Chemical modification of *Dendrocalamus asper* bamboo with citric acid and boron compounds: effects on the physical-chemical, mechanical and thermal properties

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Abstract

The effect of environmentally friendly treatment using citric acid and boron compounds on the physical-chemical and mechanical properties and thermal degradation of *D. asper* bamboo was investigated. The chemical modification using citric acid reduced the moisture uptake of bamboo by 32%, the water absorption by 26%, and thickness and width swelling by 43% and 31%, respectively, in comparison with the reference. FTIR analysis revealed the effect of the esterification process with an increase of the carbonyl/hydroxyl absorbance ratio, which explains the reductions in water absorption and swelling. No significant change was identified on the cellulose crystallinity determined by XRD, with only a small increase of the boron-treated samples. TG/DSC measurements showed that boron compounds cause a reduction of weight loss and decrease the exothermic heat flow upon heating under synthetic air flow. However, the modification with citric acid caused slightly higher thermal degradation in the same conditions of testing, which was overcome by the addition of boron compounds in the treatment solution. Enhanced mechanical performance was observed on bamboo samples treated only with boron compounds, while samples chemically modified by citric acid presented no changes or a small increase in compression and bending properties. Nevertheless, fibre detachment and structural changes on hemicellulose/cellulose caused a small decrease in shear strength and a considerable decrease, about 30%, in tensile strength. The overall results provided an insightful understanding regarding the chemical modification of bamboo, revealing new possibilities of treatment for the improvements of dimensional and thermal stability without the use of hazardous chemicals.

Keywords: bamboo; dimensional stability; esterification; treatment

1 – Introduction

To be used in construction, bamboo must be treated to enhance its resistance to fungal and insect attack. Significant developments in the area of bamboo treatment have been achieved during the last decades. These developments are attributed to increased environmental concerns, worldwide demand for ‘clean’ chemicals and high-quality bamboo products; interest in bamboo is driven by the rising prices of durable tropical timber and its limited availability (Mantanis, 2017). Various bamboo treatment techniques such as chemical, heat, and oleo-thermal treatments have been demonstrated, in both academic and industrial levels. Treatment using chemicals, as an effective way to improve durability and stability, is the most frequently investigated treatment for wood (Geraud et al., 2016; Hill, 2006; Schorr et al., 2018) and bamboo materials (Gauss et al., 2019a; Zhang et al., 2014). Chemical preservatives can permanently alter material cell wall polymers and deposit chemicals in cell voids (Feng et al., 2014; Hill, 2006).

However, most conventional bamboo and wood preservatives, such as copper, arsenic, chromium, and other chemical reagents have a high toxicity. While some chemical reagents are not toxic by themselves, they can be transformed into poisonous substances and released into the environment (Wang et al., 2018) posing a risk to ecological quality and environmental health. Chemical preservatives can be leached out and released from the material into soil, ground and surface water, and eventually into oceans, causing water and sediment pollution (Shukla et al., 2019). Appropriate disposal of such treated material at the end of bamboo or wood service life is also a significant concern (Dubey, 2010).

Novel preservative formulations are being investigated. The key target is the replacement of conventional hazardous preservatives with more environmentally safe chemicals for improving the moisture sensibility, dimensional stability, and resistance to fungal decay of bamboo. Additionally, treatment must not sacrifice the mechanical properties of the bamboo.

Chemical modification has been investigated and applied at an industrial scale to improve the durability and stability of wood products. The acetylation process with acetic anhydride, for example, is used to stabilise wood, increase hydrophobicity, improve dimensional stability and provide resistance to biological degradation, making this modified wood appropriate for exposed applications (Hill, 2006; Rowell, 2012). As in the acetylation process, an esterification process using citric acid as the primary solution can chemically modify wood or other lignocellulosic materials. This approach has been used as a binder for particleboards (Widyorini et al., 2014), wood veneers (Del Menezzi et al., 2018), and for the esterification of hydroxyl groups from wood following thermal treatment between 100 ºC and 140ºC (Despot et al., 2008; Essoua et al., 2016; Šefc et al., 2009a).

Using renewable chemical products, such as citric acid, is a significant development for treatments for the wood industry. Citric acid is widely available in nature at relatively low cost, and it satisfies requirements related to health and safety concerns (Ramirez et al., 2017; Sánchez-Rivera et al., 2017; Ye et al., 2019). Citric acid has the potential to be a cross-linking agent for cellulose (Figure 1) (Widsten et al., 2014) and to react with wood cell wall polymers (Feng et al., 2014). In the wood industry, citric acid not only improves the product but also contributes to reducing the final environmental footprint of buildings (Essoua et al., 2017).

Esterifying wood with citric acid can improve dimensional stability and biological durability. However, while compression strength parallel to the grain remains unaffected (Šefc et al., 2012), there is a decrease in tensile strength (Despot et al., 2008) and modulus of rupture in citric acid treated wood (Feng et al., 2014; Guo et al., 2019). According to studies of the reaction of citric acid with cellulosic materials conducted using FTIR spectroscopy analysis, it appears that the two adjacent carboxylic acid groups dehydrate and form a five-membered cyclic anhydride intermediate, which may further react with a hydroxyl group of cellulose via esterification (Feng et al., 2014).

Several catalysts, such as sodium hypophosphite, have been proposed to enhance the formation rate of anhydride intermediates in citric acid-modified wood to minimise cellulose degradation during the curing stages. However, it is not necessary to use the catalyst for the reaction between wood and citric acid to occur (Feng et al., 2014). Larnøy et al. (2018), impregnated pine wood with an aqueous solution containing citric acid and sorbitol and cured this at 140°C. They concluded that this combination enhances dimensional stability, durability against decay fungi and exhibits reduced susceptibility to blue-stain fungi. Essoua et al. (2016), L’Hostis et al. (2018), and Berube et al. (2017) treated different wood samples with citric acid and glycerol curing the samples at temperatures higher than 100°C. Wood treated with the combination of citric acid and glycerol exhibited improved resistance to fungal decay and higher mechanical strengths.

There are many similarities between wood and bamboo. For this reason, the agents that have shown good results in wood preservation are believed to be appropriate for the chemical modification of bamboo as well. Using citric acid as a renewable-based chemical for bamboo treatment can be an innovative alternative to the petrochemical treatment materials commonly used. Nonetheless, some components of bamboo (hemicellulose, lignin, and some other extractives) may degrade under treatment, which can negatively affect the mechanical properties of the final bamboo products; this requires investigation. Moreover, the broad-spectrum efficacy (Gauss et al., 2019a; Tondi et al., 2012) and fire-retardant properties (Donmez Cavdar et al., 2015; Yu et al., 2017; Zhou et al., 2018) of disodium octaborate tetrahydrate (DOT) and other boron compounds, which are the most common chemicals used in conventional bamboo treatment, in combination with citric acid is a matter of interest.

The main goal of the present study is to investigate the effects of citric acid treatment and compare these with DOT-treated and untreated *Dendrocalamus asper* bamboo samples. The effects were evaluated through the investigation of the physical (water absorption, swelling, and leaching) and mechanical properties (compression, tension, bending, and shear), thermal degradation under synthetic airflow, and the chemical changes, tracked by FTIR and XRD.

Figure 1 - Mechanism for the citric acid cross-linking of cellulose (Widsten et al., 2014).

2 – Materials and methods

2.1 – Materials and samples preparation

The *D. asper* bamboo species has been used for this study due to its availability in several regions in Brazil. Bamboo culms were harvested at an experimental field on the USP campus in Pirassununga, state of São Paulo, southeast region of Brazil (21°59′S 47°26′W). Pirassununga is located at an altitude of 630 m above sea level, has an annual average rainfall of 1363 mm and has a tropical climate with well-defined wet and dry seasons.

Mature culms (more than three years old) were collected and conditioned in a protected environment for drying until reaching an equilibrium moisture content. The treatment process was performed using six different internodes from the middle (more uniform) part of three different culms. Tangentially oriented strips, approximately 200 mm long and 30 mm wide, were cut from the internode sections, as shown in Figure 2.

Fibre volume fractions and the apparent densities at approximately 10% moisture content (before the conditioning steps described in section 2.2) and in the oven-dry condition are shown in Table 1. The apparent densities were measured by the water immersion method at 27 °C, as described in

ASTM D2395−17. The fibre volume fractions were determined using images obtained using an optical stereoscope and analysed using ImageJ software (Rasband, 2018), in which the same threshold procedure described by Akinbade et al. (2019) was used. A typical microstructure of *D. asper* bamboo composed of fibre bundles, parenchyma, vessels, and phloem, as well as the threshold procedure used for fibre fraction determination, is shown in Figure 3.

Figure 2 – Samples layout used for the treatment process and the number of samples obtained from each internode.

Table 1 – Apparent density and fibre volume fraction of *D. asper* bamboo samples used in this study.

Internode	Apparent density (g/cm^3)	Moisture content (%)	Oven-dry apparent density (g/cm^3)	Fibre volume fraction (%)
A	0.742	9.9	0.716	42.4
B	0.750	9.8	0.726	39.0
C	0.778	10.2	0.747	43.0
D	0.794	10.0	0.763	34.6
E	0.782	10.2	0.761	37.8
F	0.797	10.5	0.75	39.5
Average	**0.774**	**10.1**	**0.744**	**39.4**
COV	**0.04**	**0.03**	**0.04**	**0.08**

Figure 3 – Typical microstructure of *D. asper* bamboo samples used in this study and threshold procedure used for fibre volume fraction determination. V=Vessels; F=Fibre bundles; Ph=Phloem; P=Parenchyma.

2.2 – Treatment process

The samples were submitted to different treatment processes. Five samples per internode (total of 30 samples) were used for each treatment condition, using the solutions presented in Table 2. Before treatment, the samples were air-dried at 103 ± 2 °C until a constant weight was achieved; following this they were conditioned in a climatic chamber at 25 °C and 70% RH for 240 h. This procedure that was used permit weight changes after treatment to be accurately assessed and at the same time treat the samples in a more realistic moisture condition, i.e., not completely dry but with equivalent moisture content obtained by air drying (below 20%), as generally applied for bamboo treatment using vacuum/pressure methods (Kim et al., 2011; Liese and Tang, 2015a). Following conditioning, the moisture content of the samples was approximately 8% (reported later in Table 3). The samples were treated in a pressure vessel 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. Following treatment, samples were dried at room temperature for 48 h, oven-dried at 60 ±2 °C for 24 h, and finally cured at 120 ± 2 °C for 48 h in order that the reaction between citric acid and bamboo can occur. The heating initiates citric acid dehydration to form an anhydride and its carboxyl (COOH) groups, which reacts with bamboo hydroxyls forming ester bonds (Feng et al., 2014; Sánchez-Rivera et al., 2017).

For the samples treated with the presence of boron in the formulation, a combination of boric acid and disodium borate decahydrate (borax) was used in the ratio of 1: 1.54 by mass for the formation of DOT ($Na_2B_8O_{13}.4H_2O$) (Gauss et al., 2019a). In the case of CA10B5 solution, first the boric acid and borax were dissolved in the correct proportion, and then the citric acid was added.

Boric acid, disodium borate decahydrate and citric acid of analytical grade supplied by Labsynth, Brazil, were used. Reference samples were subject to the same conditioning (103^{o}C followed by 25^{o}C at 70% RH for 240 h) and curing (120^{o}C for 48 h) protocols but were not subject to the vacuum/pressure treatment cycles.

Table 2 – Impregnation schedule and treatment solutions.

Condition	Treatment solution (wt/wt)	Number of samples	Heat treatment temperature (after impregnation)
Reference	none	30	120 °C
B5	DOT 5%	30	120 °C
CA10	citric acid 10%	30	120 °C
CA10B5	citric acid 10% + DOT 5%	30	120 °C

2.3 – Moisture uptake

The treated and untreated samples were conditioned at 25 °C and 70% RH in order to observe the moisture uptake in relation to time. The samples were weighed after 48, 168, 336 and 504 hours and the moisture content calculated using the dry weight of the samples, obtained after the heat treatment process (at 120 ºC).

2.4 –Water absorption, swelling, and leaching

20 x 20 mm samples 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 of AWPA E10:16. Before this process, the treated samples were first dried at 60 °C until a constant weight was achieved. 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 immersion. The weight of the samples was determined with a precision of 0.001 g and the dimensions with an accuracy of 0.01 mm. WA, TS and WS were calculated in relation to the initial weight and dimensions of the samples after drying at 60 °C. After these measurements, the water was replaced, 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

Following treatment, samples were subjected to boron retention analyses conducted according to Brazilian Standard ABNT NBR 6232:2013. For the chemical analyses, samples extracted from the middle part of four different specimens of the samples treated with boron (leached and unleached) were ground into a powder and passed through a 60-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 laboratory of trees, wood, and furniture at the Institute of Technological Research (IPT), São Paulo, Brazil, following the same guidelines used for treated wood. The amount of equivalent B_2O_3 was calculated according to:

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

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 – Fourier Transformed Infrared (FTIR) spectroscopy

The chemical modifications involved after treatment were investigated through Fourier transform infrared (FTIR) spectroscopy. Samples extracted from the middle part of four different specimens of each condition 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 °C until a constant weight was achieved.

2.7 – Microstructural characterisation

The transverse section of the treated bamboo samples was analysed in a HITACHI model TM-3000 (with an acceleration voltage of 15 kV) scanning electron microscope (SEM) to observe possible effects of the different treatment conditions. For the analysis, small samples were cut with a diamond disc and subjected to fine grinding and polishing with (sequentially) 6, 3 and 1 µm diamond polishing suspension. After polishing, the samples were cleaned with isopropyl alcohol and dried at room temperature. The fractured surfaces of samples submitted to interlaminar shear tests (see below) with no further preparation were also submitted to microscopy analysis.

2.8 – X-ray diffraction

An X-ray diffractometer (Horiba LA-960, with CuKα radiation generated at a voltage of 40 kV and a current of 30 mA) was used to scan the samples between 5–65° 2θ at 10°/min. The samples were prepared by the same procedure described for FTIR analysis. The crystallinity of cellulose, *CrI*, was calculated using the Segal peak height method (Nam et al., 2016), according to the following equation:

$$CrI = \frac{I_{002} - I_{am}}{I_{002}}\ x\ 100 \qquad (2)$$

Where I_{002} represents the maximum intensity of the (002) plane reflection of the cellulose I structure at approximately $2\theta = 22.7^{\circ}$ and I_{am} is the intensity of the amorphous reflection at $2\theta = 18^{\circ}$.

2.9 – Thermal characterisation

The thermal characterisation was performed in order to understand the thermal degradation of bamboo treated with citric acid and boron compounds. The tests were conducted in a Netzsch TGA/DSC model STA 449 F3 Jupiter using synthetic airflow (flow rate of 100 ml/min.) from room temperature up to 800 ºC at 10 ºC/min. Differential scanning calorimeter (DSC) measurements were also performed with the thermogravimetric analysis (TGA). The samples were prepared by the same procedure used for FTIR analysis. 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 (Jiang et al., 2015; Liodakis et al., 2013, 2010; Park et al., 2015; Wang et al., 2017).

2.10 – Mechanical characterisation

Machined coupon specimens were used for compression, tension, bending, and shear tests, as presented in Figure 4. All required specimen dimensions were obtained using a digital calliper having a precision of 0.01 mm. Samples were weighed before testing and afterwards dried at (100 ± 2) °C for at least 48 h to establish moisture content at the time of test.

Figure 4 – Mechanical test methods

2.10.1 – Compression parallel to fibres

Sub-sized specimens with square transverse sections were used to investigate the effect the alternative treatments on compression behaviour parallel to the bamboo longitudinal axis (i.e. parallel to fibres). Samples with transverse sections having the same size as the culm wall (t x t) and length four times the thickness (L= 4t) were tested in a 600 kN capacity Instron universal testing machine (model 600DX) at a cross-head displacement rate of 0.5 mm/min. (Figure 4a). The samples were extracted from six different specimens (Figure 2) of each treatment condition. The tests and results calculation were conducted according to recommendations of ASTM D143-14.

The longitudinal compression strength ($f_{c,0}$) is reported as the maximum load divided by the cross-section area of the sample. The modulus of elasticity ($E_{c,0}$) in compression was determined using strain mapping obtained through a Digital Image Correlation (DIC) setup, as is described elsewhere (Gauss et al., 2019b).

2.10.2 Tension parallel to fibres

The tension parallel to fibres tests were performed based on ISO 22157-19. Radially oriented bamboo strips 200 mm in length were extracted from six different specimens (Figure 2) of each treatment condition. The strips were sanded to obtain uniform dimensions with a breadth (b) less than half of the culm thickness (t). Softwood tabs were glued on the gripped ends to facilitate gripping by the testing machine. Although ISO 22157-19 provides for prismatic specimens, because DIC was used to determine strains, the specimens were provided with a reduced section at the middle of their gauge length in order to concentrate the tension failure region (this region can be seen in Figure 4b). Tests were conducted in 10 kN capacity Testresources electromechanical universal testing machine (model 100). A displacement rate of 1.0 mm/min was used for all the tests. The longitudinal tensile strength ($f_{t,0}$) was calculated using the maximum load divided by the reduced area cross-section area at the thinnest part of the specimen. The modulus of elasticity ($E_{t,0}$) in tension was determined using the strain mapping obtained through a Digital Image Correlation (DIC) setup (Gauss et al., 2019b).

2.10.3 Three-point small coupon bending test

Samples in a prismatic form with 200 x 10 x thickness (t) mm^3 were used. They were extracted from eight different specimens (Figure 2) of each treatment condition. 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. The tests were conducted following Procedure A of ASTM D7264-15 as modified by others (Dixon et al., 2016; Gauss et al., 2019b; Gibson and Dixon, 2014) using a 10 kN capacity Testresources electromechanical universal testing machine at a displacement rate of 2.5 mm/min. The modulus of rupture (MOR), modulus of elasticity (MOE) and specific strain were calculated according to ASTM D7264-15. Tests reported in this study were conducted with the sample orientated such that the outer culm wall was in compression (OC). The displacement of midheight (t/2) of the sample at midspan was tracked using a Digital Image Correlation (DIC) setup (Gauss et al., 2019b).

2.10.4 Interlaminar shear

The behaviour of the treated bamboo samples in shear was evaluated through an interlaminar shear test. Coupon specimens are scored halfway through their depth perpendicular to the loading direction at two locations resulting in a shear plane having an area $A = L_S \times t$, as can be seen in Figure 5. Since the shear plane is at the middle of the specimen, when loaded in tension, the plane is subject to pure shear. The shear strength is then calculated using the maximum load at failure divided by the shear area A. All the interlaminar shear tests were conducted using a 10 kN capacity Testresources electromechanical universal testing machine using a displacement speed of 1.0 mm/min.

Figure 5 – Specimen layout used for interlaminar shear tests.

2.11 Statistical analyses

The averages of each test for each test condition are presented with the corresponding coefficient of variation (COV) and the number of samples. The differences among the treatment conditions on the evaluated properties were checked 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 Treatment process

Table 3 presents a summary of the solution absorption, moisture content (MC) before treatment and weight percentage gain (WPG) for all analysed conditions. The averages and corresponding COV were calculated based on 30 samples for each treatment.

Differences were observed on the average absorption of the same solution (B5, CA10, CA10B5) in different internodes sets. Even using high pressure for the treatments, this difference is explained by the different densities of the samples. In fact, by using the real density of bamboo (obtained using a helium pycnometer) and the oven-dry apparent density, it is possible to estimate the volume attributed to pores. Similar values of average real density (1.303 g/cm^3 were obtained for all internodes. By dividing the real density by the apparent density, a “void” volume of 68% for the bamboo samples used in this study was found. Higher apparent densities are closer to the maximum real density of the material (without any pores) and therefore, have less available space for the solution absorption. This effect can be observed in Figure 6, where an almost linear relation between density and solution absorption is presented. Preservative absorption is also a function of the solution molecular weight and concentration (Gauss et al., 2019a; Tondi et al., 2013). The most concentrated solution, CA10B5, had the lowest solution uptake compared with the samples treated only with DOT or CA. This effect can also be observed in Figure 6, where solution absorption is less for the CA10B5.

Table 3 – Sample conditions after the treatment processes.

Conditions (active ingredients)	Total solution concentration of active ingredient (%)	MC Bef. Treat. (%)		Solution absorption (%)		WPG After drying (%)	
		Avg.	COV	Avg.	COV	Avg.	COV
Reference	-	7.7	0.04	-	-	-	-
B5	5	8.2	0.08	59.1	0.08	0.48	0.35
CA10	10	7.9	0.05	58.7	0.09	3.55	0.11
CA10B5	15	8.4	0.07	46.4	0.11	3.45	0.12

Figure 6 – Solution uptake in relation to the oven-dry apparent density of bamboo samples from different internodes. In this plot, the error bars are the standard deviations.

3.2 – Moisture uptake

Bamboo, like wood, is a hygroscopic material that absorbs and releases moisture to the surrounding environment. In fact, the data used for wood, correlating equilibrium moisture content (EMC) to temperature and relative humidity, can also be used for the bamboo moisture uptake in some situations (Liese and Tang, 2015b). The chemical modification with citric acid is expected to decrease the equilibrium moisture content of lignocellulosic materials, as it decreases the number of available free hydroxyls through the reaction with carboxylic acid groups (COOH) from citric acid (Essoua et al., 2016). This effect can be observed in Figure 7, in which the sorption curves of all the samples (30 per condition) conditioned at 25 °C and 70% RH are presented. To the best of our knowledge, there is no publication regarding bamboo modification using citric acid. Therefore, comparisons with other bamboo species or even wood are difficult.

According to Figure 7, even after more than 500 hours of conditioning, the equilibrium moisture content was not achieved for all the analysed conditions. At 25 °C and 70% RH, conditions recommended by ISO 22157-19 and other wood Standards for material conditioning, it is expected that an EMC between 10 – 12% will be achieved (ISO, 2019.; Nguyen et al., 2012). Since the samples were dried after treatment (120 °C), including the reference samples, the collapse of cell micropores may have led to a reduction of the moisture absorption rate (Hill, 2006). The absorption curves of all conditions could be fitted to a power-law ($y = a.x^b$) with a relatively good coefficient of determination (R^2). The obtained functions for each condition are also shown in Figure 7. Treatment with citric acid clearly affected the kinetics of moisture absorption of the bamboo samples. The CA10 treatment presented the lowest moisture content after 504 h, 4.7% (COV = 0.08), while the reference had a moisture content of 6.9% (COV = 0.09), a decrease of 32%. The changes in the kinetics can also be represented by the fitting coefficients, in which a continuous decrease of the scalar (a) is observed.

Figure 7 – Moisture content change in relation to time in a climatic chamber at 25 °C and 70% RH. In this plot, the error bars are the standard deviations.

3.3 – Water absorption, swelling and leaching

Reduction in water absorption and swelling leads to increased dimensional stability, a primary goal of chemical modification of lignocellulosic materials. In Table 4 a summary of the WA, TS, and WS of all the investigated conditions is presented. The effect of citric acid on the modification of bamboo can be observed by the statistically relevant changes in WA, TS and WS.

For WA, the samples treated with CA10 show a WA reduction, in comparison with the reference, of 26% even after 288 h of immersion. After 288 h, the samples treated with DOT had no difference in comparison with the reference. The samples treated with CA and DOT (CA10B5) also had a considerable reduction of WA (16% after 288 h).

In this study, the change in dimensions was tracked measuring the thickness and width in the middle of the samples used for water absorption and swelling tests. Since bamboo is not completely flat (the samples have a natural curvature), the volumetric changes were not considered. The changes in length were almost negligible. Therefore, in Table 4, the changes in thickness and width only are reported. The samples treated with citric acid presented statistically significant changes in their dimensions. The CA10 and CA10B5 treatments had similar thickness swelling (TS) reduction after 288 h, 43% and 42%, respectively. Reductions in the width swelling (WS) were also observed: 33% and 26% for the CA10 and CA10B5 treatments, respectively. The treatment using only boron compounds showed no statistically significant difference in comparison with the reference.

Vukusic et al. (2010) modified fir and beech wood with different polycarboxylic acids. The treatments using citric acid resulted in WPG of up to 18% for Fir and 9% for Beech wood. For these conditions, anti-swelling efficiency (ASE) values of 54% and 38% and water absorption reductions of 21% and 19% for Fir and Beech wood, respectively, are reported. Šefc et al. (2009b) reported WPG between 6% and 18% also for fir and beech wood using a solution composed of citric acid and sodium hypophosphate (SHP) and curing at temperatures between 140 and 180 °C. They observed ASEs from 39% to 57% and reduction in water absorption from 15% to 22%. Pine wood treated with a solution of glycerol and citric acid presented a WPG between 30 – 35% resulting in an ASE between 50-60% (Essoua et al., 2016). Berube et al. (2017) investigated the use of citric acid and glycerol for esterification of different wood species achieving a maximum ASE of 69% for white pine, although no information about WPG is reported.

In the present study, promising values of TS and WS reductions were obtained considering the low WPG achieved (see Table 3). Furthermore, no catalyst was used while most of the papers addressing chemical modification with citric acid use SHP. Feng et al. (2014) demonstrated that the addition of SHP had little influence on the ASE of chemically-modified poplar wood: a WPG of about 4.6% resulted in an ASE close to 36%.

After the leaching process, the samples were dried at 60 °C until a constant weight was achieved and compared to the initial weight (before the test). This procedure was performed to evaluate the boron loss and mass change after leaching. The obtained results are presented in Table 5. For the samples that were treated with boron compounds, around 90% of boron was leached. The combined treatment of boron compounds and citric acid did not have an effect on boron fixation. Additionally, the weight losses of the B5 and CA10B5 treatments, 6.98% and 9.27% respectively, were higher than the reference or the CA10 treatment, which presented the lowest weight loss (5.04%). The difference between the CA10B5 and CA10 conditions is attributed to the boron loss and leaching of unreacted citric acid.

Table 4 – Summary of water absorption and swelling results. Same letters (a, b, or c) mean there is no statistical difference among treatment conditions.

Treatment conditions							
n = 16				Reference	B5	CA10	CA10B5
Water absorption (%)		12h	Avg	28.93^a	32.83^b	22.64^c	24.68^c
			COV	0.07	0.17	0.14	0.09
		24h	Avg	41.17^a	44.16^a	29.26^b	33.17^c
			COV	0.06	0.13	0.09	0.07
		288h	Avg	79.87^a	81.06^a	59.10^b	66.96^c
			COV	0.05	0.13	0.07	0.1
		WA reduction – 288 h (%)*		**-**	**+ 1.5%**	**- 26.0%**	**- 16.2%**
Swelling (%)	Thickness	12h	Avg	5.37^a	5.18^a	3.63^b	3.84^b
			COV	0.15	0.18	0.12	0.11
		24h	Avg	8.12^a	7.48^a	4.83^b	5.38^b
			COV	0.13	0.12	0.08	0.11
		288h	Avg	10.45^a	9.76^a	5.92^b	6.03^b
			COV	0.11	0.15	0.09	0.11
		TS reduction – 288 h (%)*		**-**	**- 6.6%**	**- 43.3%**	**- 42.3%**
	Width	12h	Avg	3.37^a	3.17^a	2.61^b	2.69^b
			COV	0.15	0.15	0.12	0.16
		24h	Avg	4.42^a	4.01^a	2.94^b	3.28^b
			COV	0.19	0.1	0.17	0.15
		288h	Avg	5.10^a	4.88^a	3.41^b	3.78^b
			COV	0.18	0.12	0.11	0.15
		WS reduction – 288 h (%)*		**-**	**- 4.3%**	**- 33.1%**	**- 25.9%**

Table 5 – Mass loss after leaching cycle and B_2O_3 equivalent retention before and after leaching.

Conditions		Mass loss after leaching cycle (%)	B_2O_3 eq. retention (kg/m^3)		Boron loss (%)
			Before leaching	After leaching	
Reference	Avr	5.59	-	-	-
	COV	0.07			
B5	Avr	6.98	5.47	0.46	91.6
	COV	0.08	-	-	-
CA10	Avr	5.04	-	-	-
	COV	0.06			
CA10B5	Avr	9.27	4.76	0.48	89.9
	COV	0.07	-	-	-

3.4 – Mechanical properties

In order to evaluate the effect of the chemical treatments on the mechanical properties of *D. asper* bamboo, compression, tension, three-point bending, and shear tests were performed on each investigated condition. Table 6 shows a summary of the compression, tension and shear properties. In Table 7, the results of the three-point bending tests are presented. The influence of the different treatments on the mechanical properties was assessed by ANOVA where the results with different letters are statistically different at a confidence level of 95% ($p < 0.05$). Although some influence of the low moisture content of the samples can be present on the results of the mechanical tests, the primary purpose of the mechanical characterisation in this study is a relative analysis among the different treatment conditions. In this sense, despite the differences in the samples modified by citric acid (lower EMC), the evaluated conditions presented moisture contents in the same range and therefore, are not thought to affect the relative analysis.

Through Table 6, it is possible to observe the effect of citric acid and boron treatment on the mechanical properties of bamboo. Interestingly, there is an 18% improvement in the compressive strength and modulus of elasticity of samples treated with only citric acid. This increase in the compressive properties is also reported to occur in wood modified with citric acid and SHP (Feng et al., 2014; Šefc et al., 2012). For wood, this effect is explained by the cross-linking of cell wall polymers and cell wall bulking, increasing the stiffness (Feng et al., 2014). However, the modification with citric acid had a deleterious effect on interlaminar shear strength (decrease of 19%) and especially in tensile strength (decrease of 29%). No change was observed on the tensile modulus of elasticity. Analysing the samples treated with only DOT, there was an increase in all the evaluated properties, including the modulus of elasticity in compression and tension. This effect of DOT on the mechanical properties of bamboo was evaluated in detail and reported elsewhere (Gauss et al., 2019a)

The samples treated with a combination of citric acid and DOT presented similar behaviour as the CA10 treatment. In this case, the compression properties (strength and modulus) were preserved, and shear and tensile strength were affected, with a decrease of 24% and 26%, respectively. It is possible to infer that there was a selective change in some components of bamboo, like hemicellulose or cellulose. This aspect is discussed in more detail in the next sections.

Three-point bending tests were used to determine additional features, such as a) a limit of proportionality (LOP), corresponding to the limit of the elastic region of the stress-strain curve; b) specific energy (SE), calculated as the area under the stress-strain curve up to the MOR; and c) the failure modes of the specimens, classified based on ASTM D143-14. Table 7 summarises all the results, and the failure modes are illustrated in Figure 8. As observed in other studies and the results shown in Table 7, the treatment with DOT promoted an increase in the MOR (14%), MOE (10%), LOP (22%) and SE (16%). However, most of the samples failed in a combination of splintering tension failure (ST) and horizontal shear failure (HS). The reference samples, on the other hand, exhibited mainly ST failures.

The samples treated with citric acid (alone or in combination with DOT) presented the lowest SE values, which correlates with the decrease of interlaminar shear strength (Table 6). Additionally, most samples of the CA10 and CA10B5 treatments failed as HS or ST+HS. However, MOR, MOE and LOP were preserved for the CA10B5 treatment, and an increase of LOP (21%) was observed for the CA10 samples. Although the citric acid treatment caused a decrease in the tensile strength, it did not have a deleterious effect on the bending properties.

Based on the overall results, the chemical modification of bamboo had a marginal effect on the mechanical properties, although resulted in a more brittle material behaviour (decrease in shear strength, specific energy in bending, and tensile strength). Similar results are reported related to chemical modification of wood (Feng et al., 2014; Xie et al., 2007).

Table 6 – Summary of the mechanical properties of all the analysed treatment conditions. The COV is presented in parenthesis. Same letters (a, b, or c) mean there is no statistical difference.

Condition	Average ρ	Compression // fibres n=12			Interlaminar shear n=10		Tension // fibres n=12		
		MC	$f_{c,0}$	$E_{c,0}$	MC	f_v	MC	$f_{t,0}$	$E_{t,0}$
	g/cm^3	%	MPa	GPa	%	MPa	%	MPa	GPa
Reference	0.75	6.4	97.5^a (0.06)	21.40^a (0.08)	5.9	5.9^a (0.08)	5.6	269.4^a (0.10)	23.34^a (0.04)
B5	0.77	7.1	113.4^b (0.06)	26.00^b (0.14)	6.4	6.2^a (0.07)	5.4	295.6^a (0.09)	25.91^b (0.05)
CA10	0.77	4.5	115.0^b (0.07)	25.34^b (0.07)	4.8	4.8^b (0.16)	4.7	190.6^b (0.18)	22.54^a (0.06)
CA10B5	0.74	5.4	98.3^a (0.06)	21.50^a (0.10)	5.3	4.5^b (0.16)	5.5	200.6^b (0.21)	23.19^a (0.07)

Table 7 – Summary of bending properties of all the analysed treatment conditions. The COV is presented in parenthesis. Same letters (a, b, or c) mean there is no statistical difference.

Condition	Three-point bending							
	n	MC	*MOR*	*MOE*	*LOP*	*SE*	Failure mode	
		%	MPa	GPa	MPa	kJ/m^2	ST	HS	ST+HS
Reference	14	6.1	193.9^{a} (0.07)	20.6^{a} (0.09)	127.1^{a} (0.11)	29.1^{a} (0.11)	10	4	0
B5	16	6.3	220.5^{b} (0.08)	22.7^{b} (0.04)	155.7^{b} (0.07)	33.7^{b} (0.15)	2	3	11
CA10	16	4.7	196.2^{a} (0.13)	21.9^{b} (0.09)	154.1^{b} (0.08)	24.5^{c} (0.20)	6	2	8
CA10B5	15	5.5	184.8^{a} (0.08)	21.1^{a,b} (0.05)	136.8^{a} (0.11)	24.3^{c} (0.11)	2	7	6

Where, ST = Splintering tension failure; HS = Horizontal shear failure; ST+HS = Combined ST and HS failure; LOP = Limit of proportionality; SE = Specific energy.

Figure 8 – Predominant types of failure observed in the tested bamboo samples and classified according to ASTM D143-94. Where, ST = Splintering tension failure; HS = Horizontal shear failure; ST+HS = Combined ST and HS failure

3.5 – Microstructural analysis

Following the mechanical characterisation, some of the samples were investigated through SEM analysis. One of the observable effects of citric acid treatment was the decrease in shear and tensile strength (Table 6). In Figure 9, SEM images of the interlaminar shear test fracture surfaces of B5 samples, having the highest interlaminar shear strength, and CA10B5 samples, having the lowest, are shown. Comparing these treatments, it is possible to observe a clear detachment between the parenchyma and fibre bundles on the CA10B5 sample (red arrows in Figure 9). On the other hand, on the B5 sample, fragments of the parenchyma were found attached to the fibre bundles. This observation suggests that the CA10B5 treatment affected the fibre-parenchyma interface in a deleterious manner. Analysing the cross-section of regions close to the fibre bundles from these two treatments (see Figure 10), small cracks (red arrow) along the interface between the fibre bundles and parenchyma were identified on the CA10B5 condition. The presence of inter-fibril cracks within the fibre bundle of the CA10B5 sample was also more significant than on the B5 sample. It is possible to infer that these defects played a role in the decrease of shear and tensile strength since in tension the bond of the matrix (parenchyma) and fibre bundles (reinforcement phase) is vital for maintaining continuity and permitting load redistribution between fibre bundles. Although apparently effected by treatment type in this study, inter-fibril cracks are observed in many studies having different conditioning histories; these are thought to initiate cracking in the parenchyma (Akinbade et al., 2019). Such inter-fibril cracking may increase in older (at harvest) culms (Liese and Weiner, 1996) and has been attributed to shrinkage associated with culm drying (Akinbade et al., 2019; Chen et al., 2018) but also may be an artefact of SEM sample preparation (Osorio et al., 2018).

Figure 9 – SEM images of the interlaminar shear fracture surfaces of samples from the B5 and CA10B5 conditions. F=Fibre bundles; P=Parenchyma. Red arrows indicate the P/F detachment.

Figure 10 – SEM images of the cross-section of B5 and CA10B5 samples. V=Vessels; F=Fibre bundles; P=Parenchyma. The Red arrow indicates the presence of cracks between F and P.

3.6– Fourier Transformed Infrared (FTIR) Spectroscopy

FTIR spectroscopy was used to analyse bamboo chemical functional groups and changes in these after treatments. This technique is commonly used to evaluate the efficacy of chemical modifications on wood or other lignocellulosic materials. Figure 11 presents the FTIR spectra of the reference and treatment conditions. All the spectra were normalised using the maximum absorbance.

A summary of the main functional groups between 3400 – 600 cm^{-1}, mainly assigned to stretching and vibrations of functional groups of wood and bamboo components, is presented in Table 8 (Pandey and Pitman, 2003; Xu et al., 2013). The functional region between 3800 – 2700 cm^{-1} can be attributed to different CH stretching vibration groups and O-H hydrogen bonds (Diouf et al., 2011).

Figure 11 – FTIR spectra of all the analysed conditions. The main functional groups' wavenumbers are identified.

Table 8 – Summary of the main functional groups found in wood and bamboo samples (Meng et al., 2016; Xu et al., 2013).

Wavelength (cm^{-1})	Functional group	Assignment
3345	-OH	Present in water and wood/bamboo components
2900	C=H, - CH_2 -	Stretching of the methyl and methylene groups, hydrocarbon chains
1723	− COOH (C = O)	free carbonyl groups, Stretching of acetyl or carboxylic acid (hemicelluloses)
1601	C = C	Aromatic ring (lignin)
1511	C =C	Aromatic ring (lignin), stronger guaiacyl element than syringyl
1460	C−H	Asymmetric bending in CH_3 (lignin)
1425	CH_2	Aromatic skeletal vibrations (lignin) and CH deformation in plane (cellulose)
1369	C-H	C-H deformation in cellulose and hemicellulose
1317	O−H	phenol group (cellulose)
1248	CO	Guaiacyl ring breathing with CO-stretching (lignin and hemicelluloses), esters
1163	C − O − C	Carbohydrate
1120	C−H	Guaiacyl and syringyl (lignin)
1039	C−O, C−H	Primary alcohol, guaiacyl(lignin)
896	C−H	C H deformation in cellulose

FTIR fingerprint region (1500-600 cm^{-1}) contains many well-defined peaks that provide abundant information on various functional groups present in wood/bamboo constituents. The main peaks analysed in the bamboo samples are identified in Figure 11. The main change among the investigated treatments is the increase in the peak at 1723 cm^{-1} which corresponds to the C=O stretching vibration. This effect can be better seen in Figure 12 which highlights only 1900-1300 cm^{-1}. The increase at 1723 cm^{-1} is related to the formation of esther bonds through reactions between the carboxylic groups of citric acid and bamboo hydroxyl (OH) groups (Essoua et al., 2016). In Table 9, the peak height (absorbance) ratios between the 1723 cm^{-1} peak and other relevant peaks are presented. The ratio analysis in FTIR results helps to understand chemical changes during a specific process (Morris et al., 1995; Xu et al., 2013). Comparing the carbonyl group with the hydroxyl peak at 3345 cm^{-1} there is a clear increase in the ratio, which suggests an esterification process consuming part of the available hydroxyls. The same behaviour is observed in the ratio of the 2900 cm^{-1} (C=H, CH_2), and 1317 cm^{-1} (phenol group of cellulose) peaks, which can also be used to estimate the degree of esterification of cellulose (Morris et al., 1995). If compared to the reference and boron treated samples, a higher degree of esterification was found for the samples modified with citric acid. These reactions explain the decrease in water absorption and swelling of the chemically modified bamboo samples.

Other interesting changes can be identified through the peak ratios presented in Table 9. The ratios of peaks related to cellulose and hemicellulose, I_{1369}/I_{1317} and I_{896}/I_{1317}, (where 1369 cm^{-1} corresponds to C-H deformation in cellulose and hemicellulose, 1317 cm^{-1} to O–H, phenol group in cellulose, and 896 cm^{-1} to C-H deformation in cellulose), had a small decrease in the samples treated with citric acid, which suggests structural changes in cellulose and hemicellulose may have occurred. The curing process with citric acid can also cause hydrolysis of glycosidic bonds in hemicelluloses (Azeredo et al., 2015). These changes in cellulose and hemicellulose might explain the decrease in tensile strength of the CA10 and CA10B5 samples.

Table 9 – Ratio between absorbance intensities of different functional groups.

Condition	Peak intensity ratios of different functional groups*				
	I_{1723}/I_{3345}	I_{1723}/I_{2900}	I_{1723}/I_{1317}	I_{1369}/I_{1317}	I_{896}/I_{1317}
REF	0.65	1.34	0.44	0.90	1.38
B5	0.69	1.87	0.42	0.93	1.39
CA10	1.13	2.93	0.72	0.87	1.33
CA10B5	1.34	2.83	0.80	0.88	1.30

* - Each subscript number is the wavelength relative to a specific functional group (Table 8).

Figure 12 – Detailed FTIR spectra of all the analysed conditions in the 1900-1300 cm^{-1} region. The main change among the samples is found at 1732 cm^{-1} (C=O group).

3.7 – XRD analysis

The strength of lignocellulosic materials is mainly related to cellulose because of its high degree of polymerisation and linear orientation (Winandy and Rowell, 1984). Feng Jiang by exploring wood in nanometer-scale, explained how cellulose fibrils bind into microfibrils at different angles along the axis direction and stated that these aligned cellulose microfibrils are responsible for mechanical support of the cell walls. Additionally, Since the amorphous region is lower in strength than the crystalline region in cellulose (Youssefian and Rahbar, 2015), the relationship between amorphous and crystalline cellulose may affect the mechanical properties of wood and bamboo (Jiang et al., 2018; Tang et al., 2019). During chemical or thermal treatment, changes in the cellulose structure can occur. Therefore, crystallinity index (CrI) of cellulose for each treatment condition was determined using the Segal method.

Figure 13 shows the XRD patterns of all the investigated treatments. Typical peaks assigned to cellulose Iβ structure, 22.4° (002), 16.3° (101) and 35.0° (040), can be observed (Nishiyama et al., 2003; Tang et al., 2019). All the conditions exhibited similar patterns, with minor changes in the peak height of the (002) plane, as shown in the magnified plot of the 10-30° region shown in Figure 13. The crystallinity indices of the samples are presented on the top of each diffraction pattern. Although there are no substantial changes in the CrI, the samples treated with citric acid had the lowest values. Samples treated with only boron compounds, however, presented the highest CrI, which was similar to the reference.

Changes in the CrI of cellulose are normally reported in processes involving temperature, where an increase of CrI accompanies an increase in mechanical properties. However, this effect is typically observed for treatment temperatures above around 140 °C (Fatriasari et al., 2016; Kadivar et al., 2019; Tang et al., 2019).

According to the FTIR results, it is possible to infer that minor changes of the cellulose structure occurred in the chemically modified bamboo. These changes could also be reflected in the proportion of amorphous and crystalline cellulose. Interestingly, the samples treated with boron compounds had the best overall mechanical properties and also presented the highest value of CrI, which is consistent with other studies related to cellulose structure (Tang et al., 2019). On the other hand, the bamboo samples modified with citric acid showed the lowest tensile strengths (highly dependent on the cellulose) and accordingly, the lowest values of CrI.

Figure 13 – XRD patterns of all the investigated conditions. The inset shows the 2θ positions used for cellulose crystallinity index calculation. (101) and (002) planes refer to cellulose Iβ crystal structure.

3.8 – Thermal degradation

Jiang et al. (2015) analysed the effect of urea-formaldehyde oligomer and phosphorus acid flame retardants on Chinese fir wood in terms of thermal degradation and flammability tests. Using TGA/DTA analysis, it was possible to observe the relationship among the formation of char at 400

°C (using static air), limiting oxygen index (LOI) and the temperature of the maximum of the first derivative of the TGA curve (T_{max}). There is an increase in the residual char with an increase of LOI values. This effect may be attributed to the suppression of combustibility by the addition of flame retardants, leading to the formation of more char instead of the flammable, volatile products of pyrolysis (Jiang et al., 2015). Therefore, the use of TGA under synthetic air can be a reliable tool to understand thermal degradation behaviour in more realistic conditions.

In Figure 14, the TG and its derivative with respect to time (DTG) curves of bamboo samples without any treatment using synthetic air and nitrogen flow are presented. The effect of oxygen on the thermal decomposition of bamboo is clearly evident and similar to results reported in the literature (Azadeh, 2018; LeVan and Jerrold. E., 1990; Uner et al., 2016; Wang et al., 2017). From Figure 15, comparing the TG curves with synthetic air and nitrogen flow, it is possible to observe considerable differences above 300 °C. At the temperature range between 400 °C and 500 °C, the second DTG peak in the sample tested with synthetic air is related to the combustion of volatile gases produced by the decomposition of cellulose and lignin (Wu et al., 2018). Additionally, higher temperatures of pyrolysis and/or slower weight loss at a particular temperature mean better thermal stability of wood samples (Wang et al., 2017). These effects can be achieved by using flame retardants.

Figure 14 – Comparison between TG/DTG curve of the reference sample tested with synthetic air and nitrogen flow.

Figure 15 presents the TG and DTG curves of all the investigated treatments. Firstly, it is possible to observe considerable differences among the different treatment conditions, mainly when boron compounds are used (B5 and AC10B5). In Table 10, the residual char obtained at 400 °C and T_{max} of the bamboo samples are shown. The B5 and CA10B5 samples had the highest amount of char (up to 25% increase), proportional to the boron retention, while T_{max} increased from 314 °C to 321 °C. These results show the suppression of part of the volatile gases during heating by boron compounds; this can be attributed to a flame retardancy effect. DOT, which is formed by the proportion of boric acid and borax used in this work, is a better fire retardant than pure boric acid, borax or the combination of both in other proportions (Uner et al., 2016). On the other hand, the citric acid treatment presented a lower amount of char than the reference, but similar T_{max}. The addition of boron compounds in the citric acid solution (CA10B5), however, had a positive result in terms of char formation.

Although in the work of Jiang et al. (2015) an inverse relationship between T_{max} and LOI is reported, in the present work, from Figure 15, it is possible to observe higher T_{max} for the sample tested with nitrogen flow, for which, in theory, the combustion of the sample is negligible. Materials that undergo thermal decomposition in the presence of oxygen are supposed to have higher thermal resistance if their thermal decomposition behaviour is closer to situations using an inert gas (Jiang et al., 2015). Therefore, in this work, a higher T_{max} is seen as advantageous for the flammability behaviour of the tested samples

Analysing the DTG and TG curves shown in Figure 16, it is possible to divide the temperature range into four different stages. The reference and CA10 conditions presented three stages (T1, T2, and T3) while the samples that had boron in the treatment solution also revealed a fourth stage (T4). In Table 11, the characteristics of each stage are summarised, including the initial temperature (Ti), final temperature (T_f) and corresponding weight loss for each stage.

At stage T1, between room temperature up to about 160 °C, evaporation of water is the leading cause of weight loss. Interestingly, the samples modified with citric acid ended this stage at a lower temperature than the other samples, suggesting that the modification facilitated the removal of water in the bamboo samples. At the second stage, from 160 to 370 °C, the weight loss is driven mainly by decomposition of hemicellulose and cellulose into char, CO_2, CO, CH_4, CH_3OH, CH_3COOH, and other components (Wang et al., 2017). In this case, the effect of boron compounds is evident, increasing the initial temperature and decreasing the weight loss considerably, to 47% for B5 from and 57% for the Reference conditions. At the third stage, from 370 °C and 550 °C, degradation of lignin and cellulose take place (Wang et al., 2017). In this stage, lower weight losses were also observed for the B5 and CA10B5 samples, falling to 26% for B5 from 34% for the Reference condition. Additionally, the samples treated with boron had a secondary peak within this temperature range (identified as T4), extending the degradation temperature to around 600 °C. At this fourth stage, exhibited only by the B5 and CA10B5 conditions, the maximum weight loss temperature was found to be 614 °C and 605 °C for B5 and CA10B5, respectively. Therefore, the use of boron in the formulations increased the temperature of maximum degradation, which can be explained by the suppression of combustible gases and dehydration of the formed DOT at around 600 °C.

DSC measurements can be used to observe the exothermic reactions occurring during heating. According to the DSC curves shown in Figure 16, the heat flow is smaller in the samples that were treated with boron compounds, which represents lower release of energy. Additionally, in the temperature range of 500-600 °C, the samples treated with boron presented a secondary peak; the same behaviour observed in the DTG curves of Figure 15.

Table 10 – Residual char and T_{max} of bamboo samples subjected to TG analysis.

Condition	B_2O_3 eq. retention (kg/m^3)	Residual Char (%) at 400°C	T_{max} (°C)
REF	-	34.91	314
B5	5.47	43.59	321
CA10	-	31.71	316
CA10B5	4.76	39.14	321

Table 11 – 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 (%)
REF	45	162	1.76	172	370	57.13	377	524	34.43	-	-	-
B5	41	180	2.86	211	367	47.32	380	498	26.26	498	614	14.34
CA10	38	134	2.57	164	362	56.97	379	522	33.59	-	-	-
CA10B5	44	145	3.13	173	363	50.58	391	506	26.50	507	605	9.43

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

Figure 15 – TG (a) and DTG (b) curves of different treatment conditions of bamboo samples.

Figure 16 – DSC results of the different treatment conditions of bamboo samples.

4 – Conclusions

The chemical modification with citric acid over the physical-mechanical properties and chemical composition of bamboo did not cause considerable chemical degradation, physical damage, or strength reduction. This treatment approach caused considerable improvement in water absorption, moisture uptake, and swelling properties in comparison with reference and DOT treated samples. Although higher three-point bending and compression strength were observed, caution should be adopted for the bamboo treated with citric if it is subjected to tensile and shear forces in a structural application. Furthermore, citric acid resulted in some changes in cellulose structure, with the reduction of crystallinity index, possible hydrolysis of the amorphous phase and glycosidic bonds in hemicelluloses, and detachment between the parenchyma and fibre bundle regions. Samples treated only with citric acid had higher weight losses upon heating than those of the reference samples, while the treatment only with DOT resulted in the best thermal stability. The combination of both citric acid and DOT was found to be an alternative to overcome this problem.

This work provides insights into the use of non-hazardous materials as an alternative for chemicals in bamboo treatment, opening new opportunities for the development of more durable bamboo-based materials with improved stability.

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