzii*, at a 5% concentration (w/w as Milli-Q water solution). The treatment was accomplished following a modified Bethell process in which the last vacuum of this process was not applied.

Colatan GT10 was impregnated into the wood specimens using a full cell process with vacuum 0.15 bar for 20 min at 20 °C to remove the air inside the cell wall. Afterward, the vacuum was reduced to atmospheric pressure, and the pressure was then increased to 10 bar at 20 °C for 60 min. After impregnation, the excess solution from the surface of the specimens was wiped away. The tannin retention was calculated by measuring the mass gain after oven drying the specimens at 50 °C and comparing it to their respective mass before impregnation and drying at the same temperature.

Thermal Treatment

One-third of the wood specimens previously treated with tannin (treatment 4) were exposed to later thermal modification together with specimens not previously treated as references for thermally treated wood (treatment 2). To avoid contamination, the

experiment was carried out in different stages, treating the specimens separately (w/wo tannins).

The thermal treatment was accomplished with a PARR pressure reactor, where the temperature was increased from 20 to 200 °C in a nitrogen atmosphere using a 5 °C/min gradient. For pine references, the target temperature was 220 °C. Once the target conditions were met, the specimens were exposed to two bars of pressure at 200 °C for five minutes.

Linseed Oil-based Varnish Treatment

This treatment was carried out to test the effects of linseed oil-based varnish (Suomen Luonnonmaalit Ltd) and tannin with subsequent linseed oil-based varnish treatment on wood performance. The specimens treated were either non-treated wood (treatment 3) or wood previously treated with Colatan GT10 tannin extract (treatment 5). Linseed oil-based varnish was heated until it reached 130 °C before being poured into a vessel with the wood specimens and left there for 1 h at 130 °C. To avoid contamination, the experiment was executed separately: specimens with tannins and specimens without tannins.

Leaching Test

All specimens were exposed to a leaching test that was performed following European standard EN 84 (CEN 1997). The specimens were submerged in 5:1 (v/v) of Milli-Q water for 14 days, and the water was changed nine times during the process. First changes took place after 24 and 48 h and then an additional seven times within 12 days in intervals between 24 and 72 h. Finally, the specimens were oven-dried at 50 °C until they reached a constant mass. The dry mass loss of the wood specimens due to leaching was then measured and compared to their dry mass in the previous steps.

Decay Test

The decay test was performed in a petri dish (Ø 90 mm, 15 mm height) following a modified version of the standard mini-block procedure modified by Lu *et al.* (2016). To prepare the growth media, 4% malt powder, and 2% agar were mixed in MilliQ water. The media was then autoclaved (120 °C, 15 min), and 25 mL of culture medium was poured into each petri dish under sterile conditions.

The white-rot fungus used for this test was *Trametes versicolor* (strain BAM 116), which was purchased from the Federal Institute for Materials Research and Testing (BAM, Berlin, Germany). Several cultures of this fungus were grown in a petri dish at 22 ± 2 °C and 65 ± 5%. Cultures less than four weeks old and still growing in the medium without contamination were selected for the experiment. The inoculation was performed in sterile conditions, with a fungal plug of about Ø 5.5 mm being placed in the center of the recently prepared petri dish, sealed with parafilm, and left growing in a growth chamber at 22 ± 2 °C and 65 ± 5% of relative humidity (RH**).**

The wood specimens 40 × 10 × 5 mm^3 were exposed to the fungi as soon as the mycelium covered the entire surface of the culture medium (Ø 90 mm). The wood specimens were placed over a plastic mesh inside the petri dish to avoid direct contact of the wood with the growth media. Once the specimens were introduced into the petri dish, the petri dish was kept in a growth chamber (22 ± 2 °C, 65 ± 5% RH, and no light) for 12 weeks. After the 12 weeks, the mycelium covering the wood specimens was removed with a brush and the wood specimens were dried (50 °C) until they reached constant mass.

To determine the mass loss (%), the dry specimens (50 °C) were weighed before and after decay exposure. Subsequently, Eq. 1 was applied.

$$Mass\ loss\ (\%) = (M_0 - M_1) / M_0 \quad (1)$$

where M_0 (g) is the mass before decay exposure and M_1 (g) the is mass after decay exposure.

Mechanical Test

Flexural properties were determined using the three-point bending test with a Zwick Roell Static Materials Testing Machine in which the modulus of elasticity (*MOE*) and the modulus of rupture (*MOR*) were calculated. The specimens were conditioned at a 20 ± 2 °C temperature and 65 ± 5% RH until they reached a constant mass. The equations used for calculating the *MOE* and *MOR* were as follows,

$$MOR\ (\text{MPa}) = 3PL / 2bd^2 \quad (2)$$

$$MOE\ (\text{GPa}) = d\sigma\ / d\varepsilon \quad (3)$$

where P is the maximum load (N), L is the distance between supports for the beam (mm), b is the sample width (mm), and d is the sample thickness (mm). In Eq.3, $d\sigma$ is the stress and $d\varepsilon$ is the strain.

The *MOE* loss and *MOR* loss in (GPa) and (MPa), respectively, were calculated as shown in Eqs. 4 and 5.

$$MOE\ \text{loss (GPa)} = (\mu_x - \mu_y) \pm (\sigma_x^2 + \sigma_x^2)^{1/2} \quad (4)$$

$$MOR\ \text{loss (MPa)} = (\mu_x - \mu_y) \pm (\sigma_x^2 + \sigma_x^2)^{1/2} \quad (5)$$

where μ_x is the mean before decay test, μ_y is the mean after decay test, σ_x is the standard error of the mean before decay test and σ_y is the standard error of the mean after decay test. The MOE and MOR loss due to decay were also calculated in %-values between sets of samples from same boards and randomized prior trial, half being only treated and the other half subjected to decay after treatment.

Statistical Analysis

The statistical analysis was performed with R statistical software. For each of the evaluated properties, the mean and standard error were calculated. Later, an analysis of variance (ANOVA) was performed. Tukey's range test was used as post-hoc for ANOVA to compare different treatments within the same species.

RESULTS AND DISCUSSION

Treatment Effects on Wood Specimen and Chemical Retention

The tannin impregnation was successful for all wood species (Table 2). The dry mass increment (%) of tannin-treated specimens was between 2% and 3% for *E. globulus* and *P. tremula*, while it reached a retention of over 5% in *B. pendula* and *P. sylvestris*. The thermal treatment caused the expected decrease of mass in Scots pine and less significant changes in the treated hardwood species. The effect was substantially smaller in pine when the thermal treatment followed tannin impregnation, and this subsequent thermal treatment even caused a slight mass decrease in *P. tremula* and *P. sylvestris*. Specimens treated with varnish, whether with or without tannins, increased their initial mass significantly:

Eucalyptus globulus increased its mass between 10% and 15%, *P. tremula* by approximately 20%, *B. pendula* by approximately 60%, and *Pinus sylvestris* between 39% and 44%.

After the leaching test, all treatments decreased their mass except the varnish treatment of *P. sylvestris* and *P. tremula*, which had a slight increase of 0.6%. Tannin-treated wood decreased its mass between 2.6% and 5%, depending on the species. Thermally treated specimens had a mass loss of 0.7% and 2.4%, while tannin-treated wood with subsequent thermal treatment decreased between 1.1% and 2.8%. The varnish treatment decreased its mass between 1.4% and 1.6% in *B. pendula* and *E. globulus.* Finally, tannin-treated wood with subsequent varnish treatment reached a dry mass reduction between 2% and 6.2%.

Table 2. Tannin and Linseed Oil-based Varnish Retention (%) of All Species by Treatment

Species	Treatment no.	1st Step*	2nd Step*	Retention after 1st Step** (%)	Retention after 2nd Step** (%)	Mass loss due to leaching test** (%)
Eucalyptus globulus	0	Control	-	-	-	0.6 ± 0.3
	1	Tannin	-	2.4 ± 0.1	-	3.3 ± 0.1
	2	Thermal	-	-3.4 ± 0.3	-	0.8 ± 0.1
	3	Varnish	-	10.9 ± 0.8	-	1.6 ± 0.2
	4	Tannin	Thermal	2.7 ± 0.2	0.3 ± 0.5	1.7 ± 0.2
	5	Tannin	Varnish	2.5 ± 0.1	14.1 ± 0.7	5.1 ± 0.5
Populus tremula	0	Control	-	-	-	0.8 ± 0.1
	1	Tannin	-	2.3 ± 0.3	-	2.6 ± 0.2
	2	Thermal	-	1.2 ± 2.8	-	2.4 ± 0.5
	3	Varnish	-	20.5 ± 3.6	-	-0.6 ± 0.1
	4	Tannin	Thermal	2.4 ± 0.3	-4.2 ± 0.7	1.1 ± 0.8
	5	Tannin	Varnish	3.0 ± 0.4	23.2 ± 3.5	2.8 ± 0.7
Betula pendula	0	Control	-	-	-	1.0 ± 0.0
	1	Tannin	-	5.2 ± 0.1	-	5.0 ± 0.1
	2	Thermal	-	-1.1 ± 0.4	-	0.7 ± 0.1
	3	Varnish	-	59.2 ± 1.3	-	1.4 ± 1.2
	4	Tannin	Thermal	5.1 ± 0.1	2.1 ± 0.6	2.7 ± 0.3
	5	Tannin	Varnish	5.3 ± 0.1	38.5 ± 1.2	6.2 ± 0.4
Pinus sylvestris	0	Control	-	-	-	0.9 ± 0.0
	1	Tannin	-	5.0 ± 0.1	-	4.6 ± 0.1
	2	Thermal	-	-12.8 ± 0.9	-	1.3 ± 0.2
	3	Varnish	-	39.0 ± 2.0	-	-0.6 ± 0.0
	4	Tannin	Thermal	5.1 ± 0.1	-1.4 ± 0.8	2.8 ± 0.4
	5	Tannin	Varnish	5.2 ± 0.1	43.4 ± 1.9	2.0 ± 0.0
Fagus sylvatica	0	Control	-	-	-	0.3 ± 0.0

* 1st step and 2nd step retention was compared to the initial mass; ** mean ± std. error

The tannin retention after impregnation depended significantly on the wood species treated. *Betula pendula* and *P. sylvestris* had greater retention than *E. globulus* and *P. tremula*. Thermal treatment resulted in an expected mass decrease in all species and in both treatments 2 and 4, possibly due to the evaporation of extractives and hemicellulose degradation (Yang and Liu 2020), except for *P. tremula* in treatment 2 where the mass increased, but with high standard error (Table 2). Tannin with subsequent varnish treatment reached higher retention values than varnish treatment alone in all species except *B. pendula*. The reason for this different performance of *B. pendula* remains unclear, as many reasons may be behind it, such as the different structure of the wood and presence of extractives. Since the wood was not fully impregnated during the first step of treatment, higher concentrations of tannins could be used in future tests.

After the leaching test, the tannin-treated wood with subsequent varnish treatment had a higher mass loss than mere tannin treatment in all species except in *P. sylvestris*. However, tannin-treated wood with subsequent thermal modification had a lower mass loss than tannin treatment alone in all specimens. The reason for this result could be that the thermal treatment modifies the chemical structure of the wood (Candelier *et al.* 2016), thus reducing the tannin leaching. This is similar to the findings of Kwaśniewska-Sip *et al.* (2019), who found that caffeine leaching was reduced *via* thermal treatment.

The visual appearance of the specimens changed significantly in the course of the treatments (Fig. 2). In *P. tremula* and *P. sylvestris*, the tannin-treated specimens together with thermal modification underwent a drastic change in their visual appearance, while the linseed oil-based varnish treatment barely changed its color at all. In *B. pendula* and *E. globulus*, there was no important color change between treatments.

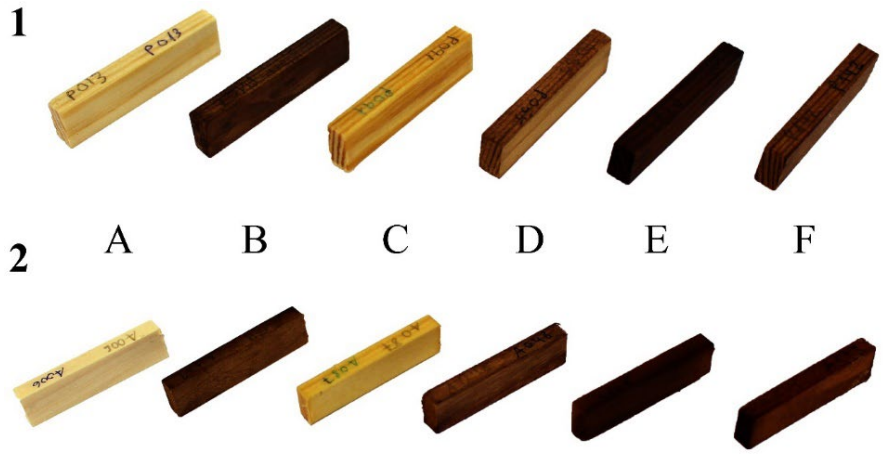

Fig. 2. Above (1) *Populus tremula* wood specimens and below (2) *Pinus sylvestris* wood specimens with different treatments. The treatments for both wood species were: control (A), tannin (B), varnish (C), thermal (D), tannin-thermal (E), and tannin-varnish (F).

Effect of Treatments on Mechanical Properties after Leaching and Decay

The specimens that were not exposed to decay fungi (Table 3) had a higher mean MOE and MOR than those exposed to the fungus. Without decay exposure, *E. globulus* had the highest MOR between 100 and 120 MPa, while control and tannin-treated specimens reached the highest values and thermal treatment the lowest. The MOE of *E. globulus* was between 4.25 and 5.50 GPa, while in *P. tremula* and *B. pendula,* it was between 3.10 to 3.50 GPa and 4.10 to 5.00 GPa, respectively. The MOR of *P. tremula* was

the lowest among the studied species, while tannin-treated *P. tremula* reached 76 MPa and tannin-treated wood with subsequent thermal modification reached a level of approximately 60 MPa. In *B. pendula*, the highest MOR was in tannin-treated wood with subsequent varnish treatment and in tannin-treated wood with subsequent thermal modification, both reaching 108 MPa, while the control specimens had an average MOR of 98 MPa. In *P. sylvestris*, tannin treatment, control, and tannin-treated wood with subsequent vanish treatment showed the highest MOR and MOE among the treatments, while thermal treatment had the lowest MOR of 59.2 MPa.

After 12-week decay exposure, Tukey's range test for post hoc analysis did not detect a significant difference in MOE between the different treatments in *E. globulus* (Table 3). In *P. tremula*, varnish and tannin-treated wood with subsequent varnish treatment had the highest values of MOE and MOR, while the controls indicated the lowest values of 1.9 GPa and 42.4 MPa. *Betula pendula* wood specimens had a lower MOE in control and tannin-treated specimens, which differed significantly from the rest of the treatments. Varnish-treated *B. pendula* reached MOE and MOR values of 5.2 GPa and 105.4 MPa, respectively, with only a small increase in MOE when comparing values before and after decay. The MOE and MOR of *P. sylvestris* varied between 3.5 to 5.1 GPa and 72.7 to 96.8 MPa, while tannin with subsequent varnish treatment reached the highest values.

The mechanical properties of the wood specimens were altered by the different treatments. With no treatments, *E. globulus* wood had the highest MOE and MOR; it was previously reported as a wood species with high mechanical properties (Majano-Majano *et al.* 2020). In addition, after the leaching test, the MOR and MOE were reduced, which agrees with the findings of previous researchers (Mauricio González *et al.* 2020).

In tannin-treated wood, there was no significant difference in MOE and MOR compared to the control even if phenolics, such as tannins, have been suggested to increase the mechanical properties of wood (Gunduz *et al.* 2011; Barbero-López *et al.* 2022). This difference between the present study and previous results might be due to the leaching of tannins during the leaching test. The MOE and MOR of varnish specimens varied depending on the species, but there was a tendency to increase the MOE, even if it was significant only in *B. pendula,* which agrees with previous research (Temiz *et al.* 2013), and to reduce the MOR (Jebrane *et al.* 2014) non-significantly in all but *B. pendula*. In the present study, without decay exposure thermal modification generated an increase in MOE in *E. globulus* and *B. pendula*, and a reduction in MOR in *E. globulus* and *P. sylvestris*, echoing the findings of Kocaefe *et al.* (2008) and Kacíková *et al.* (2013). The changes are likely due to the evaporation of extractives during the process and the degradation of hemicellulose (Yang and Liu 2020) as well as the crystallization of the of the cellulose and the cross linking of the lignin network, acting as a hardener for the microfibrils (Gunduz *et al.* 2009). Specimens with tannin and subsequent thermal modification followed the same tendency as the thermal specimens, except in the MOR of *Betula pendula*, which was significantly higher than the control, perhaps due to the fixation of tannins. Lastly, tannin with subsequent varnish treatment increased the MOE and MOR only in *B. pendula*; thus, in this wood, fixation worked better than in other species.

Table 3. MOE and MOR of Species by Treatment after Leaching Test, Without Decay Exposure, and After Decay Test

				Without decay exposure		After decay exposure	
Species	Treatment no.	1st Step	2nd Step	MOE (GPa)	MOR (MPa)	MOE (GPa)	MOR (MPa)
Eucalyptus globulus	0	Control	-	4.5 ± 0.2 [a]	123.8 ± 2.6 [b]	2.7 ± 0.3 [a]	74.3 ± 6.1 [a]
	1	Tannin	-	4.3 ± 0.2 [a]	122.3 ± 2.7 [b]	2.9 ± 0.2 [a]	74.9 ± 5.0 [a]
	2	Thermal	-	5.5 ± 0.2 [b]	99.3 ± 4.9 [a]	3.8 ± 0.3 [a]	72.7 ± 3.9 [a]
	3	Varnish	-	4.3 ± 0.2 [a]	116.2 ± 2.4 [b]	3.8 ± 0.3 [a]	88.6 ± 4.6 [b]
	4	Tannin	Thermal	4.6 ± 0.1 [a]	110.6 ± 4.4 [ab]	3.2 ± 0.2 [a]	72.7 ± 4.4 [a]
	5	Tannin	Varnish	4.4 ± 0.2 [a]	121.1 ± 2.2 [b]	3.5 ± 0.3 [a]	89.2 ± 5.0 [b]
Populus tremula	0	Control	-	3.1 ± 0.2 [a]	73.7 ± 2.9 [bc]	1.9 ± 0.1 [a]	42.4 ± 2.9 [a]
	1	Tannin	-	3.2 ± 0.2 [a]	76.0 ± 2.5 [c]	2.2 ± 0.1 [ab]	50.3 ± 2.5 [ab]
	2	Thermal	-	3.5 ± 0.2 [a]	68.0 ± 1.1 [ac]	2.2 ± 0.2 [ab]	45.0 ± 2.7 [ab]
	3	Varnish	-	3.2 ± 0.1 [a]	65.4 ± 1.4 [ab]	2.8 ± 0.2 [b]	55.4 ± 3.1 [b]
	4	Tannin	Thermal	3.3 ± 0.2 [a]	59.6 ± 3.2 [a]	2.4 ± 0.2 [ab]	46.1 ± 3.1 [ab]
	5	Tannin	Varnish	3.2 ± 0.1 [a]	69.3 ± 1.7 [ac]	2.5 ± 0.2 [ab]	55.5 ± 3.0 [b]
Betula pendula	0	Control	-	4.1 ± 0.1 [a]	98.5 ± 1.4 [a]	3.1 ± 0.2 [a]	68.8 ± 3.7 [a]
	1	Tannin	-	4.4 ± 0.1 [ab]	101.0 ± 2.0 [ab]	2.8 ± 0.2 [a]	59.7 ± 3.7 [a]
	2	Thermal	-	4.8 ± 0.1 [bc]	101.9 ± 1.2 [ab]	3.1 ± 0.3 [a]	65.7 ± 4.6 [a]
	3	Varnish	-	4.9 ± 0.1 [bc]	101.0 ± 2.5 [ab]	5.2 ± 0.1 [b]	105.4 ± 1.9 [b]
	4	Tannin	Thermal	4.9 ± 0.9 [bc]	108.4 ± 2.7 [b]	3.5 ± 0.2 [a]	71.7 ± 3.9 [a]
	5	Tannin	Varnish	5.0 ± 0.1 [c]	108.4 ± 1.9 [b]	3.4 ± 0.2 [a]	72.9 ± 3.8 [a]
Pinus sylvestris	0	Control	-	4.4 ± 0.2 [a]	89.3 ± 1.8 [c]	3.6 ± 0.2 [a]	72.7 ± 2.5 [a]
	1	Tannin	-	4.3 ± 0.2 [a]	89.7 ± 1.8 [c]	3.5 ± 0.2 [a]	74.9 ± 4.0 [a]
	2	Thermal	-	4.1 ± 0.2 [a]	59.2 ± 2.7 [a]	4.3 ± 0.3 [ab]	73.3 ± 4.8 [a]
	3	Varnish	-	4.0 ± 0.1 [a]	82.6 ± 1.7 [bc]	5.0 ± 0.2 [b]	93.4 ± 2.6 [b]
	4	Tannin	Thermal	4.1 ± 0.2 [a]	74.5 ± 2.6 [b]	4.6 ± 0.2 [b]	77.6 ± 1.9 [a]
	5	Tannin	Varnish	4.3 ± 0.2 [a]	89.2 ± 2.8 [c]	5.1 ± 0.2 [b]	96.8 ± 3.1 [b]
Fagus sylvatica	0	Control	-	6.2 ± 0.1	124.9 ± 1.8	4.2 ± 0.2	77.8 ± 3.6

Note: Values shown are means ± std. error. Different letters indicate significant differences by treatment within the species.

Effect of Treatments on Wood Mass Loss after Leaching and Decay

In *E. globulus* L. and *P. tremula* decay trials, no treatment caused a significant difference in mass loss (Table 4). However, varnish treatment in *B. pendula* retained its original mass far better, differing significantly from the other treatments. Between all species, the control specimens of *F. sylvatica* reached the highest mass loss. In *P. tremula* wood no treatment differed from control in their decay performance.

The MOE and MOR loss in *E. globulus* and *P. tremula* were similar; control specimens had the highest losses, and varnish treated samples retained their properties the most. In *B. pendula*, tannin-treated samples had the highest MOE and MOR loss, and varnish treatment again the lowest. In *P. sylvestris*, thermal, varnish and tannin with subsequent thermal modification performed the best against decay, with a mass loss only between 0% and 2%, differing significantly from the rest of the treatments for pine. The mass loss of the control specimens was approximately 10%, indicating a low susceptibility to the fungus tested.

Table 4. Decay Indicators: Mass Loss (%) (mean ± std. error), MOE Loss (%) (mean) and MOR Loss (%) (mean)

Species	Treatment no.	1st Step	2nd Step	Mass loss (%)	MOE loss (GPa)	MOR loss (MPa)	MOE loss (%)	MOR loss (%)
Eucalyptus globulus	0	Control	-	11.3 ± 1.2 [a]	1.8 ± 0.4	49.5 ± 6.6	39.1	40.0
	1	Tannin	-	12.5 ± 1.8 [a]	1.4 ± 0.3	47.4 ± 5.7	31.9	38.7
	2	Thermal	-	10.3 ± 1.8 [a]	1.7 ± 0.4	26.6 ± 6.3	31.3	26.8
	3	Varnish	-	7.6 ± 1.7 [a]	0.5 ± 0.4	27.6 ± 5.2	12.2	23.7
	4	Tannin	Thermal	13.5 ± 2.4 [a]	1.4 ± 0.2	37.9 ± 6.2	29.9	34.3
	5	Tannin	Varnish	11.3 ± 2.2 [a]	0.9 ± 0.4	31.9 ± 5.5	21.9	26.3
Populus tremula	0	Control	-	18.7 ± 1.8 [a]	1.2 ± 0.2	31.3 ± 4.1	39.8	42.4
	1	Tannin	-	13.4 ± 1.7 [a]	1.0 ± 0.2	25.7 ± 3.5	31.3	33.9
	2	Thermal	-	16.0 ± 2.1 [a]	1.3 ± 0.3	23 ± 2.9	37.1	33.9
	3	Varnish	-	11.5 ± 1.8 [a]	0.4 ± 0.2	10 ± 3.4	12.4	15.3
	4	Tannin	Thermal	11.7 ± 3.1 [a]	0.9 ± 0.3	13.5 ± 4.5	25.8	22.6
	5	Tannin	Varnish	10.1 ± 1.9 [a]	0.7 ± 0.2	13.8 ± 3.4	22.3	19.9
Betula pendula	0	Control	-	11.5 ± 2.1 [b]	1.0 ± 0.2	29.7 ± 4.0	24.6	30.2
	1	Tannin	-	17.5 ± 2.3 [b]	1.6 ± 0.2	41.3 ± 4.2	36.4	40.8
	2	Thermal	-	15.8 ± 2.4 [b]	1.7 ± 0.3	36.2 ± 4.8	35.4	35.5
	3	Varnish	-	2.0 ± 0.4 [a]	-0.3 ± 0.1	-4.4 ± 3.1	-5.4	-4.3
	4	Tannin	Thermal	12.0 ± 1.9 [b]	1.4 ± 0.9	36.7 ± 4.7	28.4	33.8
	5	Tannin	Varnish	12.6 ± 1.2 [b]	1.6 ± 0.2	35.5 ± 4.2	31.4	32.7
Pinus sylvestris	0	Control	-	9.4 ± 0.7 [c]	0.8 ± 0.3	16.6 ± 3.1	19.6	18.6
	1	Tannin	-	7.9 ± 1.0 [c]	0.8 ± 0.3	14.8 ± 4.4	18.3	16.5
	2	Thermal	-	-0.1 ± 0.2 [a]	-0.2 ± 0.4	-14.1 ± 5.5	-4.7	-23.8
	3	Varnish	-	2.0 ± 0.3 [a]	-1.0 ± 0.2	-10.8 ± 3.1	-24.5	-13.0
	4	Tannin	Thermal	0.7 ± 0.6 [a]	-0.5 ± 0.3	-3.1 ± 3.2	-10.4	-4.2
	5	Tannin	Varnish	4.8 ± 0.4 [b]	-0.8 ± 0.3	-7.6 ± 4.2	-18.9	-8.5
Fagus sylvatica	0	Control	-	19.8 ± 1.6	2.0 ± 0.2	47.1 ± 4.0	32.7	37.7

Note: Different letters indicate significant differences by treatment within the species. Each species was analyzed independently

Tannin treatment had a relatively high mass loss due to its leaching (Table 2) prior decay, as noted earlier by Tondi *et al.* (2013). The decay performance of all treated species changed due to different treatments. Tannins inhibit wood-decaying fungi (Anttila *et al.* 2013), but their effectiveness as wood preservatives is typically reduced very significantly due to leaching (Barbero-López *et al.* 2021). The tannin-treated specimens decayed even more than the control in *E. globulus* and *B. pendula*, although the differences were not significant. Similar results were found by Barbero-López *et al*. (2021), where the tannin-treated wood decayed more after a leaching test than the control specimens. This was attributed to the residual sugar content in the tannin mixes similar to those used here. In *P. tremula*, tannin-treated specimens decayed slightly less than the controls, but the performance of tannin-treated wood was not good enough against decay.

The varnish treatment was the one that performed best with the lowest values in mass loss, MOE loss, and MOR loss. These findings agree with previous studies that highlighted the effectiveness of linseed oil as a wood decay inhibitor (Humar and Lesar 2013). The thermal modification had higher mass loss values—even higher than the control in the case of *B. pendula*. Thermal modification worked the best in *E. globulus*, with the

second-lowest mass loss value of 10.3 ± 1.8% after varnish treatment. The result is in line with the previous study finding thermally modified eucalypt persistent against wood decay (Cantera *et al.* 2021). It has previously been reported that chemical changes happen during the thermal treatment, such as degradation of wood polymers in beech (Hakkou *et al.* 2006). Thermal modification can also reduce the moisture content in the cell walls (Chaouch *et al.* 2013; Thybring 2013). These changes could be responsible also of the leachability of water soluble tannins in wood.

The two tested fixation methods performed differently, but both had a lower mass loss than tannin-impregnated specimens, except in tannin with subsequent thermal modification in *E. globulus*, which had a higher mass loss than control. It is hypothesized that the higher mass loss in *E. globulus* could be related to its properties. Testing other thermal modification conditions (such as different temperatures) would be required to understand this behavior, as it is known that it also affects other properties, such as the wood durability (Hakkou *et al.* 2006). In the case of tannin with subsequent thermal modification, *P.* sylvestris and *B. pendula* performed better than tannin with subsequent varnish treatment (Altgen *et al.* 2020), whereas in *E. globulus* and *P. tremula*, it was *vice versa*. Tannin with subsequent varnish treatment in *P. tremula* had the lowest mass loss value of 10.1 ± 1.9%, which might be an indicator of tannin fixation by varnish.

Overall, the two-step impregnations tested in this experiment improved the decay resistance of some wood species, but not to the degree required by EN 113 (CEN 2021). In some wood species, tannin-treated wood with subsequent thermal or varnish treatment performed better against decay than wood specimens treated only with tannins. Even though the results did not reach the protection level required for most outdoor uses, this study demonstrates the potential use of combined thermal and varnish oil treatments as fixing agents for tannins by the wood industry. It has to be highlighted that linseed oil did not only act as a fixing agent, but it was the best treatment to prevent wood decay.

Different treatments can be effective in different wood species, but in most of the studied species, varnish treatment had a better result than thermal modification for tannin fixation. Varnish treatment performed the best relative to mass, MOE, and MOR losses. From prior studies, it is known that wood anatomy (De Ligne *et al.* 2021) and the presence of different extractives (Harju *et al.* 2003) affect the decay performance of wood. These factors could also be responsible for the varied performance of the wood species treated. As an example, the thermal treatment that performed very well against decay for *P. sylvestris* and has been developed for pine (Jämsä *et al.* 2000), did not improve the performance of the tested hardwood species. This highlights the need to test potential treatments for several different wood species to provide more reliable insight into their global performance.

CONCLUSIONS

1. The two-step impregnation processes tested in this study showed variable results depending on the wood species.
2. Both fixation methods after tannin impregnation, performed equal or better than only tannin treatment in mass loss, MOE loss, and MOR loss.
3. Leaching of tannins was reduced with subsequent thermal treatment in all wood species, but thermal treatment that performed very well for *P. sylvestris* was rather

ineffective protection against decay for the tested hardwood species.

4. The linseed oil-based varnish alone performed the best in wood against fungal decay out of the tested combinations.

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