

# Tannin-boron preservatives for wood buildings: mechanical and fire properties

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**Abstract** The remarkable biological properties of tannin-boron wood preservatives for outdoor applications have been investigated recently (Thevenon et al. in Eur. J. Wood Prod. 67:89, 2009). In the present paper mechanical and fire-proofing attributes of these formulations are determined. Mechanical properties of Scots pine and beech specimens treated with tannin-based formulations were examined in compression and bending strength tests and surface hardness was determined. The tannin-hexamine formulations reticulated into the wood structure improve the strength of the treated specimens. The treated samples which underwent compression, bending, hardness and gluing tests showed improvements of on average 20%.

Fire tests have been monitored regarding short and long flame exposure time. Short tests such as ignition, flame and ember time have allowed the ignition of the fire to be simulated, while the weight loss tests have provided a good overview of the behavior of the specimens during prolonged fire. A positive effect on fire-resistance is shown when wood is treated with tannin formulations. The fire-proofing properties of the resin have been upgraded adding boron and phosphorus. The ember time of the pieces treated using this method can be reduced by up to ten times.

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## Holzschutzmittel auf Tanninharz-Bor-Basis für Gebäude aus Holz: Mechanische Eigenschaften und Brandverhalten

**Zusammenfassung** Bestimmte mechanische Eigenschaften sowie das Brandverhalten von Holzschutzmitteln auf Tanninharz-Bor-Basis für Anwendungen im Außenbereich wurden untersucht. Deren bemerkenswerte biologische Eigenschaften wurden kürzlich beschrieben (Thevenon et al. in Eur. J. Wood Prod. 67:89, 2009). Ergebnisse wichtiger mechanischer und physikalischer Eigenschaften werden in dieser Publikation berichtet. Im Rahmen der mechanischen Eigenschaften wurden die Druck- und Biegefestigkeiten von mit Tanninharz-Bor-Formulierungen imprägnierten Kiefern- und Buchenholzproben ermittelt sowie deren Oberflächenhärte bestimmt. Bei mit kondensierten Tannin-Bor-Hexamin Formulierungen behandelten und in situ vernetzten und ausgehärteten Proben wurde eine Verbesserung der Druck- und Biegefestigkeiten sowie der Oberflächenhärte um rund 20 % ermittelt. Die Brandeigenschaften wurden bei Versuchen mit kurzer (2–3 min) und langer Einwirkzeit ermittelt. Mittels der Kurzzeitversuche konnte das Verhalten bezüglich Entflammbarkeit und Verkohlung aufgezeigt werden. Untersuchungen des Masseverlustes bei Langzeiteinwirkung gaben einen guten Überblick über das Brandverhalten der Proben. Insgesamt wurde eine signifikante Verbesserung des Abbrandverhaltens durch das in den mittels Tanninharz-Bor-Formulierungen imprägnierten Proben enthaltene Bor und Phosphor aufgezeigt.

## 1 Introduction

Tannin-based wood preservatives have been prepared since the 1980s but their high water solubility represented a drawback that was not easy to eliminate (Laks et al. 1988). In

the following decades in-depth studies on tannin chemistry meant that new opportunities for the development of these compounds in wood science could be found (Pizzi 1994). The hydroxy-aromatic chemical composition of flavonoids has a similar reactivity to that of phenols with hardeners (formaldehyde, hexamine, etc.) and it has been the key property for their development in resin formulations (Pichelin et al. 1997; Tondi et al. 2009a).

A second important feature of the flavonoids is their ability to coordinate heavy metal ions (Lotz and Hollaway 1988; Yamaguchi and Okuda 1998; Tondi et al. 2009b). The empty orbitals of metals attract the electrons of these compounds and fix them in stable complexes.

Several research groups have successfully worked on fixing boron and other metals in wood (Thevenon et al. 1998; Toussaint-Dauvergne et al. 2000; Xie et al. 1995) but no definitive solutions were found. It is only recently that the fixation of boron with cross-linkable flavonoids has been further investigated (Thevenon et al. 2010; Tondi et al. 2012a).

The use of mimosa tannin extract combined with hexamine as hardener presents two advantages, firstly to anchor the tannin in wood with a recognized non-formaldehyde-emission compound (Pichelin et al. 2006; Kamoun et al. 2003) and secondly, boron can maintain enough mobility to be active as a fungicide but not enough to be leached out (Pizzi and Baecker 1996).

These formulations were subject of more detailed investigations: The objective of the present study is to analyze the mechanical and physical properties of the treated samples for structural applications.

## 2 Material and methods

### 2.1 Materials

Scots pine (*Pinus sylvestris*) and European beech (*Fagus sylvatica*) specimens were provided by various Austrian sawmills and selected in accordance with EN 113 (1997). The samples of different dimensions were cut after one week of stabilization at 20 °C and 65% moisture content.

Mimosa (*Acacia Mearnsii* formerly *Mollissima* De Wildt) tannin extract was provided by Silvachimica srl (Italy). The other chemicals such as: Hexamethylentetramine (hexamine), boric acid, phosphoric acid and sodium hydroxide were provided by Lactan Chemikalien GmbH (Austria) and the polyvinyl acetate based D3 one-component resin GXL3 by Rakoll.

### 2.2 Impregnation

Sapwood of Scots pine and European beech specimens of different sizes were cut (according to the relevant test; see

Table 1) and were dried for a minimum duration of one week at 104 °C.

These samples were placed into a desiccator and 8 mbar vacuum was applied to remove the air trapped in the wood cells. Afterwards the desiccator was filled up with the impregnation solution and the pressure was slowly increased up to environmental pressure.

In accordance with the different species of wood treated and with the viscosity of the impregnation solutions, different vacuum and immersion times were applied to ensure the most suitable impregnation of each sample (Table 1).

The weight of the wood samples was monitored before and after the treatment to evaluate the penetration effectiveness and up-take of the impregnation solution.

The wet samples were kept for at least 12 hours at 104 °C to allow the tannin-hexamine resin to harden. Subsequently the treated specimens were stored in a climatic chamber to an equilibrium moisture content of wood (12%) for a minimum of one week before testing.

Tannin impregnation solutions were prepared with 10% and 20% w/w mimosa extract. The pH of these solutions was always corrected with NaOH 50% at a pH of 9.0. 6.0% by weight of hexamine was added as the crosslinking agent. Boric acid and phosphoric acid (5% w/w) were added in the formulations to investigate the behavior against fire, keeping the pH of the solution at the value of 9.

### 2.3 Penetration calculation

Each sample was weighed before and after the impregnation process. Real resin uptake was compared with the theoretical one and the penetration by weight ( $P_w$ ) was calculated as follows:

$$P_w = (\text{real uptake/theoretical maximal uptaking}) \times 100$$

Theoretical maximal uptaking (T.M.U.) was calculated according to the following formulas:

$$\text{T.M.U.} = V \times c \times d$$

where  $V$  is the row volume of the sample,  $c$  is the porosity of the wood sample and  $d$  the density of the impregnation solution.

Porosity ( $c$ ) of pine and beech was calculated using the formula:

$$c = 1 - (D_d/D_{cw})$$

where  $D_d$  is the density of dry wood (Scots pine = 0.515 g/cm<sup>3</sup>; European beech = 0,774 g/cm<sup>3</sup>) and  $D_{cw}$  is the average density of the cell walls (1.5 g/cm<sup>3</sup>).

Impregnation was evaluated by checking the color of the core-sample. It was determined that the pine sample can only be considered fully impregnated when at least 110% of the theoretical resin uptake is achieved and for beech this amount should be at least 130%.

**Table 1** Impregnation conditions of the samples for mechanical and fire tests**Tab. 1** Art der Imprägnierung der Proben für die mechanischen Versuche und die Brandversuche

| Sample dimensions (mm) |       |        | Wood species | Concentration of Tannin solutions (%) | Vacuum time (min) | Immersion time (h) | Penetration by weight ( $P_w$ ) (%) |
|------------------------|-------|--------|--------------|---------------------------------------|-------------------|--------------------|-------------------------------------|
| Long.                  | Tang. | Radial |              |                                       |                   |                    |                                     |
| 60                     | 20    | 20     | Pine         | 10                                    | 60                | 24                 | 91.5 ± 2.4                          |
| 60                     | 20    | 20     | Pine         | 20                                    | 60                | 48                 | 46.2 ± 0.5                          |
| 60                     | 20    | 20     | Beech        | 10                                    | 30                | 2                  | 141.9 ± 6.2                         |
| 60                     | 20    | 20     | Beech        | 20                                    | 30                | 3                  | 139.7 ± 10                          |
| 270                    | 15    | 15     | Pine         | 10                                    | 60                | 24                 | 22.4 ± 2.1                          |
| 270                    | 15    | 15     | Pine         | 20                                    | 90                | 24                 | 34.8 ± 2.7                          |
| 270                    | 15    | 15     | Beech        | 10                                    | 60                | 24                 | 49.5 ± 10                           |
| 270                    | 15    | 15     | Beech        | 20                                    | 90                | 24                 | 67.6 ± 8.8                          |
| 80                     | 20    | 5      | Pine         | 10                                    | 60                | 3                  | 95.3 ± 13                           |
| 80                     | 20    | 5      | Pine         | 20                                    | 60                | 3                  | 73.9 ± 10                           |
| 80                     | 20    | 5      | Beech        | 10                                    | 60                | 3                  | 139.1 ± 3.3                         |
| 80                     | 20    | 5      | Beech        | 20                                    | 60                | 3                  | 130.1 ± 6.6                         |
| 50                     | 25    | 15     | Pine         | 10                                    | 60                | 24                 | 110.2 ± 2.2                         |
| 50                     | 25    | 15     | Pine         | 20                                    | 60                | 48                 | 95.1 ± 7.5                          |
| 50                     | 25    | 15     | Beech        | 10                                    | 30                | 2                  | 142.7 ± 6.2                         |
| 50                     | 25    | 15     | Beech        | 20                                    | 30                | 3                  | 147.7 ± 1.7                         |
| 25                     | 25    | 25     | Pine         | 10                                    | 60                | 24                 | 115.6 ± 1                           |
| 25                     | 25    | 25     | Pine         | 20                                    | 60                | 24                 | 109.7 ± 1.9                         |
| 25                     | 25    | 25     | Beech        | 10                                    | 30                | 1                  | 126.5 ± 1.3                         |
| 25                     | 25    | 25     | Beech        | 20                                    | 30                | 1,5                | 123.3 ± 0.9                         |

## 2.4 Mechanical and surface properties

The evaluation of the structural properties of tannin-treated samples was performed on small specimens and it was always compared with untreated specimens. The most important mechanical features such as compression and bending resistance were studied and useful surface properties for wood workability such as hardness and gluing capacity were also examined.

### 2.4.1 Compression tests

60 × 20 × 20 mm<sup>3</sup> pieces of Scots pine and European beech were tested in compression according to the standard DIN 52185 (1976). Six samples for each formulation were tested using a Zwick/Roell Z 250 universal testing machine with a compression rate of 2 mm/min.

### 2.4.2 Three point bending tests

270 × 15 × 15 mm<sup>3</sup> Scots pine and European beech samples were tested according to DIN 52186 (1978). The number of annual rings in the square radial surface was 12–15 for pine and 5–7 for beech samples. Six samples for each formulation were tested using a Zwick/Roell Z 250 universal testing

machine with a compression rate of 2 mm/min. Maximal flexion and the modulus of elasticity (MOE) were then determined.

### 2.4.3 Hardness tests

The hardness of Scots pine and European beech samples (60 × 20 × 20 mm<sup>3</sup>) was tested on lateral sides (tangential and radial) according to the Brinell test EN 1534 (2000). The “emco-test automatic” was specifically employed in this study to investigate the Brinell hardness of the six samples for each formulation.

### 2.4.4 Gluing tests

The gluing capacities of the treated surface were evaluated by means of a shearing test. Samples of Scots pine and European beech (80 × 20 × 5 mm<sup>3</sup>) were impregnated with two concentrations of tannin resin and then glued in couples with 250 g/m<sup>2</sup> of polyvinyl acetate based resin. At least five glued samples for each formulation were obtained and tested. The shearing test was performed at a rate of 2 mm/min on a 20 × 10 mm<sup>2</sup> glued surface.

## 2.5 Fire-proofing properties

Lab-scale tests were carried out to evaluate the most important parameters of the treated samples regarding fire exposure.

### 2.5.1 Short-time exposure fire tests

$50 \times 25 \times 15 \text{ mm}^3$  samples of Scots pine and European beech were tested against fire, therefore the larger surface (radial) was exposed to the 100% oxidant flame of a Bunsen burner. The distance between Bunsen burner and sample was set at 9 cm and the burning times were controlled with a stop-watch. Ignition, flame and ember time were recorded for each sample whereby the ignition time was the minimum exposure time necessary to activate unaided burning.

The flame time measures the time that the sample requires to extinguish the flame after 2 and 3 minutes of continued exposure. Ember time measures the time required for complete extinction (no more red spots, no more fumes).

Each value was recorded after at least three specimens had undergone each tested formulation.

### 2.5.2 Long-time exposure fire test: weight loss

Cubic samples of 25 mm per side of Scots pine and European beech were impregnated with different tannin formulations. The specimens were exposed to direct flame in a lab-made instrument. The vertex of the sample was exposed to the top of the roaring blue flame of the Bunsen burner ( $d = 8\text{--}10 \text{ cm}$ ).

The weight of the sample was registered every 30 seconds and the weight-loss curve was extrapolated.

The test was repeated at least three times for each formulation.

## 3 Results and discussion

### 3.1 Concept of penetration

An important parameter for the evaluation of the impregnation is the penetration by weight as this feature influences all tests performed.

Samples of varying dimensions were weighed before and after the impregnation process. The porosity of the wood species was considered to facilitate the calculation of the maximum amount of resin that could penetrate the wood.

In the majority of cases, the real value obtained was more than the calculated amount because tannin tends to create complexes with the hemicelluloses of the cell walls (Taira et al. 1997). This phenomenon explains why, in the case of beech, the easy accessibility of vessels enables a higher

amount of wood cells to be impregnated than in Scots pine. The analysis in Table 1 shows that most samples can be fully impregnated under the conditions reported. The only samples that are not impregnated in depth are the pine pieces prepared and treated with 20% of tannin solution and all series of samples for bending tests. Further information concerning the mechanism of penetration of these species can be found in Tondi et al., Tondi et al. (2012a, 2012b).

The vacuum time of 30 to 60 minutes is generally sufficient to remove the air from the wood samples whilst a long impregnation time (up to 48 h) is preferable when the impregnation solutions are viscous and the samples are larger, particularly in the longitudinal direction.

### 3.2 Mechanical properties

Beech and Scots pine samples differ in appearance after tannin impregnation treatment.

The most apparent changes are the darker color and smoother surface.

The quantification of the mechanical properties is fundamental in consideration of tannin-boron formulations for application in wood construction. For this reason, compression tests, bending tests, hardness and gluing capacity measurements were performed.

Figure 1 represents the strength performance in compression resistance when 0, 10 and 20% tannin solutions were impregnated. The most immediate result is that an improvement in compression resistance occurs for every tannin formulation applied and for every wood species treated.

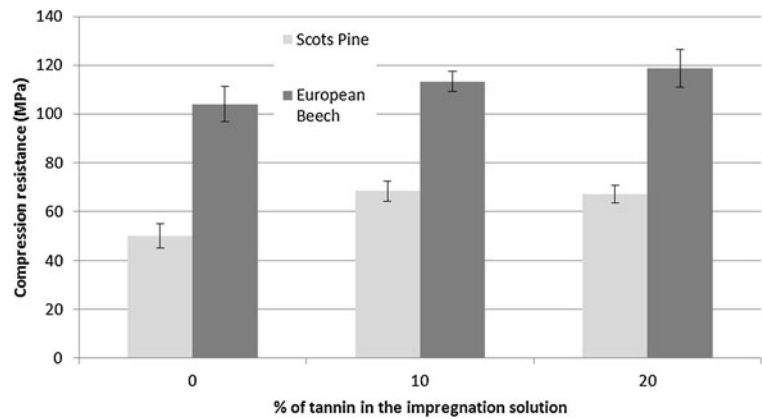
It is apparent that the reticulation of the tannin-hexamine resins in the wood cells reinforces the mechanical properties of the treated specimens.

The solution with 10% of tannin penetrates in depth and produces a homogeneous distribution of the network after curing. Mechanical resistance improvements are high, namely 35% for Scots pine and 10% for beech. Unfortunately, when the viscosity of the solution increases, the penetration in Scots pine is incomplete and the distribution of the resin is no longer homogeneous. The mechanical resistance is still increased, but there is no proportionality between the tannin applied and the strength achieved.

In the case of beech, the penetration of the 20% tannin formulations is complete and therefore the compression resistance is increased. This improvement is approx. 15% and this enhances its value, considering that untreated beech is naturally around two times more resistant to compression than pine.

Three point bending test results are reported in Table 2. Also in this case it can be observed that tannin resin impregnation always increases Young's modulus of the specimens. The impregnation of the samples for the bending tests was always incomplete. At the moment that most of the penetration occurs longitudinally, the differences in resin uptake do

**Fig. 1** Compression strength in relation to tannin impregnation  
**Abb. 1** Druckfestigkeit in Abhängigkeit der Tanninimprägnierung



**Table 2** Bending tests of Scots pine and European beech wood samples

**Tab. 2** Ergebnisse der Biegeprüfungen der Kiefern- und Buchenholzproben

| Wood species   | Concentration of tannin impregnation solution (%) | Solid released after impregnation (%) | Young's modulus MOE (MPa) | Max flexion (mm) |
|----------------|---|---------------------------------------|---------------------------|------------------|
| Scots pine     | 0   | 0                                     | 99.2 ± 4.3                | 10.1 ± 1.4       |
| Scots pine     | 10  | 4.2                                   | 111.8 ± 12.5              | 7.2 ± 1.1        |
| Scots pine     | 20  | 3.7                                   | 120.9 ± 10.8              | 9.9 ± 1.7        |
| European beech | 0   | 0                                     | 124.3 ± 6.4               | 10.8 ± 0.9       |
| European beech | 10  | 4.9                                   | 156.6 ± 4.74              | 9.5 ± 0.4        |
| European beech | 20  | 5.6                                   | 145.5 ± 8.1               | 9.4 ± 0.7        |

not affect the bending properties of the specimens significantly because the external sides of the sample are not influenced by the three points where the mechanical stress is applied. Only the lateral penetration can play a significant role in the impregnation of the central part of the sample (Scholz et al. 2010). For these reasons, the effective penetration in pine is higher and the results in bending are proportionally increased with the amount of solid resin applied. The treated pine specimens achieve an improvement in MOE of up to 21.8%.

Lateral penetration in beech is much lower but the results show that tannin treatments allow an increase of up to 25% of the Young's modulus. In this case, it is possible that some large vessels enable the resin to reach the central part of the sample and reinforce the whole structure.

Another interesting aspect of this test relates to the analysis of the maximal flexion of the specimens. It can be observed that the higher flexion is always obtained by untreated samples. The presence of the tannin resins increases the rigidity of the specimens. Hence, the tannin treatment increases the mechanical stress resistance and decreases the flexion deformations.

However, it should be emphasized that all the mechanical features tested are improved. Consequently the treatment can be considered not only as an innovative and eco-friendly method to increase durability (Thevenon et al. 2009), but also as a means to render the wood more resistant in building constructions or flooring applications.

### 3.3 Surface properties

The surface properties of the treated wood were tested in order to evaluate their hardness and gluing capacities.

Hardness was studied according to the Brinell method and the results are reported in Fig. 2.

Even for this surface phenomenon, the proportionality between the hardness and the tannin concentration of the impregnation solution is respected only when the penetration is complete. Therefore, the treatment of Scots pine with a too highly concentrated (20%) solution of tannin does not give the results expected. Notwithstanding the fact that hardness is a surface property, harder surfaces are achieved when the samples are homogeneously filled.

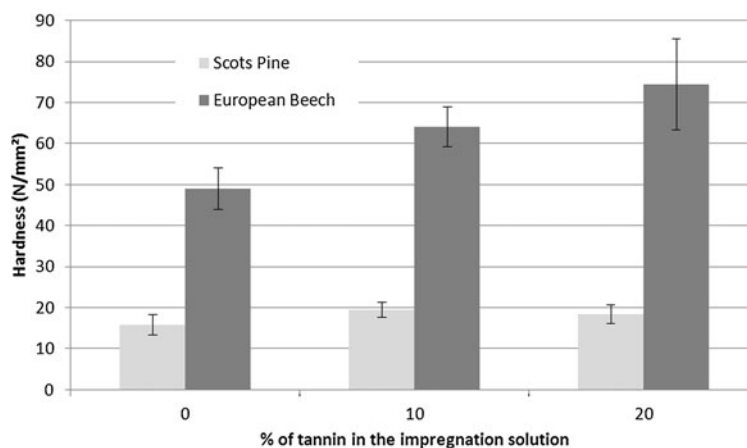
In general, however, the treated samples always increase their hardness after tannin impregnation treatment and also their resistance to mechanical surface solicitations is upgraded.

Another important factor to be analyzed in treated wood is its bonding potential. The adhesion properties of glue can be compromised if the wood substrate is treated. The test was performed with a vinylic D3 glue to simulate several possible exterior applications. The results of the shearing tests related to these investigations are shown in Table 3.

In the large majority of tests there was a significant percentage of wood failure. In the case of pine, the shearing tests showed that the treated surfaces remain sufficiently glueable. Wood failure occurs at around 6.0 N/mm<sup>2</sup> and the glue-line can resist this stress in most cases.



**Fig. 2** Brinell hardness in relation to tannin impregnation  
**Abb. 2** Brinell-Härte in Abhängigkeit der Tanninimprägnierung



**Table 3** Gluing properties of tannin-treated surfaces  
**Tab. 3** Klebeeigenschaften Tannin imprägnierter Proben

| Wood species   | Tannin in the impregnation solution (%) | Wood failure (%) | Shearing resistance (N/mm <sup>2</sup> ) |
|----------------|---|------------------|--|
| Scots pine     | 0                                       | 88               | 4.59                                     |
| Scots pine     | 10                                      | 66.25            | 4.68                                     |
| Scots pine     | 20                                      | 98               | –  |
| European beech | 0                                       | 72.5             | 12.64                                    |
| European beech | 10                                      | 24               | 9.63                                     |
| European beech | 20                                      | 20               | 7.99                                     |

In contrast, the beech samples treated are less gluable and the shearing resistance diminishes when more preservative is penetrated.

For both the wood species tested, the tannin resin renders the surface of the wood smoother and the roughness for the grip of the vinyl resin decreases significantly. Another significant aspect of the tannin treatment is the modification of the surface energy. Indeed, the surface becomes more hydrophobic and then it reduces the penetration of the water-based PVAc adhesives.

### 3.4 Fire-resistant properties

A key question for wood building preservatives is their behavior against fire.

This characteristic is always studied when the samples are of large dimensions, in order to evaluate their mechanical stability. Unfortunately, large dimension autoclaves are required to impregnate structural wood beams in depth. Thus, more simplified lab-scale tests were conducted to gain a comparative analysis of fire resistant properties. Two types of simulation tests were considered: short- and long-time exposure tests.

Short-time exposure tests simulate the lighting of the fire, while the weight loss test allowed a clearer understanding of

the behavior of the wood specimens in the case of prolonged fire.

The dimensions of the samples were selected because they allow limited edge effects and achieve a good impregnation rate.

Ignition, flame and ember time represent a good evaluation of the ignition process (Tables 4 and 5).

An analysis of these tables shows that the effect of tannin increases the fire resistance of the samples. The ignition time significantly increases when the concentration of tannin increases. In the case of Scots pine (Table 4), the flame does not penetrate into the sample within two minutes when 20% of tannin is applied for most of the sample. For this reason, the flame time is also particularly limited. When three minutes of fire are applied, the flame time increases more significantly, because this allows the fire to reach some untreated parts of the sample. Only little or no effect can be observed for the ember time. The red spots are small in treated wood, but they last longer because they burn into an inner protected zone.

When the formulations are enriched with 5% of boric acid or with 5% of phosphoric acid, there is a significant decrease in the ember time, meaning that complete extinction takes place in less than 1 minute.

Beech shows similar behavior against fire (Table 5). The only significant difference can be seen in the extinguishing time when a 3-minute fire is applied. In this case, beech keeps the flame and the spots for a longer period. The fire-retardant effect of tannin is also evident for this wood species: the flame time decreases up to ten times. Unfortunately this fire-proofing aspect does not always have the same efficacy against ember. Longer fire exposure requires the presence of inorganic compounds in the preservation resin to reach a sensible fire-proofing degree.

Wood is not a homogeneous material, hence the tests have a considerable standard deviation. The information achieved with this method allows only a preliminary notion of the general behavior of treated wood against fire.

**Table 4** Short exposure fire tests for Scots pine

**Tab. 4** Ergebnisse der Kurzzeit-Brandbeanspruchungsversuche der Kiefernproben

| Parameters                  | Ignition time (s) | Flame time 2 min (s) | Flame time 3 min (s) | Ember time 2 min (min) | Ember time 3 min (min) |
|-----------------------------|-------------------|----------------------|----------------------|------------------------|------------------------|
| Untreated                   | 12 ± 3            | 140 ± 30             | 120 ± 25             | 4.0 ± 1.0              | 3.9 ± 1.0              |
| 10% Tannin                  | 75 ± 15           | 35 ± 10              | 130 ± 30             | 2.5 ± 0.5              | 6 ± 1.5                |
| 20% Tannin                  | > 120             | 20 ± 10              | 80 ± 20              | 2.5 ± 0.5              | 7 ± 1.5                |
| 20% Tannin + Boric Ac. 1%   | > 120             | 25 ± 5               | 30 ± 5               | 0.8 ± 0.2              | 1.5 ± 0.5              |
| 20% Tannin + Phosph. Ac. 1% | > 120             | 15 ± 5               | 27 ± 5               | 0.9 ± 0.2              | 2.5 ± 0.8              |

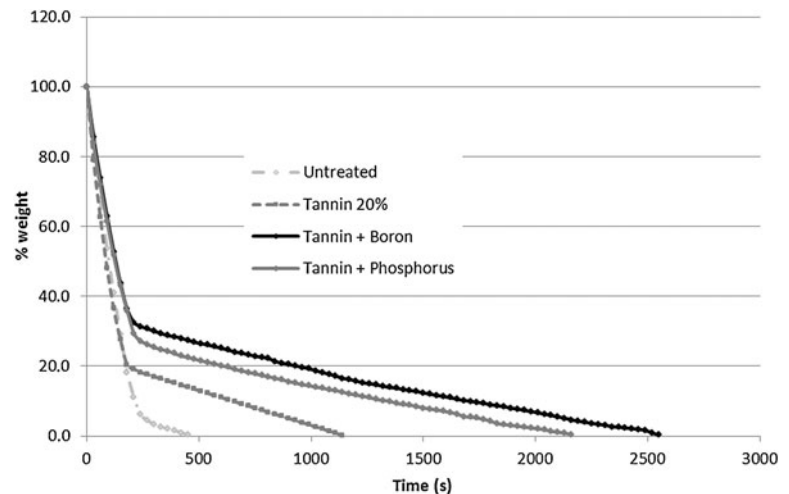
**Table 5** Short exposure fire tests for European beech

**Tab. 5** Ergebnisse der Kurzzeit-Brandbeanspruchungsversuche der Buchenproben

| Parameters                  | Ignition time (s) | Flame time 2 min (s) | Flame time 3 min (s) | Ember time 2 min (min) | Ember time 3 min (min) |
|-----------------------------|-------------------|----------------------|----------------------|------------------------|------------------------|
| Untreated                   | 12 ± 3            | 250 ± 60             | 310 ± 60             | 9 ± 2                  | 13 ± 2.5               |
| 10% Tannin                  | 40 ± 10           | 60 ± 10              | 180 ± 30             | 2.5 ± 0.5              | 11 ± 1.5               |
| 20% Tannin                  | 75 ± 20           | 15 ± 5               | 80 ± 20              | 3.5 ± 1.0              | 10 ± 1.5               |
| 20% Tannin + Boric Ac.1%    | > 120             | 25 ± 5               | 90 ± 15              | 0.8 ± 0.2              | 3 ± 1.0                |
| 20% Tannin + Phosph. Ac. 1% | > 120             | 22 ± 5               | 80 ± 15              | 1 ± 0.2                | 2.8 ± 1.0              |

**Fig. 3** Long fire exposure tests: Weight loss of Scots pine samples treated with different formulations

**Abb. 3** Langzeit-Brandbeanspruchungsversuche: Masseverlust der Kiefernproben in Abhängigkeit der Art der Imprägnierung



The weight loss for Scots pine samples is shown in Fig. 3.

The constant monitoring of these long-term exposure tests produces curves with the same tendency. During the initial time there is a high loss of weight, then the carbonized part protects the core wood from fire and consequently, the weight decrease occurs much more slowly.

In the case of tannin impregnation, the curve changes its slope significantly prior to that of the untreated sample. Even if this shift happens when the weight loss is already substantial (80%), it still allows the sample to resist the burning process for at least twice the time required to complete the burning.

This retardant effect can be further improved when inorganic compounds are added. The effect of boron appears to be stronger than that of phosphorus. Considering that boron is already included in the formulation for its high performing anti-biological properties, it means that there is a doubly

beneficial effect for the presence of boron in wood preservatives.

The data recorded for beech are similar to the ones for Scots pine. It has to be mentioned that in beech samples, the hardened tannin resin modifies the elasticity of the structure. When treated beech is exposed for a long time (> 3 minutes) to a flame it has the tendency to suddenly break.

This flame retardant action of tannin copolymers was already reported for other materials (Tondi et al. 2009a). However, the fire properties of tannin-hexamine copolymers have never been tested before and these preliminary tests show positive potential for further investigation, also in wood composite industries.

## 4 Conclusion

Tannin-boron-hexamine formulations were investigated to be effectively useful as preservatives for wood constructions

(Thevenon et al. 2009). This combination, which has already shown very good properties in wood preservation, seems to be really interesting for its mechanical and fire-retardant properties.

It has been seen that from the mechanical point of view there are no contra-indications. On the contrary, an increase in mechanical properties between 10 and 30% is indicated.

Scots pine increases its compression resistance by around 30% in compression and by 10% in bending resistance when impregnated with 10% tannin formulations.

Beech also increases its mechanical properties: 15 to 20% improvements are reported for samples treated with 20% tannin solutions.

The surfaces of the treated wood specimens become harder after each tannin-hexamine impregnation. The gluing properties of treated specimens are affected by the decrease in roughness of the treated wood, but especially in the case of pine, the shearing resistance is comparable with the one for internal resistance of this wood.

The most interesting aspect, however, is represented by the use of tannin as a fire retardant agent. In each test, there appeared to be clearly positive results. The presence of mimosa tannin in wood provides a broad, positive fire-retardant effect. In general, ignition and flame time are significantly diminished, while the loss of weight under continuous exposure to fire occurs more slowly. The use of boron and phosphorus in the formulation breaks down the ember time and slows down the loss of weight significantly.

The improvements gained in the mechanical and physical properties studied will serve to stimulate more interest in tannin-boron formulations for outdoor building preservation. All these considerations could open up new possibilities for the up-scaling of this technology based on tannin-boron synergies.

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## References

- DIN 52185 (1976) Testing of wood. Wood—compression tests—parallel to grain. German standard 09/1976
- DIN 52186 (1978) Testing of wood. Bending test. German standard 06/1978
- EN 113 (1997) Wood preservatives. Test method for determining the protective effectiveness against wood destroying basidiomycetes. Determination of the toxic values. 06/1997
- EN 1534 (2000) Wood and parquet flooring. Determination of resistance to indentation (Brinell). Test method. 06/2000
- Kamoun C, Pizzi A, Zanetti M (2003) Upgrading of MUF resins by buffering additives. Part I. Hexamine sulphate effect and its limits. *J Appl Polym Sci* 90:203–214
- Laks P, Peggy A, Hemingway RW (1988) Flavanoid biocides: wood preservatives based on condensed tannins. *Holzforschung* 42:299–306
- Lotz WL, Hollaway DF (1988) Wood preservation. US patent No. 4732817
- Pichelin F, Kamoun C, Pizzi A (1997) Hexamine hardener behaviour: effects on wood glueing, tannin and other wood adhesives. *Holz Roh- Werkst* 57:305–317
- Pichelin F, Nakatani M, Pizzi A, Wieland S, Despres A, Rigolet S (2006) Thick wood panels bonded industrially with formaldehyde free tannin adhesives. *For Prod J* 56:31–36
- Pizzi A (1994) Advanced wood adhesives and technology. Dekker, New York, pp 149–217
- Pizzi A, Baecker AW (1996) A new boron fixation mechanism for non-toxic wood preservatives. *Holzforschung* 50:507–510
- Schol G, Krause A, Militz H (2010) Exploratory study on the impregnation of Scots pine sapwood (*Pinus sylvestris L.*) and European beech (*Fagus sylvatica L.*) with different hot melting waxes. *Wood Sci Technol* 44:379–388
- Taira S, Ono M, Matsumoto N (1997) Reduction of persimmon astrin-gency by complex formation between pectin and tannins. *Posthar-vest Biol Technol* 12:265–271
- Thevenon MF, Pizzi A, Haluk JP (1998) Non-toxic albumin and soja protein borates as ground-contact wood preservatives. *Holz Roh- Werkst* 55:293–296
- Thevenon MF, Tondi G, Pizzi A (2009) High performance tannin resin-boron wood preservatives for outdoor end-uses. *Eur J Wood Prod* 67:89–93
- Thevenon MF, Tondi G, Pizzi A (2010) Environmentally friendly wood preservative system based on polymerized tannin resin-boric acid for outdoor applications. *Maderas* 12(3):253–257
- Tondi G, Zhao W, Pizzi A, Du G, Fierro V, Celzard A (2009a) Tannin-based rigid foams: a survey of chemical and physical properties. *Bioresour Technol* 100:5162–5169
- Tondi G, Oo CW, Pizzi A, Trosa A, Thevenon MF (2009b) Metal absorption of tannin based rigid foams. *Ind Crop Prod* 29:336–340
- Tondi G, Wieland S, Wimmer T., Thevenon M.F., Petutschnigg A (2012a) European Journal of Wood and Wood products Journal ID: 107, Article ID: 603, Date: 2012-02-23, Proof No: 1
- Tondi G, Thevenon MF, Wieland S, Pizzi A, Mies B, Standfest G, Petutschnigg A (2012b) Impregnation of scots pine and beech with tannin solution: high potential in wood preservation. *Wood Sci Technol* (submitted)
- Toussaint-Dauvergne E, Soulounganga P, Gérardin P, Loubinoux B (2000) Glycerol/glyoxal: a new boron fixation system for wood preservation and dimensional stabilization. *Holzforschung* 54:123–126
- Xie C, Ruddick JNR, Rettig SJ, Herring FG (1995) Fixation of ammoniacal copper preservatives: reaction of vanillin, a lignin model compound with ammoniacal copper sulphate solution. *Holz-forschung* 49:483–490
- Yamaguchi H, Okuda K (1998) Chemically modified tannin and tannin-copper complexes as wood preservatives. *Holzforschung* 52:596–602