Accepted version.
Published version: Constr Build Mater 2021;282:122723.
https://doi.org/10.1016/j.conbuildmat.2021.122723.

Assessment of *Dendrocalamus asper* (Schult and Schult f.) (Poaceae) bamboo treated with tannin-boron preservatives

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Abstract

Tannin-boron based preservative solutions were used for the treatment of *D. asper* bamboo by vacuum/pressure impregnation. Samples treated with tannin/hexamine-based solutions presented low weight losses after decay tests with *P. sanguineus* and *G. trabeum* decay fungi, and were classified as resistant and highly resistant, respectively, even after leaching. However, a high boron loss after severe leaching cycles was observed. Samples treated with tannin/hexamine/boron had superior mechanical properties and increased thermal stability. The use of tannin-based solutions in combination with boron compounds showed promising results in terms of mechanical properties improvement and increased fungal decay resistance, bringing new possibilities for bamboo preservation.

Keywords: bamboo; fungi decay; mechanical properties; treatment; thermal stability

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Accepted version.
Published version: Constr Build Mater 2021;282:122723.
https://doi.org/10.1016/j.conbuildmat.2021.122723.

1. Introduction

Although the use of bamboo as a sustainable material has received more attention in the last ten years (based on the numbers of related publications in this field), the potential of bamboo has been questioned due to several drawbacks. Owing to its chemical composition with high amount of starch (2-6%), sugar (2%) and protein (1.5-6%) and low contents of resin, wax and tannin [1–4], bamboo is very vulnerable to deterioration. Biological degradation bydecay fungi, termites and powderpost beetles (*D. minutus*), is the major restriction on bamboo use, especially in the construction industry [5–7]. Therefore, it needs preservative treatments.

Investigations on bamboo degradation when exposed to biological attack or outdoor conditions lead to use of different preservative methods and solutions to protect bamboo [6,8,9]. Chemical treatment methods serve as the most appropriate bamboo preservation methods and are recommended for large-scale construction projects [10,11]. However, careful considerations should be given to the selection of the materials to avoid human health-related problems related to hazardous chemicals [12,13]. Sustainability, as well as its effect on the physical and mechanical properties of bamboo, must be considered. Accordingly, less hazardous preservatives such as boron salts and tannins are becoming increasingly critical to diminish environmental impact [6,8,14].

Boron salts are very common for wood and bamboo treatment and are recommended worldwide for structural use, in situations where the bamboo is protected from external adversities, such as water and sun exposure, and without contact with the ground/soil [15–17]. Tannins, which are naturally derived substances [18,19], have been used as preservatives in wood products offering protection against light and weathering factors, and against deterioration by insects, fungi and bacteria [14,20–23]. Tannin extracts can be obtained from different sources, especially from tree barks, such as *Acacia mearnsii* [19,24]. They usually are used for leather production, animal feed, wood resins and other chemicals [19].

Although these two materials are efficient against termites, beetles and some fungi, they are extremely leachable when used alone [23,25,26], which limits the application of bamboo in more exposed conditions. Several alternative formulations have been developed to overcome this negative aspect in the wood industry. In the early studies on the use of tannins, it was found that

Accepted version.
Published version: Constr Build Mater 2021;282:122723.
https://doi.org/10.1016/j.conbuildmat.2021.122723.

condensed tannins were effective against decay fungi only when complexed with copper (II) ions [27]. Nevertheless, the use of tannin extracts in combination with boron has been highlighted to reduce the leaching of boron and tannin compounds because of in-situ polymerisation within the wood structure [14,23,28–32]. This combined preservative solution with a cross-linking agent (formalin, hexamine) at elevated temperature creates a material with improved characteristics and properties compared to the characteristics of the individual components, possessing positive results in terms of leachability, fungi decay resistance, and stability [30,32].

The tannin forms an insoluble polymerised network, while boron compounds such as boric acid can facilitate this reaction and be partially incorporated in the polymerised tannin [23,33]. The hard polymerised material partially occupies the wood's cavities, improving the mechanical properties of tannin-boron treated wood. However, there is a lack of information focused on this treatment for bamboo. Although bamboo is also a porous material whose main chemical composition is similar to wood [34], its decay resistance is quite different from that of wood [4].

Tannin and boron-based treatments have been explored as a viable and interesting method to improve wood degradation resistance. This treatment process is also hypothesised to be adequate for bamboo-based materials for higher added-value products. Therefore, this work focuses on assessing the treatability of bamboo with tannin and tannin-boron solutions and the corresponding mechanical and physical properties, fungi decay performance, and thermal stability of *D. asper* bamboo.

2. Materials and methods

2.1. Materials and samples preparation

Mature culms (more than three years old) of *D. asper* bamboo were collected in June (winter in Brazil) and conditioned in a protected environment. The culms were harvested at an experimental field in the University of Sao Paulo campus, Pirassununga, Brazil. Pirassununga is located at an altitude of 630 m above sea level, with an annual average rainfall of 1363 mm and a tropical climate with well-defined seasons (rainy summer and dry winter). Samples of six different

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https://doi.org/10.1016/j.conbuildmat.2021.122723.

internodes from the middle part (more uniform) of three different culms were used for this study. Tangentially oriented strips (20 per internode) were cut from the internode sections.

The apparent densities at approximately 7% MC and in the dry condition, the real density, fibre volume fraction, and chemical composition are shown in Table 1. The apparent densities were measured by the water immersion method at 27 °C (water density = 0.9965 g/cm^3), as described in ASTM Standard D2395−17. The fibre volume fractions were determined using images obtained by an optical stereoscope and analysed through ImageJ analysis software [35]. The real density was determined using a helium pycnometer, in which bamboo particles (dried at 60 °C for 48 h) representative of all the internodes (A-F) were used for the analysis. The same particles were used for chemical analysis that was carried out following the methodology proposed by Van Soest (1994) [36] described in Salman et al.(2010) and also used in other works to characterise lignocellulosic materials [37–39]. This method basically consists of separating cellular (lipids, fats, starch, water-soluble and nitrogen compounds) and cell-wall contents (holocellulose, lignin, insoluble protein) by using neutral and acid detergent solutions. First, the sample as a dry powder is heated in a neutral detergent solution and the cellular and cell-wall constituents are separated by filtration. The neutral detergent fibres (composed of alpha-cellulose, hemicellulose, and lignin) are then heated in an acid detergent solution to solubilise hemicellulose, which is separated from lignin and cellulose by filtration. The cellulose of the obtained acid-detergent fibres is then dissolved with a 72% H_2SO_4 solution. The balance between the solubilised and filtered fractions is used to calculate alpha-cellulose, hemicellulose, lignin, and extractives. The percentage of ash was obtained by burning the sample at 500 °C for 4 h.

Accepted version.
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Table 1 - Physical properties and chemical composition of D. asper bamboo used in this work.

Internode	Apparent density (g/cm^3)	MC (%)	Oven-dry apparent density (g/cm^3)	Real* density (g/cm^3)	Fibre** volume fraction (%)	Chemical composition*				
						α-C	L	H	E	A
A	0.978	7.5	0.949	-	-	-	-	-	-	-
B	0.979	7.6	0.942							
C	0.853	7.4	0.827							
D	0.882	7.5	0.845							
E	0.887	7.4	0.867							
F	0.894	7.8	0.864							
Avg	0.912	7.5	0.882	1.303	44.82	54.8	20.2	13.7	9.6	1.7
COV	0.06	0.02	0.06	0.03	0.08	-	-	-	-	-

α-C: alpha-cellulose; L: lignin; H: hemicellulose; E: extractives; A: ashes

* Real density and chemical composition were determined using ground material obtained from all internodes. ** Determined by the analysis of eight samples randomly chosen.

2.2. Tannin, boron compounds and hexamine reaction

Before bamboo treatment, the polymerisation of tannin with hexamethylenetetramine (hexamine) and the boron compounds boric acid (BA) and disodium octaborate tetrahydrate (DOT) (1.54:1 ratio borax/boric acid) was explored. Several formulations were prepared with different hexamine, boric acid, and DOT concentrations in relation to tannin (Table 2).The concentration of hexamine was based on the dry weight of tannin, and the concentrations of boric acid and DOT were based on the total solution weight. All the solutions were adjusted to pH = 9 using a 50% wt/vol NaOH solution. After preparation, the solutions were oven-dried at 103 ± 2 °C and then maintained in this temperature for 48 h for a complete polymerisation reaction.

After drying/curing process, the samples were crushed into particles (28 mesh) and subjected to a leaching process. For each condition, 4 g of solid material and 80 mL of distilled water were added into glass beakers. The samples were stirred every 24 h and maintained immersed for 72 h. Then the samples were filtered and dried to a constant weight at 103 °C. The

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https://doi.org/10.1016/j.conbuildmat.2021.122723.

obtained materials were submitted to a second leaching cycle (using the same previous procedure) and again filtered and dried at 103 °C. One replicate per formulation was tested.

The polymerisation of the tannin-based formulations were investigated through Fourier transform infrared (FTIR) spectroscopy. Samples were ground into a powder and passed through a 100-mesh sieve. The analyses were conducted using a PerkinElmer Spectrum One FTIR with the ATR (Attenuated Total Reflectance) universal sample accessory. For each analysis, 32 scans were used in the spectral region of 4000-600 cm^{-1} with a resolution of 4 cm^{-1}. Before the measurements, all the samples were dried at 60 ^{o}C until a constant weight was achieved.

The unleached and leached samples were analysed using a colourimetric method [40], which is also used to determine boron in plants [41]. The samples were calcined in a furnace at 550 °C for 4 h, and the ash was then digested with 25 mL of HNO_3 solution (0.1 M). Then, 1 mL of the obtained solution was diluted to 100 mL in HCl (0.1 M), and a buffer solution was added to control the pH. Azomethine-H was added to the diluted solution to react with boron. The solution was analysed in a UV-Visible spectrophotometer at 430 nm, and the obtained absorbance was used to calculate the boron concentration according to a previously prepared calibration curve.

Boric acid, borax, hexamine, and sodium hydroxide of analytical grade supplied by Labsynth®, Brazil, were used. *Acacia mearnsii* tannin powder (Phenotan AG) was gratefully provided by Tanac®, Brazil.

Table 2 - Tannin-based solutions used for the leaching test.

Sample	Solution composition
1	Tannin 10% + Hexamine 6%
2	Tannin 10% + Hexamine 10%
3	Tannin 10% + Hexamine 6% + Boric acid 1%
4	Tannin 10% + Hexamine 6% + Boric acid 5%
5	Tannin 10% + Hexamine 10% + Boric acid 1%
6	Tannin 10% + Hexamine 10% + Boric acid 5%
7	Tannin 10% + Hexamine 6% + DOT 1%
8	Tannin 10% + Hexamine 10% + DOT 1%
9	Tannin 10% + Hexamine 6% + DOT 5%
10	Tannin 10% + Hexamine 10% + DOT 5%

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https://doi.org/10.1016/j.conbuildmat.2021.122723.

Obs.: % of hexamine in relation to the dry mass of tannin and % of DOT and BA in relation to the total solution weight

2.3. Treatment process

Five samples per internode (total of 30 samples) 200 mm in length (parallel to the fibres), 30 mm in width, and thickness varying between 10-15 mm were used for each treatment condition . The same number of samples were used as references, i.e., bamboo without any treatment.The samples were oven-dried at 103 ± 2 °C until constant weight before the treatment and then conditioned at 25 °C and 70% RH for 240 h. This procedure was used to track weight changes after treatment. The samples were pressure treated following a vacuum/pressure schedule: initial vacuum (-650 mmHg) without any solution for 15 min, vacuum phase with the solution for 60 min, pressure phase (14.1 kgf/cm^2) for 180 min and final vacuum phase for 15 min. The obtained samples of each treatment were dried at room temperature for 48 h, oven-dried at 60 ±2 °C for 24 h, and finally cured at 103 ± 2 °C for 48 h for the reaction of tannin polymerisation to occur.

The treatment solutions were prepared by dissolving the tannin extract in 8 L of distilled water (10% wt/wt solution) and adding the cross-linking agent hexamethylenetetramine (hexamine) to the solution. For the tannin solution (T10H), 6% (by dry tannin weight) of hexamine was used. For the samples treated with the presence of boron (B5 and T10HB5) in the formulation, boric acid and disodium borate decahydrate (borax) in the ratio of 1: 1.54 by mass were used for the formation of DOT ($Na_2B_8O_{13}.4H_2O$). The tannin-boron solution (T10HB5) was prepared by first dissolving the boric acid and borax (5% wt/wt) and then adding the tannin extract (10% wt/wt) and hexamine (10% on dry tannin weight). The pH of all the tannin-based solutions was maintained at pH=9 using a NaOH 50% wt/vol solution.

2.4. Water absorption, swelling and leaching test

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Published version: Constr Build Mater 2021;282:122723.
https://doi.org/10.1016/j.conbuildmat.2021.122723.

The water absorption and swelling behaviours of treated bamboo were determined during a leaching test procedure. Sixteen 20 mm x 20 mm x thickness (t) samples per condition were extracted from the middle part of four different specimens after treatment. These samples were subjected to a leaching process for 12 days according to recommendations described in AWPA Standard E10:16. The treated samples were first dried at 60 °C to constant weight. The samples were then immersed in distilled water for the determination of water absorption (WA) and thickness and width swelling (TS and WS, respectively) after 12 h and 24 h of immersion. The dimensions of the samples were measured (± 0.01 mm) and then weighted (± 0.001 g). WA, TS, and WS were calculated in relation to the initial weight and dimensions of the samples after drying at 60 °C. After the measurements, the water was changed, and the samples were conditioned in a steel vessel where a vacuum (-650 mmHg) was applied for 60 min to guarantee total penetration of water. Following this, the water was replaced after 12 h and then every 24 h for 12 days. After the completion of the leaching process, the final weight and dimensions of the samples were obtained, and they were again dried at 60 °C until a constant weight was achieved.

2.5. Boron retention analysis

The samples treated with formulations based on DOT were subjected to boron retention analyses conducted according to Brazilian Standard ABNT NBR 6232:2013. For the chemical analyses, samples (20 mm x 20 mm x thickness) extracted from the middle part of four different specimens treated with boron-based formulations (leached and unleached) were ground into a powder and passed through a 28-mesh sieve. The obtained material was subjected to sulphuric acid digestion, diluted and analysed by atomic absorption spectroscopy. The chemical analyses were performed in the Trees, Wood, and Furniture Laboratory at the Institute for Technological Research (IPT), São Paulo, Brazil, following the same procedures used for treated wood. The amount of equivalent B_2O_3 was calculated according to:

$$Retention\ (B_2O_3) = \left(\frac{B \times \rho}{100}\right) \times 3.22 \qquad \text{Eq. 1}$$

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Where B is the weight percentage of boron in the analysed sample (in %), ρ is the oven-dry apparent density of the sample (in kg/m^3), and 3.22 is a stochiometric factor for obtaining the amount of B_2O_3 based on the amount of boron.

2.6. Accelerated fungi decay test

A modified fungal decay test was performed in the Institute for Technological Research (IPT), São Paulo, Brazil, based on a previous method [42]. This methodology is conducted by placing the samples directly on agar medium inoculated with fungi, similarly to the agar block test described in BS Standard EN 113:1997. Small samples of 20 x 3 x thickness (t) mm³ were extracted from the middle section of four different specimens and tested in Petri dishes. Samples extracted from the specimens submitted to the leaching cycles described in 2.4 were also tested. Sixteen samples per condition were tested against the fungi strains *Pycnoporus sanguineus* (white-rot) and *Gloeophyllum trabeum* (brown-rot), obtained from IPT. First, the fungi were cultivated in potato dextrose agar (PDA) for two weeks in Petri dishes. Before the exposure of the samples, they were conditioned at 26 °C and 70% RH for two weeks until a constant weight (initial weight). The samples were then sterilised at 120 °C for 15 min and allocated aseptically in the Petri dishes (four Petri dishes with four samples per condition per fungus) to be exposed to the fungi. After eight weeks of test, the samples were removed from the climatic chamber, cleaned, dried at 60 °C for 2 hours, and then conditioned at 26 °C and 70% RH until a constant weight (final weight). The initial and final weights were used to calculate the weight loss.

2.7. Mechanical characterisation

Machined coupon specimens, representing the full wall thickness, were used for compression, bending, and shear tests. For all the tests, the samples were extracted from six to eight different specimens, representing all the internodes. All required specimen dimensions were measured using a digital calliper (± 0.01 mm). The moisture contents at the time of test were determined by weighing the samples before testing and after drying at (100 ± 2) °C for at least 48 h.

Accepted version.
Published version: Constr Build Mater 2021;282:122723.
https://doi.org/10.1016/j.conbuildmat.2021.122723.

Compression tests parallel to the bamboo longitudinal axis (parallel to fibres) were performed with samples with transverse sections having the same size as the culm wall (t x t) and length four times the thickness (L= 4t). Twelve samples per condition were tested in a 600 kN capacity Instron universal testing machine (model 600DX) at a cross-head displacement rate of 0.5 mm/min. The tests and calculations followed the recommendations of ASTM D143-14. The longitudinal compression strength (f_c) is reported as the maximum load divided by the cross-section area of the sample.

Three-point bending tests were conducted using samples in a prismatic form with 200 x 10 x thickness (t) mm^3. A span of 190 mm was used for all the tests, which resulted in an average shear span to depth ratio exceeding 10 in every test. For the sake of comparison to other studies, the samples were oriented such that the outer culm wall was in compression (OC). This orientation also results in higher modulus of elasticity and modulus of rupture [43]. The tests were conducted following Procedure A of ASTM D7264-15 as modified by others [43–45] using a 10 kN capacity Testresources electromechanical universal testing machine at a displacement rate of 2.5 mm/min. Sixteen samples per condition were tested. The modulus of rupture (MOR), modulus of elasticity (MOE) and specific strain were calculated according to ASTM D7264-15. The displacement of midheight (t/2) of the sample at midspan was tracked using a Digital Image Correlation (DIC) setup [43].

The shear behaviour of the treated bamboo samples was evaluated through an interlaminar shear test by tension [46,47]. Coupon specimens were scored halfway through their depth perpendicular to the loading direction at two locations resulting in a shear plane having an area A = $L_s \times t$. Since the shear plane was at the middle of the specimen, the plane was subjected to pure shear when loaded in tension. The shear strength was then calculated using the maximum load at failure divided by the shear area A. Ten Samples per condition were tested in a 10 kN capacity Testresources electromechanical universal testing machine using a displacement speed of 1.0 mm/min.

2.8. Thermal characterisation

Accepted version.
Published version: Constr Build Mater 2021;282:122723.
https://doi.org/10.1016/j.conbuildmat.2021.122723.

The thermal characterisation was performed to understand the thermal degradation of bamboo treated with DOT and tannin-based solutions. For the analyses, samples extracted from the middle part of four different specimens of each condition were ground into a powder, passed through a 60-mesh sieve and dried at 60 °C for 48 h. The tests were conducted in a Netzsch TGA/DSC model STA 449 F3 Jupiter using synthetic air (79.5% N_2 and 20.5% O_2) at a flow rate of 100 mL/min from room temperature up to 800 ºC at 10 ºC/min. The synthetic airflow was used to better understand the behaviour of the material in a real environment, in the presence of oxygen. This procedure has been demonstrated to be correlated with limiting oxygen index (LOI) flammability tests [48–52].

2.9. Statistical analyses

The averages of each test for each test condition were calculated with the corresponding coefficient of variation (COV) and the number of samples. The differences among the treatment conditions on the evaluated properties were analysed by a Tukey test and analysis of variance (ANOVA) for significant ($p < 0.05$) differences. All analyses were performed using MINITAB Release 18 Statistical Software.

3. Results and discussion

3.1. The polymerisation reaction of tannin, boron compounds and hexamine

Previous studies have reported the use of tannin solutions based on mimosa tannin extract (10-35% solution), hexamine (6% by mass on dry tannin), and boric acid (5% on total solution weight) as a boron source [31,33,53,54]. The pH of the solution can also influence the polymerisation process. Usually, a pH correction of the tannin-based solutions to a pH = 9 is performed with a NaOH solution before the curing heat treatment [53,54]. In fact, pH can influence the solubility of the formed compounds and solution viscosity before polymerisation [54–56].

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Another important aspect is that ordinarily, only boric acid is utilised in the formulations reported in the literature.

The results obtained after the leaching process are presented in Table 3. Firstly, it can be seen that the increase of the hexamine concentration in the formulation had no influence on the solubility of the formed compounds, especially when observing samples 1 and 2. Samples with higher concentrations of boric acid and DOT showed the highest losses after leaching, which may be related to boric acid or DOT in excess or unreacted with the tannin polymer network. Regarding the loss of boron, all formulations had a considerable boron loss but retained more than 50% of the original boron even after the leaching process. It should be noted that both boric acid and DOT are very soluble, and if not in combination with tannin, the loss of boron would be total. Increased hexamine concentration in samples 4, 6 and 10 was associated with reduced boron leaching, especially in sample 4. However, among the formulations with higher concentrations of boric acid and DOT, sample 10 presented the lowest boron and weight losses after leaching.

Figure 1 depicts the FT-IR spectra of tannin-based compounds; pure tannin and samples 2 (T10H1.0), 6 (T10H1.0B5), and 10 (T10H1.0DOT5). The addition of hexamine alters the tannin structure, due to the differences in the obtained spectrum and consequently of the chemical bonds. It is mainly noted a difference regarding the groups C = C of aromatics (1600 cm^{-1}) and the absence of peaks between 1450 cm^{-1} and 1500 cm^{-1} in tannin samples with DOT and BA + Hexamine, which is related to the tannin polymerisation process [55,57]. A difference in the 1600 cm^{-1} peak (aromatics) is observed in the samples with and without boron. The more pronounced hump between 1350-1500 cm^{-1} of the TH1.0DOT5 and TH1.0BA5 samples may be attributed to B–N stretching (1465–1330 cm-1) and B–O stretching (1380–1310 cm-1) [58]. However, there is no noticeable difference between the samples with BA and DOT.

Concerning the results presented in Table 3, solutions based on the formulations of the samples 1 and 10 were used for bamboo treatment by vacuum/pressure process. For the tannin + hexamine samples, the amount of hexamine did not change the weight loss after leaching, and therefore, a higher amount of hexamine is unnecessary. In the case of the tannin + hexamine + boron samples, sample 10 had the lowest weight loss (among the high boron content samples), and the increase of hexamine helped to reduced boron loss.

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https://doi.org/10.1016/j.conbuildmat.2021.122723.

Table 3 - Results of weight loss and boron analysis of all the conditions submitted to the leaching cycles.

Sample	Solid composition (%)				Weight loss after leaching (%)	Boron analysis (mg/kg - ppm)		
	Tannin	Hexamine	DOT	BA		Unleached	Leached	Boron loss (%)
1	94.3	5.7	-	-	1.99	-	-	-
2	90.9	9.1	-	-	1.94	-	-	-
3	86.2	5.2	-	8.6	3.04	11,478	8,744	23.81%
4	83.3	8.3	-	8.3	2.74	12,973	11,542	11.03%
5	64.1	3.9	-	32.0	24.84	33,055	16,768	49.27%
6	62.5	6.3	-	31.2	23.96	34,535	18,536	46.32%
7	86.2	5.2	8.6	-	0.29	12,137	7,136	41.20%
8	83.3	8.3	8.3	-	0.68	11,044	6,477	41.35%
9	64.1	3.9	32.0	-	19.19	33,570	17,668	47.37%
10	62.5	6.3	31.2	-	18.48	31,030	18,552	40.21%

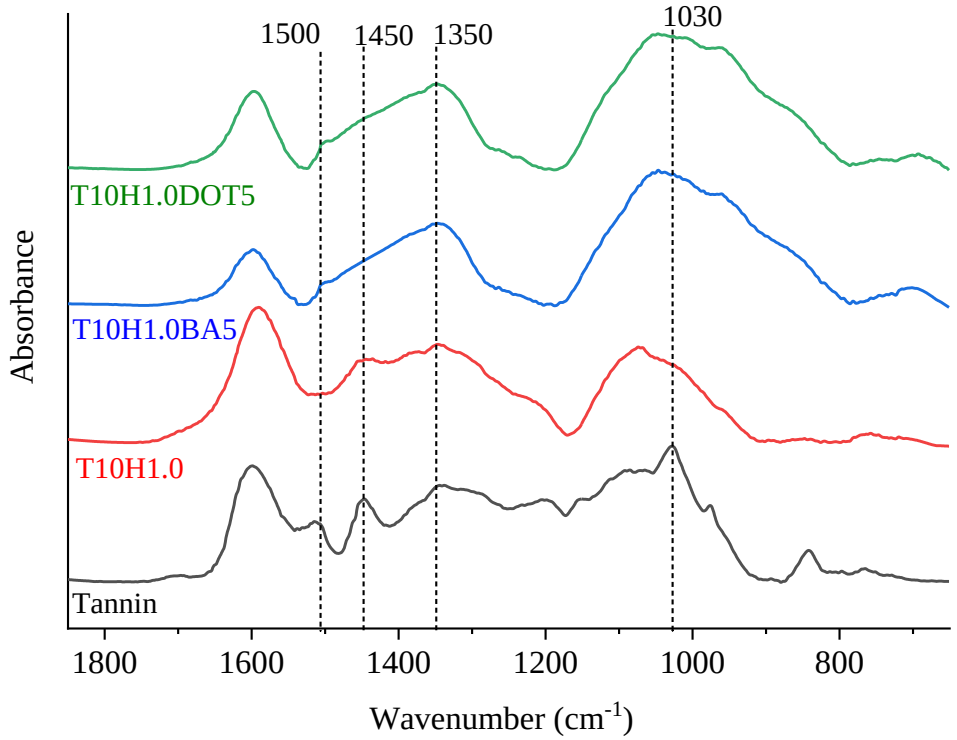

Figure 1– FT-IR spectra of polymerised tannin formulations.

3.2. Bamboo treatment

Accepted version.
Published version: Constr Build Mater 2021;282:122723.
https://doi.org/10.1016/j.conbuildmat.2021.122723.

Table 4 gives the solution absorption (weight of preservative solution absorbed in relation the weight of the samples before treatment) and weight percentage gain (WPG) (the relation between the dry weight of the samples after and before treatments). Before treatment, the samples had an average moisture content of 7.1% (COV=0.05).

Bamboo has a high amount of extractives, which can leach during treatment and explain the low WPG values. For the tannin based solutions, the WPG were equivalent to retention values (R) of 24.17 kg/m^3 and 24.7 kg/m^3 for TH10 and TH10B5, respectively, calculated by the formula: $R\left(\frac{kg}{m^3}\right) = \frac{W_{A.I}\,(g)}{\rho_{a\,(\frac{g}{cm^3})}}.10$, where $W_{A.I}$ is the weight of retained active ingredient and ρ_a the dry apparent density of bamboo. Tondi et al. (2013) reported absorptions of up to 180% and 120% for scots pine and beech woods respectively, using 10% tannin extract solutions and vacuum impregnation. These wood species have a porosity of 65.7% (scots pine) and 48.4% (beech) [30]. In comparison, the porosity of the bamboo used in this study, using the dry apparent density and real density (Table 1), was 32.3%, which explains the lower absorption values observed in bamboo. Additionally, since bamboo does not have pathways for radial penetration, like in wood, the penetration within the bamboo microstructure mainly occurs in the metaxylem vessels and the access to parenchyma is limited [59,60]. Therefore, the accessibility of the solutions into the bamboo structure is limited by anatomical features, even using vacuum/pressure impregnation for treatment.

Table 4 - Sample conditions after the treatment processes.

ID	Treatment solution composition	Solution absorption wt (%)		WPG After drying (%)	
		avg.	COV	avg.	COV
B5	DOT 5%	49.5	0.09	0.04	-
TH10	Tannin 10% + Hexamine 10%	42.6	0.10	2.74	0.12
TH10B5	Tannin 10% + Hexamine 10% + DOT 5%	38.9	0.11	2.80	0.10

Obs.: % of hexamine in relation to the dry mass of tannin and % of DOT and BA in relation to the total solution weight

Accepted version.
Published version: Constr Build Mater 2021;282:122723.
https://doi.org/10.1016/j.conbuildmat.2021.122723.

3.3. Water absorption, swelling and leaching

Table 5 gives the results of water absorption (WA), thickness (TS) and width swelling (WS) after 12, 24, and 288 h (end of the leaching process). The statistical analysis presented in the Tables refers only to the comparison among the treatment conditions (Reference, B5, T10HB5, and T10H) for each analysed property. The change in dimensions was tracked measuring the thickness and width in the middle of the samples. Because of the bamboo samples natural curvature, the volumetric changes were not considered. The changes in length were negligible (less than 0.4% in all treatment conditions after 288h) and, therefore, were not included in Table 5.

The three treatments had a small positive effect on WA, TS, and WS reduction. In the properties measured at 12 h, all the results are similar. However, at the end of the experiment (t = 288 h) the treatments caused a small decrease in WA, TS, and WS, especially the T10HB5 condition. The change in WA and dimensions were more evident in the first 24 h of immersion.

Tondi et al. (2012c) studied the dimensional stability of wood in different values of relative humidity treated with 10% and 20% tannin solutions. They concluded that there is no considerable difference in comparison to the reference, with only a small increase in radial swelling of the treated wood [53]. To the best of our knowledge, there is no available data in the literature about physical properties of bamboo treated with tannin and boron preservatives. From the obtained results, we can conclude that the treatments investigated in this work had little effect on the hydrophilicity behaviour of bamboo.

Table 5 - Summary of water absorption and swelling results. Same letters in the same row (a, b, or c) mean there is no statistical difference among treatment conditions.

Treatment conditions						
n = 16			Reference	B5	T10HB5	T10H
Water absorption (%)	12h	Avg.	28.96 [a,b]	27.67 [b]	29.37 [a]	30.23 [a,b]
		COV	0.06	0.13	0.08	0.05
	24h	Avg.	39.72 [a]	36.09 [b]	37.61 [a,b]	38.56 [a,b]
		COV	0.05	0.10	0.07	0.04
	288h	Avg.	67.43 [a]	59.18 [b]	59.62 [b]	61.96 [b]
		COV	0.05	0.07	0.06	0.03

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https://doi.org/10.1016/j.conbuildmat.2021.122723.

Swelling (%)	Thickness	12h	Avg.	6.81 [a]	6.09 [a,b]	5.86 [b]	5.96 [a,b]
			COV	0.11	0.18	0.13	0.10
		24h	Avg.	10.13 [a]	8.49 [b]	8.11 [b]	7.94 [b]
			COV	0.10	0.14	0.14	0.11
		288h	Avg.	13.12 [a]	11.19 [b]	10.35 [b,c]	9.70 [c]
			COV	0.08	0.16	0.15	0.13
	Width	12h	Avg.	3.93 [a]	3.92 [a]	3.67 [a]	3.85 [a]
			COV	0.16	0.14	0.09	0.14
		24h	Avg.	5.43 [a]	5.12 [a,b]	4.54 [b,c]	4.76 [c]
			COV	0.14	0.09	0.10	0.13
		288h	Avg.	6.95 [a]	6.75 [a]	5.67 [b]	5.81 [b]
			COV	0.11	0.08	0.08	0.13

Water causes severe leaching of wood preservatives, especially for boron-based formulations. Therefore, leaching tests are essential to evaluate the performance of treated wood/bamboo. Table 6 shows the results of the leaching tests with the corresponding boron loss. This was a severe leaching test, with the main idea of testing the treated materials in harsh conditions. After the test, the samples treated with T10HB5 had the lowest weight loss among all the analysed conditions. However, the boron loss was the same as the B5 samples, treated only with DOT. Although the primary purpose was to reduce boron leaching by using a polymerised tannin network, the leaching cycles used in this study seemed to be capable of solubilising most of boron. Interestingly, when tested independently (results of section 4.2.3.1), the same formulation preserved 60% of boron. In the work of Tondi et al. (2012c), they reported that approximately 20% of tannin was leached using 20% tannin solution and 35% was leached using a 10% tannin solution. Although using hexamine as a cross-linking agent, the tannin loss was attributed to unreacted tannin within the wood's structure. After leaching cycles according to the standard EN 1250-2 (1995), Tondi et al. 2012a reported a boron loss of approximately 30% for scots pine and approximately 22% for beech wood after 80 h of test with the water changed 6 times. In the same work, it is possible to observe that most part of unreacted boron leaches out in the first leaching cycles. Although the tannin-based solutions significantly reduced boron leaching

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https://doi.org/10.1016/j.conbuildmat.2021.122723.

in the investigated conditions, the effect of longer-term and harsher leaching tests were not performed, which could lead to further boron loss.

The polymerisation of tannin network within bamboo's structure could have had its reaction affected by the presence of bamboo constituents and therefore, affected the boron fixation. Nevertheless, we can observe that a small amount of boron is still present in the leached samples.

Table 6 - Mass loss after leaching cycle and B2O3 equivalent retention before and after leaching.

Conditions		Weight loss after leaching (%)	B_2O_3 eq. retention (kg/m^3)		Boron loss (%)
			Before leaching	After leaching	
Reference	Avg.	6.65	-	-	-
	COV	0.07			
B5	Avg.	6.63	4.66	0.82	82.4
	COV	0.10	-	-	-
T10H	Avg.	6.77	-	-	-
	COV	0.10			
T10HB5	Avg.	5.66	3.01	0.55	81.7
	COV	0.08	-	-	-

3.4. Fungal decay tests

Bamboo samples were tested in pure cultures of *P. sanguineus* and *G. trabeum* to evaluate the efficiency of the proposed treatments against fungi decay.

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Table 7 shows the weight loss results (WL), with the corresponding ANOVA analysis, of all the conditions (leached and unleached) for both *P. sanguineus* and *G. trabeum* fungi. The first thing to notice is that *P. sanguineus* caused higher WL than *G. trabeum* in all treatment conditions. The effect of the leaching process is also clearly noticeable. Interestingly, even with the high boron loss of the T10HB5 samples (see Table 6), this condition presented the lowest WL among the leached samples in both fungi tests. On the other hand, although the B5 samples had the best performance in the unleached condition (4.50% and 3.37% for the *P. sanguineus* and *G. trabeum* respectively), the leached samples had WLs similar to the reference.

Table 7 - Results of fungi decay tests presented in weight loss percentage. Same letters (a, b, or c) mean there is no statistical difference among treatment conditions.

Weight loss – WL (%)								
Condition	*P. sanguineus* n=16				*G. trabeum* n=16			
	Unleached		Leached		Unleached		Leached	
	Avg.	COV	Avg.	COV	Avg.	COV	Avg.	COV
Reference	9.26 [a]	0.23	15.03 [a]	0.22	6.02 [a]	0.11	10.52 [a]	0.66
B5	4.50 [c]	0.28	10.51 [a,b]	0.51	3.37 [c]	0.39	13.37 [a]	0.53
T10H	6.98 [b]	0.25	9.79 [b]	0.65	3.81 [b,c]	0.27	3.48 [b]	0.63
T10HB5	5.28 [c]	0.27	7.58 [b]	0.88	4.47 [b]	0.21	1.35 [b]	0.90

White-rot fungi (such as *P. sanguineus*) degrade lignin and hemicellulose while brown-rot fungi (such as *G. trabeum*) are selective for cellulose [61]. Results of bamboo fungi decay are scarce, especially about treated bamboo. Suprapti (2010) subjected different bamboo species were

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https://doi.org/10.1016/j.conbuildmat.2021.122723.

subjected to decay by white-rot, brown-rot and soft-rot fungi [62]. For *D. asper* bamboo the highest weight losses were caused by the white-rot fungus *P. sanquineus*, and the materials was classified as non-durable. On the other hand, Wei et al. (2013) found weight losses below 5% of *D. asper* bamboo tested against the brown-rot fungus *G. trabeum*.

Tiburtino et al. (2015) tested *B. vulgaris* and *D. giganteus* (commonly confused with *D. asper* in Brazil) samples treated with CCB against *Rhodonia placenta* (brown-rot) and *Polyporus fumosus* (white-rot). For the reference (control) samples, they reported a weight loss in *D. giganteus* of 10.83% and 8.35% for *R. placenta* and *P. fumosus* respectively. *B. vulgaris* presented similar values; 8.33% and 11.24% for *R. placenta* and *P. fumosus* respectively. They also tested the effect of different treatment methods using 1% and 3% CCB (oxide based) solutions. The 3% CCB treated samples had the best results for both species (lowest weight loss in both fungi).

Tannin treatments also presented promising results in wood. In the work of Silveira et al. (2017), acacia wood samples treated with A*cacia mearnsii* tannin extract showed good results in terms of fungi decay by *P. sanguineus*. The treatment using a tannin solution of 10% decreased the WL from 28.07% (reference without treatment) to 5.96%. In comparison, CCB (2.5% solution) treated samples presented a WL of 2.67%. By using tannin-hexamine-boron formulations, Tondi et al. (2012b) studied fungi degradation of treated European beech and pine woods. Pine wood treated with solutions with different compositions (between 10-20% of tannin and 0.1-4.1% of boric acid), decayed by *Coniophora puteana* fungi (brown-rot) after leaching, presented WL between 0.1-3.2%. The reference (without treatment) had an average WL of 42.6%. Tannin-only solution was not tested. Similar values are reported for European beech decayed by *C. versicolor* (white-rot).

The data from Table 7 can be better visualised in the boxplot of Figure 2. There is a considerable deviation of the weight loss data, especially on the leached samples, which may be attributed inhomogeneous leaching of the preservatives. Nonetheless, we can see the positive effects of the tannin-based treatments even after the leaching cycles, especially on the samples decayed by *G. trabeum* fungi. It is also possible to notice graphically that the leached reference and B5 samples have the same behaviour.

The samples treated with tannin-based formulations can be classified (as per EN 350-1:1996) as durability Class 2 (durable – 5% < WL ≤ 10%) against *P. sanguineus* and Class 1

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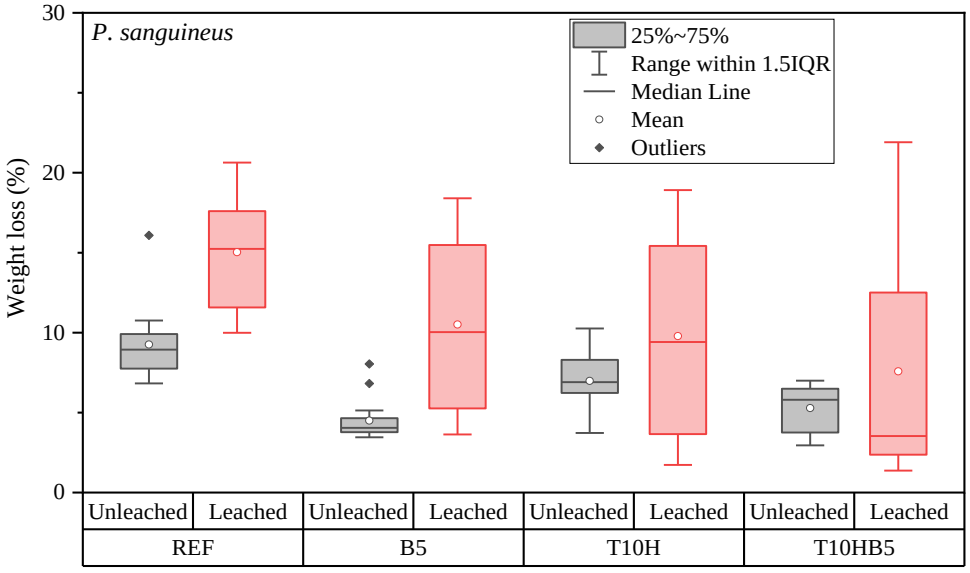
(highly durable - WL < 5%) against *G. trabeum* for both leached and unleached samples. Although Class 1 is achieved against both fungi for the unleached B5 samples, the leached ones had the same classification as the reference, Class 3 (moderately durable - 0% < WL ≤ 15%). A high boron loss was observed in the T10HB5 samples after leaching but both tannin-based formulations presented satisfactory results after fungi decay test. It suggests that part of the polymerised tannin was stable even after the leaching cycles and sufficient to reduce the fungi decay on bamboo.



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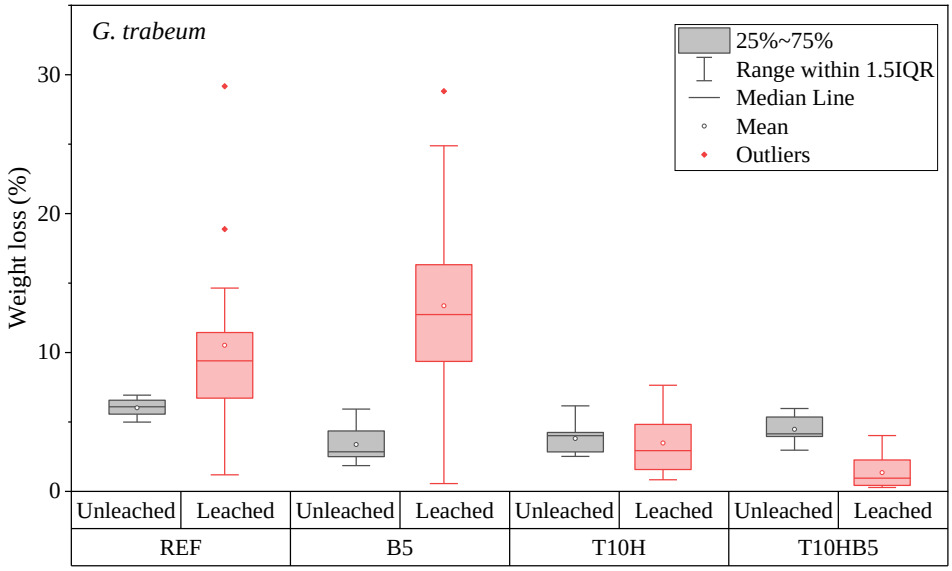

Figure 2 - Boxplot of the results Comparing weight losses of untreated or boron/tannin treated bamboo samples exposed to *P. sanguineus* or *G. trabeum* in an agar block test.

3.5. Mechanical properties

Table 8 presents a summary of the mechanical properties obtained by compression, inter-laminar shear and three-point bending of all the investigated conditions. The first thing to notice is the small increase in the density of the treated samples, which may be attributed to the solid particles of boron and tannin occupying part of the voids. In bamboo and wood, the increase in density is generally accompanied by an improvement of the mechanical properties. Figure 3a presents an optical microscopy image of a typical microstructure of the bamboo used in this study, mainly composed of parenchyma, fibre bundles and vessels. The tannin-based solutions were found to be concentrated in bamboo vessels, as indicated in Figure 3b on the left. However, some of the vessel walls collapsed on the samples treated with tannin-based solution, which is assumed to be caused by the high pressure used for impregnation.

An increase in the compression strength (f_c) of all the treated samples was observed; 24.12%, 10.45%, and 18.90% for the B5, T10H, and T10HB5, respectively. In the bending tests, there appeared to be clearly positive results for all three treated samples groups. The T10HB5 treatment presented the highest values for MOR and MOE, with an increase of 13.38% and 8.9% respectively, in comparison with untreated samples. The observed increase on the f_c, MOR and

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MOE of the samples treated with boron corroborates with our previous results confirming that DOT improves the overall mechanical properties of bamboo [7].

According to the results of inter-laminar shear, although it was observed a slight increase of 1.19% in the case of DOT treated samples and a slight decrease of 5.95% and 7.14% in the case of T10H and T10HB5 samples, respectively, this difference is not statistically significant ($p > 0.05$). The small reduction in f_v may be caused by the collapse of part of the conductive vessels (Figure 3b).

The improvement of the mechanical performance by using tannin-based treatments is in line with the outcome of research performed by Tondi et al., where especially hardness is improved because of the reticulation of the tannin-hexamine resins in the wood cells [30]. The polymerisation reaction of tannin-hexamine within bamboo's structure is also thought to contribute to strength improvement.

Table 8 - Summary of mechanical properties results. Same letters (a, b, c, or d) mean there is no statistical difference among treatment conditions.

Condition	ρ (g/cm^3)	MC (%)	Compression // fibres n=12		Interlaminar shear n=10		Three-point bending n=16			
			f_c (MPa)		f_v (MPa)		MOR (MPa)		MOE (GPa)	
			Avg.	COV	Avg.	COV	Avg.	COV	Avg.	COV
Reference	0.88	7.2	105.3^{a}	0.05	8.4^{a}	0.11	215.3^{a}	0.09	21.45^{a}	0.04
B5	0.92	7.1	130.7^{d}	0.04	8.5^{a}	0.13	242.6^{b}	0.09	23.34^{b}	0.05
T10H	0.90	7.0	116.3^{b}	0.03	7.9^{a}	0.13	222.5^{a,b}	0.13	22.01^{a,b}	0.05

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https://doi.org/10.1016/j.conbuildmat.2021.122723.

T10HB5	0.91	7.3	125.2[c]	0.03	7.8[a]	0.11	244.1[b]	0.10	23.36[b]	0.04

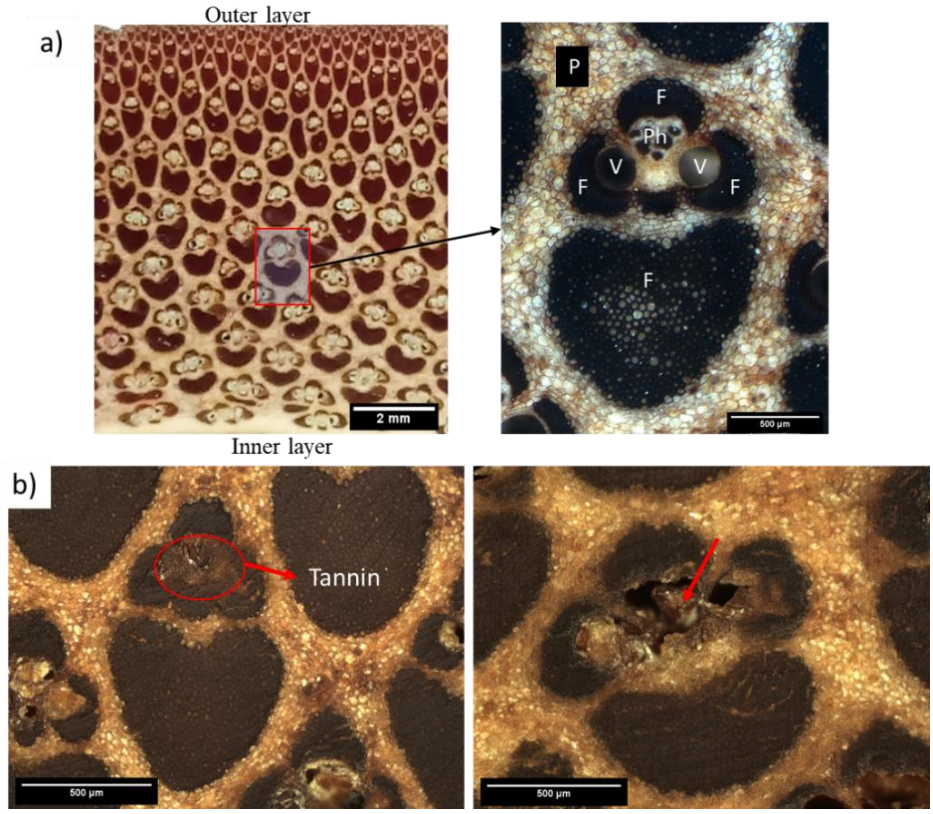

Figure 3 - Optical microscopy of *D. asper* bamboo and a) its main constituents (F – Fibre bundles; Ph – Phloem; V – Vessels; P – Parenchyma) and b) samples treated with a tannin-based solution.

3.6. Thermal degradation

Thermogravimetric analysis (TGA) can be a powerful tool to understand the thermal stability of bamboo. Characteristics from the TG curve can be correlated with flammability tests by using synthetic air during the test [49]. Jian et al. (2015) studied the effect of flame retardants on Chinese fir wood and reported an increased char formation at 400 °C in the TG test under synthetic air as the limiting oxygen index (LOI) increased. Higher pyrolysis temperatures and slower weight loss at a specific temperature range imply better thermal stability of wood. Flame retardants are used to achieve these properties [48]. By using urea-formaldehyde oligomer and

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phosphorus acid flame retardants, for example, the combustibility in wood is suppressed, leading to the formation of more char over flammable pyrolysis products[49].

Figure 4 shows the TG curves and its derivative with respect to time (DTG) for the reference and treated samples. Differences in weight loss behaviour among the treated conditions in relation to the reference can be observed, especially the samples with boron (B5 and T10HB5). Table 9 gives the residual char at 400 °C, and the T_{max} (temperature of maximum weight loss rate) obtained using the TG and DTG curves. The boron retention values are also presented. The B5 and TH10B5 samples showed the highest char yield, with an increase of 25.9% and 14.7%, respectively, in relation to the reference. T_{max} also increases in both conditions, proportionally with boron retention values. These results can be attributed to the suppression of part volatile gases by the boron compounds. The effect of boron compounds as fire retardant is well known [48,63]. The flame-retardant mechanism of boric acid is primarily physical. During heating, it forms a glassy coating (boron trioxide) on the solid surface trapping volatile pyrolysis products which decreases oxygen diffusion and, consequently, prevents the propagation of exothermic combustion reactions [63]. It is worth mentioning that DOT had demonstrated better fire retardant effect than pure boric acid or borax [64].

Notably, although no boron is present in the T10H condition, there is an increase of 14.7% in the percentage of residual char but no change in the T_{max}. In fact, Tondi et al. (2012a) reported the positive effects of polymerised tannin-hexamine treatment on the reduction of ignition, flame and ember times of Scots pine and European beech woods (tannin only and tannin with boric acid/phosphoric acid).

The TG and DTG curves in Figure 4 can be divided into different stages. The samples without boron presented 3 stages while the B5 and T10HB5 conditions presented 4 stages (delimited in Figure 4a). Table 10 summarises the characteristics of each stage, showing the weight loss, initial temperature (T_i), and final temperature (T_f). Between room temperature and around 160 °C (T_1) the weight loss is mainly caused by the evaporation of water. The second stage (from 160 to 370 °C) is characterised by the decomposition of hemicellulose and cellulose into char, CO_2, CO, CH_4, CH_3OH, CH_3COOH, and other components [48]. In this phase, the positive effects of the presence of boron are evident. The decrease in weight loss and T_f are proportional to boron retention. The T10H condition also had a decrease in weight loss, which corroborates with the

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result of residual char. Lignin and cellulose degrade in temperatures between 370 and 550 °C (T_3) [48]. Although the TH10 condition had an increase in the temperature of maximum degradation ($T4_f$), the weight loss in this stage was similar to the reference. In this temperature range, the samples B5 and T10HB5 presented a fourth stage (T_4), which extended the temperature of maximum degradation to 590 °C and 578 °C for the B5 and T10HB5 conditions respectively. This effect can be related to the suppression of combustible gases and dehydration of DOT in this temperature range, increasing the temperature of maximum weight loss.

Table 9 - Residual char and Tmax of bamboo samples subjected to TG analysis.

Condition	B_2O_3 eq. retention (kg/m^3)	Residual Char (%) at 400°C	T_{max} (°C)
Reference	-	35.77	288
B5	4.66	45.05	320
T10H	-	41.04	286
T10HB5	3.01	42.88	307

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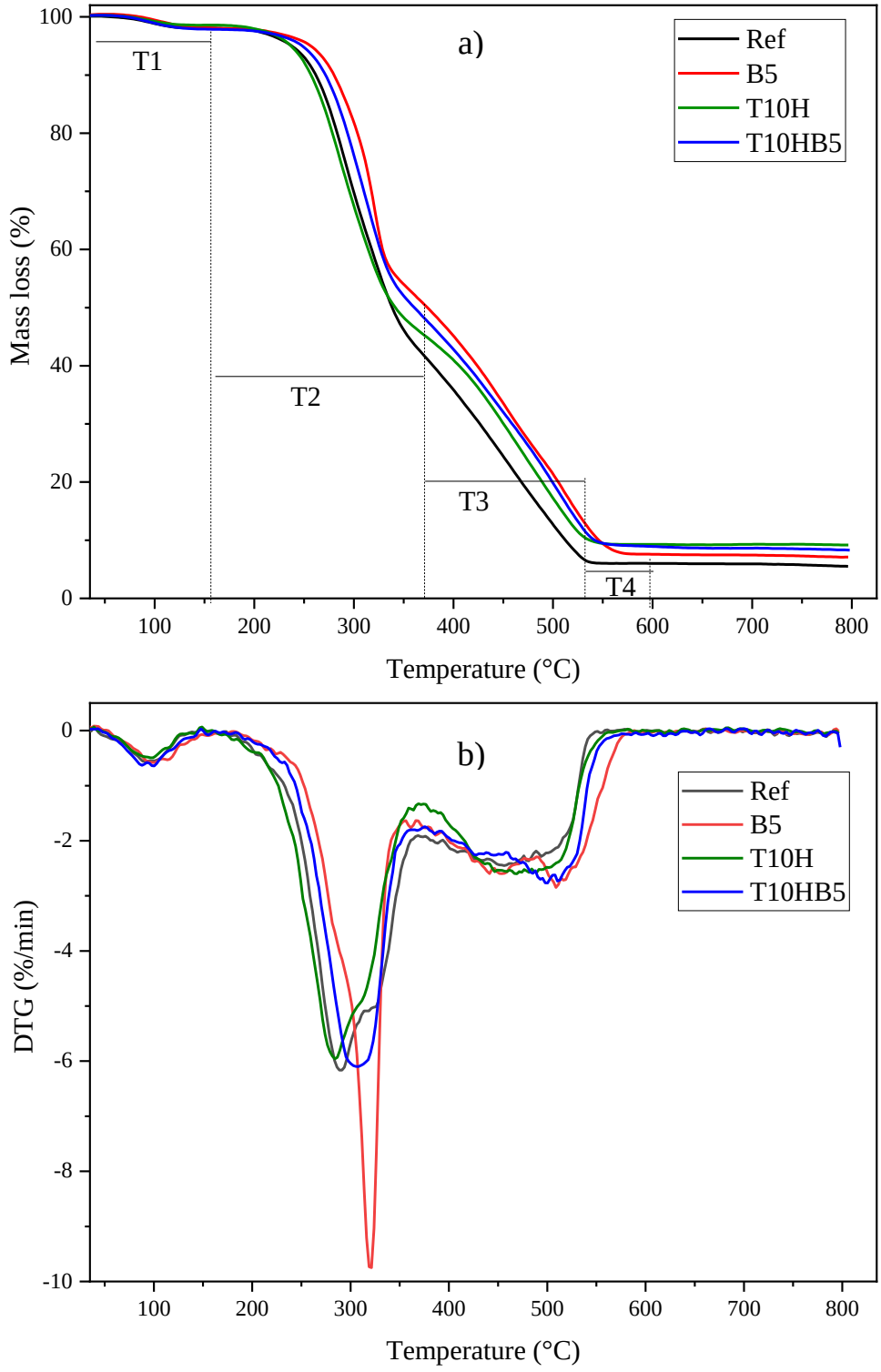

Figure 4 - TG (a) and DTG (b) curves of the bamboo samples with different treatment conditions.

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Table 10 - Characteristics of thermal decomposition stages. The ranges were determined according to the DTG curve.

Condition	$T1_i$ (°C)	$T1_f$ (°C)	WL_1 (%)	$T2_i$ (°C)	$T2_f$ (°C)	WL_2 (%)	$T3_i$ (°C)	$T3_f$ (°C)	WL_3 (%)	$T4_i$ (°C)	$T4_f$ (°C)	WL_4 (%)
Reference	40	134	2.02	184	371	56.29	376	549	34.65	-	-	-
B5	43	166	2.40	191	353	44.42	371	484	25.35	489	590	16.39
TH0.6	40	135	1.66	172	369	53.04	376	563	35.25	-	-	-
TH1.0B5	44	154	2.38	184	359	47.45	372	460	18.19	460	578	20.72

Where WL = Weight loss at a specific stage; T_i = Initial temperature; T_f = Final temperature.

4. Conclusions

Tannins are believed to play important roles in tree defence against potential pathogens. They may also have promise for protecting wood-based materials, including bamboo. In this work, we presented an alternative treatment method for bamboo based on the combination of polymerised tannin and boron.

- In comparison to wood, the treatability of bamboo is more difficult. The low solution uptake of bamboo is thought to be related to its anatomical structure and lower porosity. The treatments did not cause meaningful differences in water absorption (WA) and dimensional stability. However, the tannin/hexamine/boron samples had the lowest values of WA, thickness and width swelling.

- A mixture of 10% tannin, 10% hexamine (based on dry tannin) and 5% boric acid+ borax was resistant to boron loss. However, it was not capable of fixing boron in bamboo after leaching cycles.

- Decay tests showed that the samples treated with tannin-based solutions (leached and unleached) could be classified as durable and highly durable, showing better performance

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https://doi.org/10.1016/j.conbuildmat.2021.122723.

than untreated and boron treated samples. The effect of remnant polymerised tannin was enough to decrease the weight loss against the tested fungi.

- The mechanical tests suggested positive effects of all the investigated treatments, improving the compression strength, modulus of rupture (MOR) and modulus of elasticity (MOE) in bending. Tannin-hexamine-boron treated samples had the highest MOR and MOE values.

- Thermogravimetric analyses using synthetic airflow revealed that boron improved the thermal stability of bamboo in the evaluated conditions. Tannin/hexamine treatment also caused a mild increase in the char yield at 400 °C and, consequently, positively affected thermal degradation.

Along with its wide range of applications, tannin-based solutions can be an interesting option for bamboo treatment, especially where leaching is a problem. Nevertheless, more research is necessary to improve the reaction for a tannin-boron network and the treatability of bamboo materials.

Acknowledgements

The authors acknowledge the funding provided by FAPESP Grant No 2016/26022-9 and 2018/18571-8, which supported the first author's work at the University of São Paulo. Institute for Technological Research (IPT) and Prof. Kent A. Harries from the University of Pittsburgh are also acknowledged for the fungi decay tests and the support on the mechanical characterisation, respectively.

Accepted version.
Published version: Constr Build Mater 2021;282:122723.
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Accepted version.
Published version: Constr Build Mater 2021;282:122723.
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