

## Article

# Quebracho-Based Wood Preservatives: Effect of Concentration and Hardener on Timber Properties

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**Abstract:** Tannin polyphenols are produced by plants to protect themselves against natural decay. It is expected that impregnating low-durable timber with tannin extracts of more durable species such as quebracho (*Schinopsis balansae*) will enhance the durability of the specimens. This biomimetic approach combined with the in situ polymerization of quebracho–hexamine formulations can be a valid alternative to synthetic wood preservatives. In this work, we aim to evaluate the impregnation mechanism as well as the impact of tannin and hardener concentration on the mechanical and leaching resistance properties of treated wood. Compression resistance, surface hardness and leaching resistance of four different common non-durable wood species: spruce (*Picea abies*), pine (*Pinus* spp.), poplar (*Populus alba*) and beech (*Fagus sylvatica*) impregnated with different concentrations of extract and hexamine are presented. The results show that the mechanical properties of tannin-impregnated timber are enhanced, especially for timber with lower densities. Tannin and hardener concentrations tendentially do not contribute significantly to further increase MOE (modulus of elasticity), MOR (modulus of rupture) and Brinell hardness. Similar results are also obtained when the specimens are tested against leaching: tannin is significantly more water-resistant when cured with hexamine, but higher amounts of hardener do not further improve its water resistance. These findings suggest that quebracho tannin–hexamine formulations are already effective at low concentrations (5 to 10% extract with 2.5 to 5% hexamine).

**Keywords:** timber protection; treatment; eco-friendly; bio-based; flavonoid; wood anatomy



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## 1. Introduction

Although the major worry of these years is the pandemic situation, we are all aware that climate change is already happening and its consequences will be dramatic for the life on our planet [1,2]. After the Paris Agreement, the reduction of CO<sub>2</sub> emissions became a must for many countries, and a more sustainable use of the resources is yet required [3]. It is expected that bioresources will soon replace most of the fossil derivatives, and the wood production chain, which is already registering important growths, will further expand [4]. Timber is and will be a fundamental source of energy and materials, and its correct exploitation will be the key for the future of our species [5].

For these reasons, it will be important to sustainably extend the service life and the applicability of timber by increasing its durability and its mechanical performance. Succeeding in this purpose will involve a decrease in concrete and plastics in the building sector with a consequent reduction in carbon footprint [6].

The use of tannins for improving wood durability has been known for decades [7]. This approach is an example of biomimicry because tannins, which are naturally produced by superior plants to protect against biotic and abiotic decay, are infiltrated into the wood structure of low-durable timber species [8,9].

The use of tannin formulations for the protection of wood would be a real breakthrough in the industry of protective coatings and impregnation chemicals because the

market is at present still dominated by synthetic polymers such as polyacrylates and polyurethanes [10,11] and by heavy-metal solutions based on copper and chromium [12,13].

The first studies performed by applying tannin extracts as wood preservatives showed an interesting increase in durability against fungi, but their solubility hindered their use as preservatives for moist environments and outdoors [14,15]. In the 1970s it was discovered that condensed tannins undergo similar polymerization chemistry to phenolics [16,17]. In particular, it was observed that hexamine was able to establish stable networks in an alkaline environment when combined with mimosa extracts to produce bio-based adhesives [18,19]. The tannin–hexamine polymer produced is stable and highly water-resistant because it is characterized by nitrogen-containing bridges which connect flavonoid units through methylene anchorage [20].

Recently, tannin-based formulations were fixed in wood through in situ polymerization, producing timber samples with extended resistance against mechanical stress, leaching, fire and biologic attacks [21–24].

Despite the attractive properties achieved by mimosa tannin-treated timber, also by modifying the formulations, resistance against weathering is still the major drawback hindering the long-term exposure outdoors [25]. This is principally due to the rigid network produced by the mimosa extract, which breaks after several dimension changes in wood exposed to weathering [26].

The second-most abundant, commercially condensed tannin extract, due to its outstanding extraction yields [27], is quebracho (*Schinopsis balancae*). This dark-brown powder belongs chemically to the condensed tannin [28], and it presents high phenolic content [29] and also higher amounts of low-molecular-mass sugars than mimosa [30]; therefore, it is expected that they could facilitate the interaction with wood in their use as a preservative.

In this study we aimed to impregnate different low-durable wood species such as spruce (*Picea abies*), pine (*Pinus* spp.), poplar (*Populus alba*), and beech (*Fagus sylvatica*) with a commercial extract of quebracho tannin extract in order to understand the impregnation mechanisms and the retentions. Furthermore, the mechanical properties and the leaching resistances will be observed after the addition of different concentrations of tannin and hexamine (used as hardener).

## 2. Materials and Methods

### 2.1. Materials

Wood pieces of  $50 \times 15 \times 15$  mm<sup>3</sup> of 4 different wood species were obtained from local sawmills: Norway spruce (*Picea abies*), pine (*Pinus* spp.), white poplar (*Populus alba*) and European beech (*Fagus sylvatica*).

Fintan 373b commercial tannin of quebracho (*Schinopsis balancae*) was kindly provided by Silvateam (S.Michele Mondovì, Italy). The pH of a 40% water solution of the extract was 6.7. Sodium hydroxide and hexamine (hexamethylenetetramine) were purchased from AlfaAesar (ThermoFisher, Waltham, MA, USA).

### 2.2. Preparation of the Tannin-Based Formulations

Solutions of concentrations of 5%, 10%, 15% and 20% of quebracho extract were obtained by quickly adding deionized water to the quebracho extract and then adding NaOH (33%) until the pH was 8. Hexamine was added to the tannin formulations in different proportions by weight of tannin extracts, specifically 2.5%, 5.0%, 7.5% and 10%.

### 2.3. Wood Impregnation

Dry samples of different wood species were placed into a 2 L beaker, divided by plastic nets in order to avoid surface contact between samples. A load was put on top to avoid floating. The tannin solution was then added, and the whole system was transferred into a desiccator. Air was removed from the samples by applying a vacuum of 100 mBar in the desiccator for 30 min. Then, the system was slowly brought to atmospheric pressure again and the wood specimens were left dipping in the tannin solution for 24 h.

Finally, the impregnated specimens were recovered from the tannin bath and wiped with blotting paper.

The wet retention ( $R_{\text{wet}}$ ) of the samples was calculated according to the following formula:

$$R_{\text{wet}} [\text{g}] = W_{\text{wet}} [\text{g}] - W_0 [\text{g}] \quad (1)$$

where  $W_0$  and  $W_{\text{wet}}$  are the weight before and after impregnation, respectively.

Then, the impregnated wood samples were oven-dried at  $102 \pm 2$  °C for an additional 24 h. This heating stage allowed the tannin–hexamine formulation to in situ polymerize, enhancing the mechanical properties of the specimens.

The dry retention ( $R_{\text{dry}}$ ) was calculated according to the following formula:

$$R_{\text{dry}} [\text{g}] = W_{\text{dry}} [\text{g}] - W_0 [\text{g}] \quad (2)$$

where  $W_{\text{dry}}$  is the weight of the impregnated sample after drying.

Each test involved the repetition of 8 samples which were conditioned before characterization.

## 2.4. Microscopic Analysis

### 2.4.1. Sample Preparation

Spruce and beech microcuts were obtained with a Leica CM1950 cryostat working at around  $-30$  °C. Finally,  $5 \times 30$  mm<sup>2</sup> slices of 15–20 µm thickness were obtained with a rotary microtome.

### 2.4.2. Optical Apparatus

A mechanically focused upright microscope (Leica DM4B) was used for slice observation. The instrument mounted transmitted light LED illumination with BF, PH, DF, and POL transmitted light contrast methods and fully automated fluorescence axis. The microscope was coupled to a Leica DMC4500 5 megapixels Sony CCD-ICX282 digital camera. The sensor allowed  $2560 \times 1920/3.4$  µm  $\times$   $3.4$  µm resolution and  $8.7$  mm  $\times$   $6.5$  mm scanning area.

## 2.5. Mechanical Tests

The mechanical analyses were performed with a Galdabini Quasar 25 universal testing machine on  $50 \times 15 \times 15$  mm<sup>2</sup> stabilized samples. The appliance is composed of a rigid double-column system with a maximum capacity of 25 kN. The execution of the tests and the monitoring of the results were controlled using Labtest software (Galdabini, Cardano al Campo, Italy).

### 2.5.1. Compression Resistance Test

The stabilized samples were compressed along the grain according to the ISO13061-2 [31]. Compression rate of 2 mm/min and maximum load (MOR) and modulus of elasticity (MOE) in compression were registered. Every experiment was repeated for at least 8 specimens.

### 2.5.2. Brinell Surface Hardness

Surface hardness tests (HBS) were performed on both radial and tangential faces. This test was carried out according to EN 1534 [32]. For the spruce, pine and poplar (soft), the spherical indenter was used at a rate of 25 N/s up to a maximum load of 48 N, while for beech (hard), a rate of 120 N/s up to a maximum load of 980 N was applied. For both methods, the test time once the maximum load was reached was 30 s. Through the calculation of orthogonal diagonals derived from the spherical imprint, hardness values were calculated and expressed according to the Brinell scale. Every test was repeated at least 8 times.

### 2.6. Leaching Resistance

The leaching process was carried out by dipping 8 impregnated specimens in around 20 mL of deionized water per sample (24 samples in 500 mL), and applying 10 min of 100 mbar pressure, and then keeping them under water for 3 h. The leached samples were removed from the bath and exposed to 103 °C for 24 h. The final weight of the leached sample was registered ( $W_{\text{leach}}$ ), and the leaching resistance (L.R. %) was calculated according to the following formula:

$$\text{L.R. [\%]} = \left( 1 - \frac{W_{\text{dry}} [\text{g}] - W_{\text{leach}} [\text{g}]}{R_{\text{dry}} [\text{g}]} \right) \times 100 \quad (3)$$

### 2.7. Statistical Analysis

As the data are not normally distributed, a non-parametric test was chosen in order to compare the dependent variables. In particular, the Kruskal and post hoc Dunn tests were selected. The software used was RStudio Team (2021) [33].

## 3. Results

The influence of the tannin concentration for wood impregnation was initially assessed using spruce and beech as examples of coniferous and deciduous wood, respectively. An amount of 5% tannin weight of hexamine was used as a hardener (Section 3.1). The second part of the study was dedicated to understanding the effect of the amount of crosslinker on the mechanical properties of four wood species (Section 3.2).

### 3.1. Influence of Tannin Concentration on Impregnation

Wet and dry retention of the specimens impregnated with different concentrations of tannin are reported in Table 1. It can be observed that by raising the tannin concentration, the amount of solution which impregnates the sample decreases (wet retention), while the amount of tannin inserted in wood is higher (dry retention).

**Table 1.** Solution and tannin uptake for different concentrations of tannin–water solution for spruce (*Picea abies*) and beech (*Fagus sylvatica*).

Tannin (%)	Spruce		Beech	
	$R_{\text{wet}}$ (g)	$R_{\text{dry}}$ (g)	$R_{\text{wet}}$ (g)	$R_{\text{dry}}$ (g)
5	6.70	0.23	6.99	0.24
10	5.72	0.38	6.43	0.41
15	4.64	0.51	5.43	0.58
20	4.18	0.54	6.19	0.80

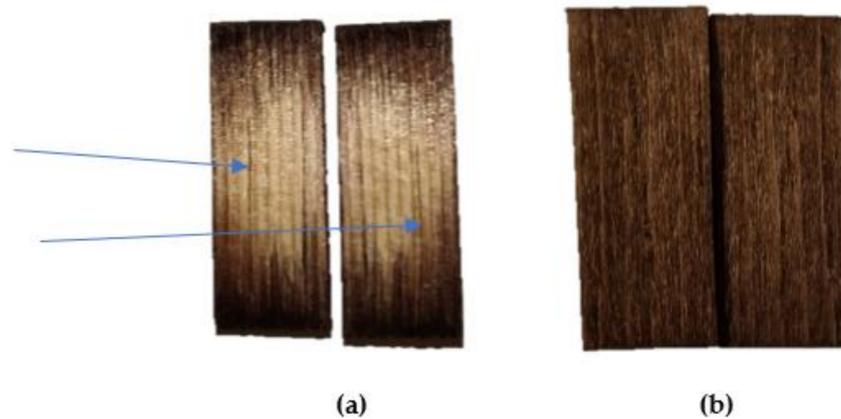
In the case of spruce, the wet retention drastically decreases while the dry retention increases by a factor of 2.35. In particular, there is no significant dry retention increase between 15% and 20% of tannin solution, suggesting that the higher viscosity decreases the penetration and the tannin accumulates on the surface. Conversely, beech wet retentions remain almost constant, and the dry retentions increase by a factor of 3.33. This means that the solution penetrates beech independently of the tannin concentration and hence the dry retention increases with the concentration of the formulation.

These results show that the wood permeability is correlated with the species: while beech is easy to impregnate, spruce is generally hard [34].

Anatomic observations were performed in the two wooden structures to understand the different absorption mechanisms for spruce and beech.

### 3.1.1. Optical Analysis

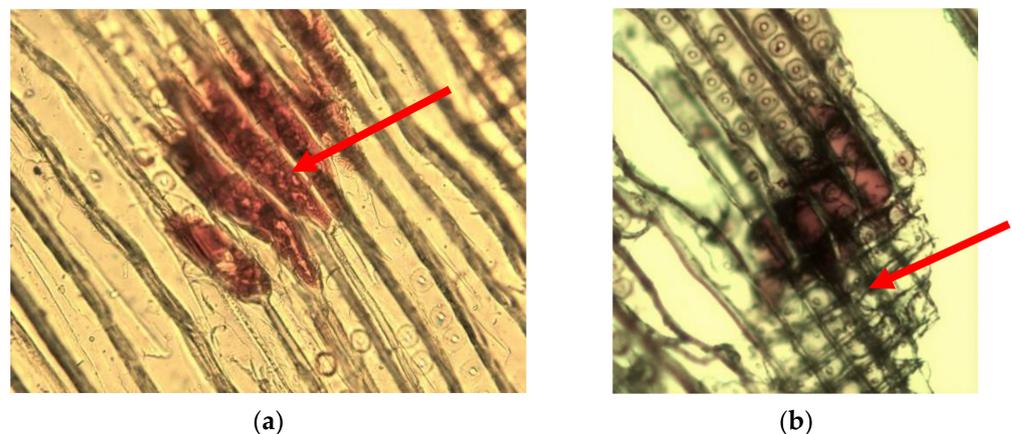
Figure 1 shows the core cut of impregnated spruce (a) and beech (b) specimens. The tannin seems to be completely penetrated in the beech specimens while a partial penetration from the grains is visible in spruce.



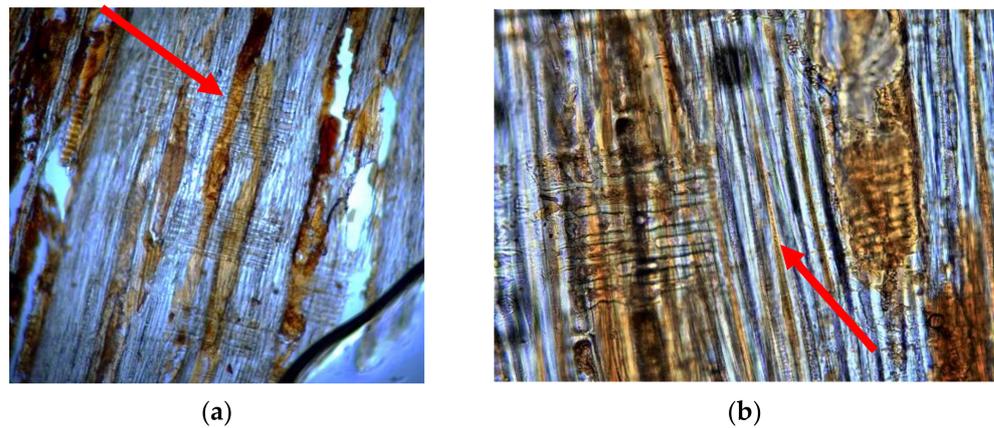
**Figure 1.** (a) Longitudinal section of spruce (*Picea abies*) sample impregnated with 10% of tannin water solution. (b) Longitudinal section of beech sample impregnated with 10% of tannin water solution.

Wood cell pore sizes depend on species, radial position and environmental factors. Generally, the diameter of beech vessels is around  $50\ \mu\text{m}$  [35], while the mean tracheid diameter (latewood and earlywood) in spruce is around  $30\ \mu\text{m}$  [36]. Considering the conduction elements, the hardwood vessel cells are in open contact with each other, establishing a sort of tube which allows the longitudinal conduction, whereas softwood tracheids are connected only through bordered pits. Indeed, water flow in spruce occurs through bordered pits which generally close when they dry. Eventually, the narrower diameter of lumina tracheids, coupled with the resistance of the pit membrane, reduces the flow in softwood, resulting in a difficulty to impregnate. It can also be observed that the darker longitudinal traits in Figure 1a (blue arrows) are large resiniferous ducts into which the impregnating agent easily penetrates.

The preferred penetration paths for the two species can be better highlighted at higher magnifications (Figures 2 and 3).



**Figure 2.** (a) Spruce (*Picea abies*) with 5% tannin solution  $400\times$ . Tannin solution accumulated at the ends of tracheids; (b) Tannin solution does not enter in rays (radial parenchyma cells, uncolored).



**Figure 3.** Beech (*Fagus sylvatica*) wood impregnated with 10% of tannin solution. (a) Tannin solution in vessels, 100 $\times$ ; (b) Few narrow fiber tracheids contain a small amount of tannin solution, 400 $\times$ .

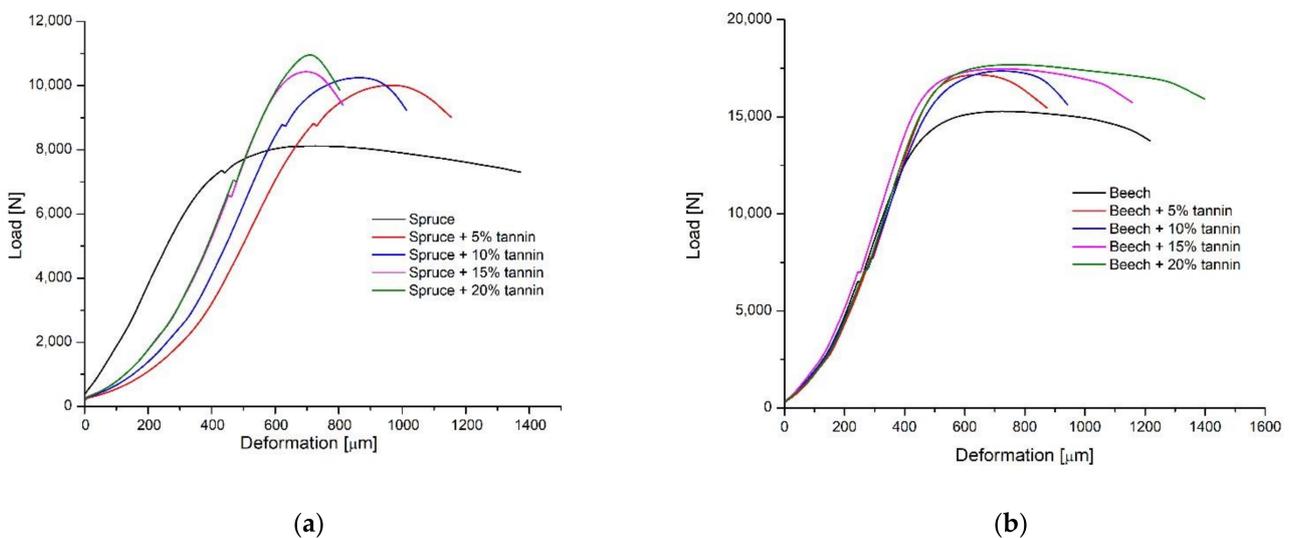
Figure 2a shows that the tannin solution flows in a non-linear way from one tracheid to another, passing through the bordered pits in spruce samples. The cell walls appear to be the same color, which suggests that the tannin solution accumulates in the cell lumen and does not infiltrate into the cell wall. Additionally, the solution flows until it reaches the bottom of the tracheids, where it appears to form granular masses on the inner surface of the cell wall (red arrow). The rays (radial parenchyma cells) do not appear to contain the tannin solution. However, in the spruce there are also radial tracheids, which can allow a contained radial flow of the solution (Figure 2b).

The preferred impregnation route for beech are the vessels, and in a smaller amount the fiber tracheids. The tannin solution concentrates mainly in the vessels (Figure 3a), (red arrow) while in the parenchymatic tissue, the tannin solution seems absent (Figure 3a,b).

These observations confirm that the impregnation of spruce is harder and less homogeneous than that of beech due to the structural differences between coniferous and deciduous trees [36].

### 3.1.2. Mechanical Properties

In Figure 4, the stress vs. strain behavior for impregnated spruce (Figure 4a) and beech (Figure 4b) is reported.



**Figure 4.** Compression resistance behavior of spruce (a) and beech (b) treated with different concentrations of tannin-hexamine solutions.

For both wood species, the presence of tannin–hexamine solutions enhances the maximum compression resistance, but the concentration of tannin does not significantly affect the performances. In the case of spruce, the presence of tannin–hexamine polymers renders the specimens initially weaker, but then the elastic region lasts longer with the consequent increase in maximal load. Conversely, the increase in tannin concentration contributes to produce stiffer specimens, with no improvement in its modulus of rupture. The impregnation of beech simply extends the elastic region and consequently its maximum load. A higher concentration of tannin only extends the plastic deformation before collapsing.

Hardness also shows improvement after impregnation. While spruce samples have an average hardness of 1.78, the hardness of impregnated samples is between 2.56 and 2.74, independently on the concentration; beech has an average hardness of 3.48, with its impregnated samples between 3.57 and 3.72. The increase in hardness for spruce is around 50%, while for beech it is just 5%.

### 3.2. Influence of Hexamine Amount on Impregnation

Once the effects of tannin concentration were defined, the influence of the hexamine was investigated in terms of retention, mechanical properties and leaching resistance by keeping the tannin concentration fixed at 10%. In this second part, poplar and pine are included in the study.

Wet and dry retentions of tannin–hexamine formulations with different concentration of hardener are shown in the Table 2 for the four wood species.

**Table 2.** Wet and dry retentions for different wood species treated with 10% quebracho tannin solutions with different hexamine concentrations.

Hexamine (%)	Wood Species							
	Beech <sup>1</sup>		Poplar <sup>2</sup>		Spruce <sup>3</sup>		Pine <sup>4</sup>	
	R <sub>wet</sub>	R <sub>dry</sub>	R <sub>wet</sub>	R <sub>dry</sub>	R <sub>wet</sub>	R <sub>dry</sub>	R <sub>wet</sub>	R <sub>dry</sub>
2.5 <sup>a</sup>	5.71	0.48	6.14	0.49	6.53	0.48	3.45	0.25
5 <sup>b</sup>	4.98	0.33	6.27	0.50	6.88	0.50	3.59	0.29
7.5 <sup>c</sup>	5.93	0.40	6.16	0.47	6.38	0.44	4.26	0.29
10 <sup>d</sup>	4.68	0.30	6.40	0.48	6.56	0.46	3.78	0.26

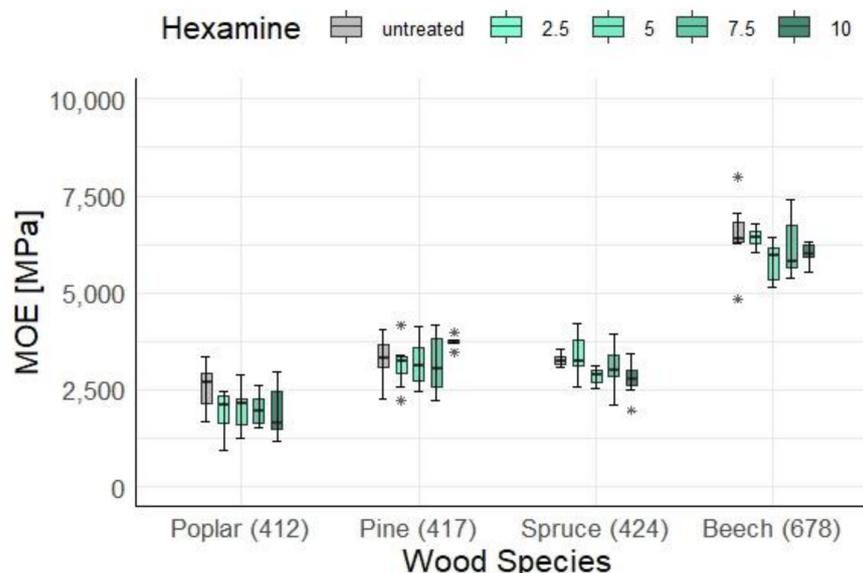
The numbers and letters used for species and cross-linking concentration, respectively, identify statistically significant differences in the following tables.

The increase in hardener concentration does not seem to affect the wet and dry retentions. The *p*-values of 0.7383 and 0.2914 are registered for solution and tannin penetration. A strong effect on wet, and consequently on dry, retention is due to the wood species. In particular, pine was harder to impregnate, while no significant difference was observed for poplar and spruce (*p*-value > 0.05).

#### 3.2.1. Mechanical Properties

The impregnated samples with 10% tannin and hardened with different amounts of hexamine (2.5%, 5.0%, 7.5%, 10.0% *w/w* related to tannin) were tested to understand the influence of the amount of hexamine in terms of modulus of elasticity (MOE) and modulus of rupture (MOR) on compression and Brinell hardness (HB).

The graphic in Figure 5 reports the MOE for the four species untreated (0%) and impregnated with 10% tannin and variable amounts of hexamine (2.5%, 5%, 7.5% and 10%).



**Figure 5.** Boxplot chart of modulus of elasticity for different wood species at various hexamine amounts. The symbol “ \* ” indicates the outliers of the tests performed.

From this plot, it is possible to highlight that the impregnation with tannin formulation does not affect the MOE of the samples ( $p$ -value 0.7758). Statistical differences were observed between species, except for spruce and pine that register an average of 3064 and 3300 MPa (Table 3). Although the MOE was not affected by the treatment, MOR results were enhanced after impregnation (Figure 6).

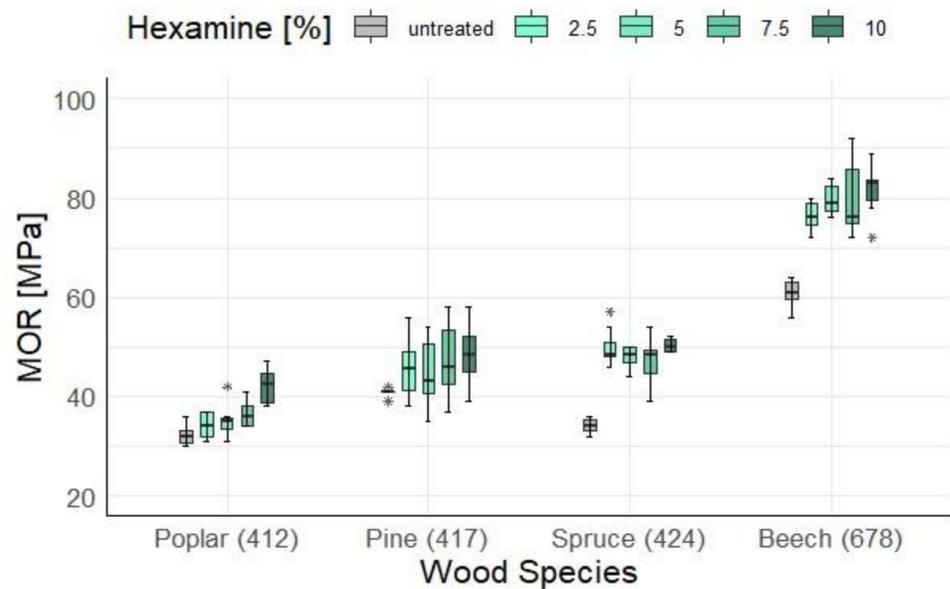
**Table 3.** Kruskal and post hoc Dunn tests for MOE, MOR and HBS as a function of wood species and amount of hexamine.

	MOE		$p$ -Value > 0.05	MOR		$p$ -Value > 0.05	HBS		$p$ -Value > 0.05
	$\chi$			$\chi$			$\chi$		
Hexamine	1.8		a × b × c × d	18.0		a × b × c × d	9.2		Untreated-a × b × c × d
	$p$ -value	0.8		$p$ -value	$1 \times 10^{-3}$		$p$ -value	$1 \times 10^{-3}$	
Wood species	115.0		3-4	108.2		3-4	88.4		2-3; 2-4; 3-4
	$p$ -value	$2 \times 10^{-16}$		$p$ -value	$2 \times 10^{-16}$		$p$ -value	$2 \times 10^{-16}$	

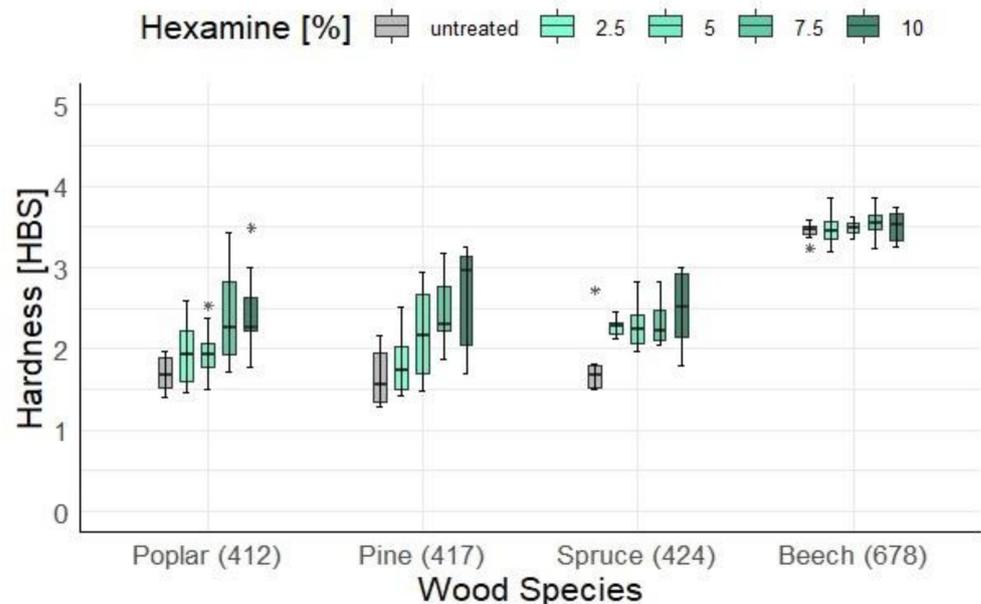
In particular, the correlation between hexamine concentration and MOR shows a  $p$ -value of  $1 \times 10^{-3}$ , confirming a significant difference following impregnation (Table 3). The Dunn’s test returned a significant difference ( $<0.05$ ) between the non-impregnated samples and the specimens treated with a hexamine content of 2.5% or more in the solutions, but no difference was found between the different concentrations of hardener used.

From Figure 6, it can be seen that spruce and beech significantly increase their MOR, even when a contained concentration of hexamine is applied. In poplar, a direct proportionality between the amount of crosslinker and MOR was observed, which could be due to the limited mechanical performances of the untreated wood.

To complete the mechanical properties, the surface hardness of the untreated and tannin–hexamine-treated specimens is summarized in Figure 7.



**Figure 6.** Boxplot chart of modulus of rupture for different wood species at various hexamine amounts. The symbol “\*” indicates the outliers of the tests performed.



**Figure 7.** Boxplot chart of Brinell surface hardness for different wood species at various hexamine amounts. The symbol “\*” indicates the outliers of the tests performed.

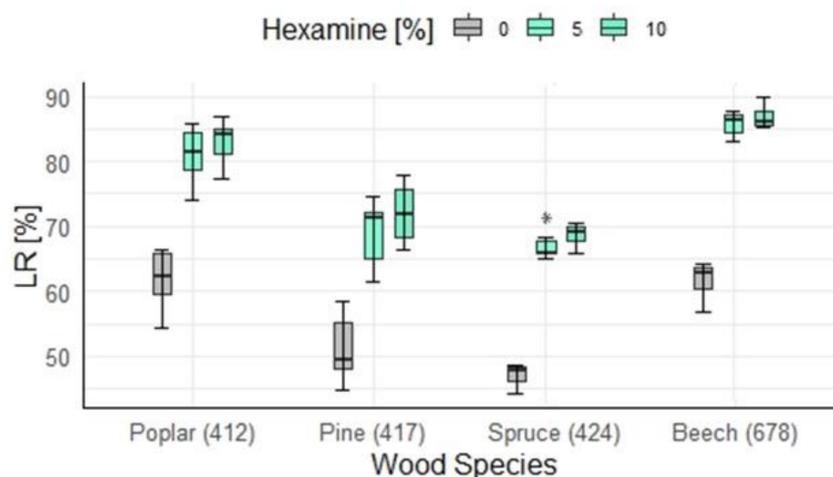
In this experiment, a significantly higher hardness was observed for beech. It clearly appears that the beech surface hardness is not affected by any tannin treatment.

Conversely, the surface hardness of the weaker species is positively influenced by the impregnation and by the amount of hexamine applied. Significant differences between the amount of hardener and HBS is reported by Kruskal test with a  $p$ -value of  $1 \times 10^{-3}$  (Table 3).

### 3.2.2. Leaching Resistance

The leaching resistance of the quebracho-tannin impregnated samples is presented in Figure 8. It can be seen that the presence of hexamine significantly increases the leaching resistance of the polymer. This can be observed for every timber species, and the increase can be quantified as between 20% and 30%. Even though slightly higher leaching resistance

is observed when 10% of hardener is applied, the concentration of hexamine does not show statistically significant consequences on the leaching resistance (Table 4). A further observation indicates that softwoods show major leaching compared with hardwoods. This is because the hindered penetration involves the deposition of higher amounts of polymer in the surface layer; therefore, the proportion of tannin polymer that contacts water will be higher.



**Figure 8.** Leaching resistance of timber-impregnated samples in function of the concentration of hexamine. The symbol “\*” indicates the outliers of the tests performed.

**Table 4.** Kruskal and post hoc Dunn tests for leaching resistance as a function of wood species and amount of hexamine.

		LR	<i>p</i> -Value > 0.05
Hexamine	$\chi$	43.9	5–10
	<i>p</i> -value	$2 \times 10^{-10}$	
Wood Species	$\chi$	19.0	1–2; 3–4
	<i>p</i> -value	$2 \times 10^{-4}$	

#### 4. Discussion

The presence of in situ crosslinked tannin-based polymers improves the mechanical properties of the impregnated wood samples. This finding was expected and already observed by other researchers with non-polar waxes as well as with thermoset resins [37–40]. However, this enhancement depends on the wood species, the mechanical tests performed and the amount of hardeners. Considering that the dry retention is almost independent from the amount of hardener and from the wood species (except pine), it is possible to summarize that:

- While spruce, pine and poplar have similar mechanical behavior, beech registers higher MOE, MOR and hardness, independently, on the impregnation. As expected, the wood species and the density are key for the mechanical properties of specimens [41]. In other words, due to lower density, poplar mechanical properties are more similar to that of spruce and pine, despite it taxonomically belonging to hardwood [42].
- The presence of a tannin–hexamine network embedded in the wood structure contributes to the enhancement of the mechanical properties of spruce and beech, although the concentration of tannin does not affect the intensity of this improvement. In the case of spruce, the presence of tannin polymer is significantly more important, involving a 30% increase in MOR and 50% in HBS against the 15% in MOR and 5% in HBS registered for beech. This is due to the lower density of spruce and the higher concentration of tannin on the surface.

- The MOE is not significantly affected by the presence of different amounts of hexamine. Conversely, MOR and hardness improve when more hardener is applied. The importance of hexamine is more significant for timber species at lower density. This suggests that the tannin polymer supports the wood structure when the elastic region expires, meaning that when the deformation becomes irreversible, the tannin network contributes to maintaining the wood structure before collapsing. Brinell hardness enhancement is especially contained for beech, because the easy penetration in the inner part of the wood dilutes the polymer accumulation on the surface.
- Hexamine also has a dominant impact at low concentration for MOR of spruce and beech; otherwise, its increase only slightly affects the property of the impregnated timber. This suggests that contained amounts of hexamine are already sufficient to create most of the supporting network of tannin [43]. However, using higher amounts brings further advantages that could be considered, especially for increasing the hardness of low-density species. This contained effect of polymerization with higher amounts of hexamine was unexpected. Other scientists applied hexamine to phenol-formaldehyde and pyrocatechol resins and observed that higher concentrations involved an increase in networking [44,45].
- The leaching resistance highlights that, as expected, the presence of hexamine significantly contributes to increasing the water resistance of the flavonoid-based network for every wood species tested [19,20]. However, the increase in concentration does not involve significant water resistance improvements. This confirms the observation of the previous point that for this property also, the excess of hexamine does not significantly contribute to strengthening the polymer network.

These quebracho tannin-based wood preservatives are almost completely bio-based products presenting enhanced mechanical and water resistance properties. Despite these interesting properties, these products cannot be easily compared with other promising bio-based preservatives. However, compared with a study of Barbero-Lopez et al. [46], quebracho tannin–hexamine registered retention between 20 and 70 kg/m<sup>3</sup>, which is in line with other tannin quebracho (Colatan GT10) and pine oil measurements of the study, especially considering that we impregnated the wood without extra external pressure. Mechanical enhancement registered was contained, compared with that observed by Noel et al. [47], who treated wood with lactic acid polymer. However, the retentions and the polymerization conditions considered were higher [47]. Furthermore, more consistent comparisons will be addressed when the efficacy of these formulations are tested against biologic attacks.

## 5. Conclusions

In this work, the impregnation of different wood species with quebracho–tannin formulations was observed. We found that the concentration of the impregnating solution affects the wet retention of spruce, while beech is easier to penetrate. This was due to the transportation tissues of the two species. While the beech structure can be easily accessed from broad vessels, spruce was hindered by most of the tracheids that presented closed bordered pits. The presence of quebracho tannin networked with hexamine embedded in the structure contributes to enhance the mechanical properties of timber, especially the modulus of rupture and the surface hardness of the samples with lower density. An increased concentration of tannin and hexamine in the impregnating solution did not involve significant enhancement, suggesting that for improving mechanical properties and leaching resistance, 10% quebracho tannin formulations containing 2.5–5% of hexamine (*w/w*. tannin) are already sufficient [48]. These novel formulations will be tested for their biological and weathering resistance to understand their efficacy as wood preservatives and their position in the market. At present, the major limitation is the more contained yet still important leaching sensibility that could be reduced by crosslinking the polymer at higher temperatures.

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