Effects of Alkali Treatment and Drying Method on Densification Process of Bamboo

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Abstract

In this study, a two-step process of delignification and densification was carried out on *Dendrocalamus Asper* bamboo specimens. It is aimed to investigate the densification properties of the bamboo samples after removing the lignin. To delignify the samples, two different approaches were applied. The first group was treated in a room-temperature NaOH + NaSO3 solution, while the second group was treated in the same solution at 100 ^{O}C. Afterward, the samples were dried in either an oven with 100 ^{O}C or at room temperature of 25 ^{O}C. Hence, a total of four different groups of delignified and dried samples were produced with an average moisture content of 7 - 10 %. The samples were then densified to 50 % of their original thickness having the thickness reduction determined a priori using a thermo-mechanical press system at 160 ^{O}C. The results indicated that all alkali treated samples required a lower load for the densification process compared to the reference. Average compression stress of 17.0 MPa for the reference, 10.3 MPa for the samples treated with alkali solution at room temperature, and 7 MPa for the boiled alkali solution treated samples were applied to achieve a densification degree of 50%. The drying process also affected the compression resistance of bamboo and oven-dried specimens showed an increase of 30% and 17% for room temperature and boiling temperature treatment respectively. The modulus of rupture, limit of proportionality, and elastic modulus of densified bamboo were all negatively impacted by the pre-treatment, according to the results of the bending test. Overall, untreated and treated bamboo displayed similar behavior for physical attributes in densified samples. After being treated with alkaline solution, bamboo showed reduced levels of lignin as well as hemicellulose and cellulose, according to chemical tests. In conclusion although the treatment facilitates the densification process, the time employed for the treatment and the final properties of the material did not prove to be advantageous

Highlights

- Dendrocalamus asper bamboo was subject to a two-step process of delignification and densification.
- Effects of NaOH + NaSO3 solution temperature and drying process were compared.
- Fiber volume and microstructure were analyzed.
- Physical, mechanical and chemical characteristics were studied.

1. Introduction

Bamboo has promising properties to be used as an alternative and sustainable material for construction and building purposes. Despite that, a few factors hinder its use in large scale, such as: inhomogeneous geometry and physical and mechanical properties along the culm, dimensional instability, natural degradation, and anisotropy. These characteristics must be overcome to promote a wider use for bamboo in construction industry [1].

By modifying the physical and mechanical properties of bamboo through controlled processes, alternative products can be produced with greater standardization and reliability. Modifications such as chemical treatments and densification are alternatives that has been explored in the wood and bamboo industry to minimize the heterogeneity of these materials and increase their performance [2–5].

The densification process consists of compressing the samples in an open thermo-hydraulic press system, in the radial direction, resulting in the decrease of the internal volume of the material due to either the plasticization or collapse of cell walls [4, 6, 7]. To enhance wood quality, densification is employed in various processes such as wood shaping, molding, friction welding, embossing, and wood bending. These applications serve to dissipate internal stresses, improve key wood characteristics, including dimensional stability, strength, surface hardness, durability, and facilitate the drying and plasticization of the wood. However, while processing in an open system, it is impossible to appropriately regulate the process parameters such the moisture content of the materials. Whether the process is open or closed will affect the densification processing's outcome [8].

The delignification process involves extracting lignin from vegetal-based resources and disintegrating the lignocellulosic structure into fibrous components [9]. The delignification process can be carried out in two ways, the solvent process, and the chemical process. The most used in industry is the chemical process using sulfite and alkaline pulping [10]. The delignification process using solvent-based pulping such as sodium hydroxide, anthraquinone, and methanol usually has higher efficiency, is less expensive, presents lower emissions and by-products. Nonetheless, this process is mainly used on small scale [10]. The use of water as a pretreatment to extract lignin before densification of bamboo have been studied to increase the plasticity of bamboo, consequently facilitating the process of densification [11].

The two-step process of delignification/densification involves the partial removal of lignin and hemicellulose from the lignocellulose materials followed by thermo-mechanical pressing. This process have been used usually for wood or bamboo in order to achieve a more efficient densification using less energy and slightly modifying their structure, resulting in better performance such as better biological resistance, better dimensional stability, low equilibrium moisture content, decreased contraction and expansion, and better weather resistance [12].

A two-step process of delignification with NaOH + Na2SO3 solution, followed by densification, improved the strength of wood. For instance, densified basswood with lignin removal of 45% presented an ultimate tensile strength of 587 MPa, in comparison to 51.6 MPa for natural wood, and 175.0 MPa for densified wood without delignification [13]. For *Phillostachys Bambusoides* bamboo species, an improvement in tensile (770 MPa) and flexural strength (327 MPa) was found after the delignification and densification processes, in comparison to natural bamboo (298 MPa and 148 MPa, for tensile and flexural strength, respectively) [14].

This paper aims to study chemical modification and delignification through NaOH based solutions with different temperatures, and two types of drying process prior to densification, and evaluate its effects on bamboo physical, mechanical, chemical, and thermal properties of *Dendrocalamus asper* bamboo. Is expected to achieve total cell wall collapse and complete bamboo densification with highly aligned cellulose fibers and material with improved dimensional stability and mechanical properties.

2. Materials and methods

2.1. Material and sample acquisition

Three-year-old mature bamboo poles of Dendrocalamus asper species were harvested at an experimental field in the state of São Paulo, Brazil (21°59'S 47°26'W). The harvested culms, boasting an average diameter of 18 cm, underwent treatment utilizing the method elucidated in [15]. This method entails immersing bamboo poles in a Dissodium octaborate tetrahydrate (DOT) solution for a period of 5 days, succeeded by a subsequent 3-day drying phase at room temperature, to ensure the durability of the bamboo. The treated bamboo poles were stored in a protected environment at room temperature for four months until they reached an equilibrium moisture content of 9 to 11%. Samples with average dimensions of 100 mm in length and 30 mm in width were extracted from different internodes located in the middle part of the culms (Fig. 1). The wall thickness of all samples varied between 13 and 14 mm.

2.2. Methods

The samples were submitted to delignification, drying and densification process, and evaluated through physical, mechanical, chemical, and thermal tests. Before testing the samples were conditioned at 25 ± 2 ºC and 65 ± 3% of relative humidity. Each group received a code to facilitate its identification and analysis (Fig. 2). The order of treatment and groups obtained are represented in Fig. 3. A summary of the number of samples and its dimensions for each evaluation can be found in Table 1.

Table 1
Distribution of samples for evaluation.

Type of test	Dimensions (L x W x T) (mm)	Number of samples per group	Total number of samples	Treatment
Physical properties	21 x 21 x t	5	25	Densified
	21 x 21 x t	3	15	Undensified
Image analysis	21 x 21 x t	1	5	Densified
	21 x 21 x t	1	5	Undensified
Three point bending test	100 x 8 x 7	9	45	Densified
TGA and FT-IR	Bamboo powder	-	-	Densified

2.2.1. Delignification

The solution that was used for the delignification process is sodium hydroxide 2.5 mol.L-1 mixed and Na2SO3 0.4 mol.L-1. Bamboo samples were divided in two groups immersed in the solution. One group with boiling aqueous solution for approximately 1 hour, and the other with the aqueous solution at room temperature with the same composition (Fig. 4) for 1 hour. To remove the solution after treatment, both processes were followed by immersion in boiling deionized water repeatedly until a neutral pH was achieved.

2.2.2. Drying process

Bamboo blocks obtained from each delignification process were submitted to two different drying processes. The first method was conditioning the samples in a controlled environment with 65 ± 3% of relative humidity at room temperature (25 ± 5 ºC) for 30 days. consisted in leaving the samples in the oven at a temperature of 100 ºC for 24 hours, as shown in Fig. 5.

2.2.3. Densification process

The samples are compressed radially in an open thermo-hydraulic press system as part of the densification process, which causes a reduction in the material's internal volume as a result of either plasticization or cell wall collapse. [6]. Following the same process as Kadivar et al. 2021 [7], universal testing machine EMIC DL-30000 with a load cell of 300 kN, was equipped with a small press plates system for heating the samples and applying the desired pressure.

The pressure was applied at a compression rate of 6.7 mm/min until the samples reached a densification degree of 50%, where the average compression stress of 17 MPa for the reference, 10.31 MPa for the samples treated with alkali solution at room temperature, and 6.95 MPa for the boiled alkali solution treated samples were applied. The temperature of the plates was set to 160°C [7]. Stress-strain plot was obtained until the densification degree of 50%.

After reaching the desired densification degree, the equipment was set to stop applying load and maintain the displacement.

When the applied load is removed and the displacement is constant, the internal stress begins to decrease until it approaches a constant value. The time required for the internal stress to reach a constant value is called relaxation time. Data about the load applied was gathered for 10 minutes to analyze the relaxation behavior and obtain the relaxation curves.

2.2.4. Physical properties

Samples with the size of (21 × 21 × t) mm were prepared and dried in an oven for 24 hours at 100 ± 5°C. For density, water absorption and thickness swelling, dimensions and weight of bamboo samples were taken after oven drying and after immersion in water for 1 hour and 24 hours with a digital caliper (± 0.5 mm precision) and a digital scale (± 0.5 g precision).

Density was calculated based on ASTM Standard D2395-17 recommendations [16]. Thickness swelling and water absorption values after 1 hour and 24 hours of water immersion were calculated in relation to the weight and dimensions of the samples after oven drying at 100 ± 5°C.

For statistical comparison between groups, one-way ANOVA and post-hoc Tukey tests were applied for each physical property. All the comparisons were made within the same condition (oven dried, 1 hour, or 24 hours water immersion).

2.2.5. Mechanical characterization

Samples with the size of 7 mm thickness, 8 mm width and 100 mm length extracted from the middle layer of specimens were prepared to perform three point bending tests with a span of 80 mm, following ASTM D790 test method [17] recommendations. A mechanical servo-hydraulic testing machine (MTS Model 370.02, Eden Prarie, MN) was used to perform the tests (Fig. 6a).

Modulus of Rupture (MOR), Modulus of Elasticity (MOE), and Limit of Proportionality (LOP) were calculated, which equations can be found on Fig. 6b. Specific Energy (EE) was calculated as the area under the stress-strain curve divided by the cross-section of the samples. One-way ANOVA and post-hoc Tukey tests were applied to assess statistical differences between groups for each mechanical property.

2.2.6. Image analysis

A Hitachi TM-3000 Scanning Electron Microscope (SEM) using an accelerating voltage of 15 kV and a backscattered electron detector were used to obtain images from the cross-sectional area of the samples.

To prepare the samples, the Struers Tegra Pol-11 machine was used for sanding and polishing. To achieve a highly reflective surface, samples were passed through different grit size paper (from P320 - P2000) with water, and polycrystalline diamond suspension solutions were used to finish the polishing process.

ImageJ software was used to calculate the fiber volume fraction of bamboo. First, the images from the samples were collected and the image was focused on the usable area Fig. 7a. Secondly, the image was transformed into an 8-bit (grayscale) image to separate the fiber portion from the holes and parenchyma using the software command limit Fig. 7b. The software automatically detects the darkest part, which is the parenchyma and the empty spaces.

2.2.7. Chemical analysis

Fourier Transform Infrared Spectroscopy (FT-IR) analysis was performed on densified groups after delignification and drying process. Particles of bamboo were obtained from the analytical mill Quimis - Q298A, and a PerkinElmer Spectrum One spectrometer with ATR accessory was used to perform scans along the range of 4000 to 600 cm-1, with a resolution of 4 cm-1.

2.2.8. Thermogravimetric Analysis

Natural and treated densified bamboo were used to perform simultaneous TG-DSC measurements, using a NETZSCH STA 449F3 apparatus, within a temperature range from 25 to 600°C under a nitrogen environment, purged at 40 mL min − 1. A constant heating rate of 10°C min − 1 was maintained.

3. Results and discussions

3.1. Physical properties

Values of density of all groups are shown in Fig. 8 for oven drying condition. Complete statistical analysis and density values for oven dried, 1 hour and 24 hours water immersion conditions can be found on Table 2. It can be observed that, all treated samples presented a lower density in comparison to the reference ones, with no statistical difference for non-densified condition and with significant difference after densification, except for T25D100D group. This result can be related to the removal of lignin from the bamboo structure by the action of the alkaline solution, which will be discussed further on chemical analysis.

Table 2: Density values.

Density (g/cm³) - Mean (SD)			
Undensified groups			
Treatment	Oven dried	1 hour	24 hours
RefUN	0.731 ^{a} (0.004)	0.773 ^{a} (0.021)	0.907 ^{a} (0.005)
T25D25UN	0.656 ^{a} (0.010)	0.714 ^{a} (0.008)	0.897 ^{a} (0.012)
T25D100UN	0.704 ^{a} (0.005)	0.747 ^{a} (0.020)	0.945 ^{a} (0.014)
T100D25UN	0.683 ^{a} (0.007)	0.792 ^{a} (0.0007)	0.946 ^{a} (0.024)
T100D100UN	0.703 ^{a} (0.011)	0.788 ^{a} (0.022)	0.969 ^{a} (0.015)
Densified groups			
Treatment	Oven dried	1 hour	24 hours
RefD	1.083 ^{a} (0.057)	1.078 ^{a} (0.022)	1.076 ^{a} (0.042)
T25D25D	0.963 $^{b, c}$ (0.047)	1.009 ^{a} (0.039)	1.067 ^{a} (0.022)
T25D100D	1.024 $^{a, c}$ (0.031)	1.039 ^{a} (0.049)	1.289 ^{a} (0.421)
T100D25D	0.791 ^{d} (0.062)	0.740 $^{b, c}$ (0.333)	1.017 ^{a} (0.055)
T100D100D	0.934 ^{b} (0.017)	1.001 $^{a, c}$ (0.013)	1.083 ^{a} (0.026)

$^{a, b, c}$ letters indicate significant statistical differences between values in the same column (Tukey).

Regarding water absorption (Fig. 9 and Table 3), undensified reference samples showed less absorption either after 1 hour or 24 hours in comparison to all treated groups. The densification process raised bamboo water absorption, but this trend was not confirmed for a few treated groups, namely T25D25 and T100D25.

Densified reference samples presented an expected higher water absorption in relation to non-densified samples, however, its values for 1 hour immersion are lower than all the values from densified and non-densified treated samples (Fig. 9). Even though without statistical difference, after 24 hours of immersion reference samples presented lower mean values in comparison to treated ones. This effect can be related to damage caused by alkaline treatment, which leads to more gaps in the bamboo structure. Also, since the sclerenchyma has a higher water absorption than the parenchyma, the removal of lignin does not influence this parameter [18].

Table 3: Water absorption values.

Water Abs (%) - Mean (SD)		
Undensified groups		
Treatment	1 hour	24 hours
RefUN	9.51 ^{a} (0.50)	43.63 ^{a} (2.00)
T25D25UN	20.36 $^{b, c}$ (0.88)	68.21 ^{b} (0.59)
T25D100UN	17.29 ^{b} (1.25)	52.56 $^{a, c}$ (2.22)
T100D25UN	25.27 ^{c} (1.48)	62.46 $^{b, c}$ (4.16)
T100D100UN	23.40 $^{b, c}$ (3.18)	60.32 $^{b, c}$ (3.94)
Densified groups		
Treatment	1 hour	24 hours
RefD	8.23 ^{a} (1.41)	53.92 ^{a} (3.20)
T25D25D	17.59 ^{b} (3.16)	54.51 ^{a} (4.84)
T25D100D	16.59 ^{b} (2.69)	58.21 ^{a} (2.25)
T100D25D	20.93 ^{b} (4.79)	58.95 ^{a} (8.65)
T100D100D	20.80 ^{b} (2.29)	61.40 ^{a} (6.03)

$^{a, b, c}$ letters indicate significant statistical differences between values in the same column (Tukey).

The thickness swelling results reveal that densified reference samples exhibit lower dimensional stability compared to treated ones. Notably, there is a statistically significant difference observed only within the T100D25D group. Samples treated in a boiling alkaline solution and dried at room temperature (T100D25D), have a significant higher stability in comparison to other treatment conditions and reference. On the other hand, for non-densified samples, bamboo samples without any pretreatment have similar stability in comparison to treated ones (Fig. 10 and Table 4) after 24 hours immersion.

Table 4: Thickness swelling values.

Thickness Swelling (%) - Mean (SD)		
Undensified groups		
Treatment	1 hour	24 hours
RefUN	1.98 ^{a} (0.71)	8.75 ^{a} (1.43)
T25D25UN	6.29 ^{a} (1.90)	13.53 ^{a} (1.02)
T25D100UN	4.52 ^{a} (1.09)	7.68 ^{a} (0.58)
T100D25UN	5.34 ^{a} (1.21)	10.08 ^{a} (1.27)
T100D100UN	4.97 ^{a} (1.10)	8.55 ^{a} (0.76)
Densified groups		
Treatment	1 hour	24 hours
RefD	6.46 ^{a} (5.39)	40.79 ^{a} (10.85)
T25D25D	9.56 ^{a} (3.72)	32.55 ^{a} (7.79)
T25D100D	11.81 ^{a} (4.24)	34.50 ^{a} (3.33)
T100D25D	7.81 ^{a} (3.08)	19.05 $^{b, c}$ (2.33)
T100D100D	9.74 ^{a} (2.63)	31.15 $^{a, c}$ (6.44)

$^{a, b, c}$ letters indicate significant statistical differences between values in the same column (Tukey).

Figure 11 displays the test body of six sample groups post-physical tests and a 24-hour water immersion. Notably, both undensified and densified groups reveal that the chemical treatment resulted in defibrillation within the bamboo structure.

3.2. Mechanical characterization

Table 5 presents modulus of rupture (MOR), limit of proportionality (LOP), modulus of elasticity (MOE) and specific energy (EE) for densified reference and treated samples after three point bending test.

Table 5: Mechanical properties of densified bamboo with different pretreatments.

Treatment	MOR (MPa)	LOP (MPa)	MOE (GPa)	EE (kJ/m²)
RefD	266.7 ^{a} (27.8)	174.2 ^{a} (23.5)	19.2 ^{a} (2.6)	19.5 ^{a} (10.5)
T25D25D	190.9 ^{b} (13.9)	118.3 ^{b} (9.71)	14.7 ^{b} (1.3)	20.4 ^{a} (3.3)
T25D100D	162.5 ^{c} (19.2)	118.7 ^{b} (17.8)	15.8 ^{b} (2.6)	20.2 ^{a} (5.9)
T100D25D	144.6 ^{c} (18.3)	90.9 ^{c} (10.9)	12.9 ^{b} (3.2)	14.1 ^{a} (6.9)
T100D100D	154.2 ^{c} (20.0)	102.1 $^{b, c}$ (23.2)	14.6 ^{b} (2.3)	13.0 ^{a} (0.8)

$^{a, b, c}$ letters indicate significant statistical differences between values in the same column (Tukey).

The results indicate that densified reference samples have higher mechanical properties then all treated ones. This can be related to the removal of lignin due to alkali effect of the pretreatment. Although lignin is a weak component on bamboo structure in comparison to cellulose, its removal causes a degradation of the interface between matrix and bamboo fibers, reducing the composite strength. Average fiber fraction image analysis (section 3.4), showed that the fiber content of treated and densified samples decreased due to the attack of the treatment in the fibers, meaning that there was a removal of cellulose after treatment, which also justify the negative impact of the delignification process on mechanical properties.

MOR and MOE for untreated and undensified *Dendrocalamus asper* bamboo species found on literature are 215.3 MPa and 21.45 GPa, respectively [19]. Results found on this work shows an improvement in MOR after densification, but a decrease in both modulus of rupture and elastic modulus for chemically treated groups. These findings are opposite to results found for *Phyllostachys Bambusoides* [20], in which pretreated and densified samples presented an improvement flexural strength. It is important to mention that the immersion time on alkaline solution, densification time and densification degree were different from this study.

Failure patterns for all groups can be seen on Fig. 12. A small number of individual fibers were seen, because of the tension fibers that work as bundles in the crack propagation. The interface between the fibers and the parenchyma shows good adhesion and the failure happens most often in the parenchyma. In the compression area, the bending caused a crack propagation in the compacted fibers, causing fiber breakage.

Almost all samples showed a brittle fracture, and shear failure presenting a very small plastic deformation before the crack. Despite that, treated samples showed plastic deformation, which was not observed in the reference group. The crack propagation also happened slower than the reference, being the groups with boiling solution the ones with more plastic deformation.

3.3. Effects of pretreatment on densification process

The stress-strain curve is shown in Fig. 13. The reference group presents the higher value for stress until the strain of 0.5 mm/mm (17 MPa). The samples which underwent boiling treatment needed less load application to achieve the densification degree of 50%, being the samples that dried at room temperature with the lowest amount of stress (7 MPa), approximately 40% in comparison to reference samples. This indicates that the removal of lignin due to alkaline treatment facilitates the process of densification, allowing to decrease the load applied on bamboo and total energy needed to densify the material.

The applied stress and also internal stress relaxation within the bamboo matrix during the process of densification are shown in Fig. 14. The relaxation curves depicted in Fig. 14 highlight that the THM process is an intensive method for bamboo modification. This process induces internal stresses within the bamboo structure. This phenomenon is because of its structural transformation. The same trend was observed for all the samples; Relaxation eliminated some part of the stresses with a high elimination rate at the first 50 seconds for all the samples and then became asymptotic to some different residual values. The residual stress value after 550 seconds was around 8MPa for the reference and this value decreased by using pretreatments. The group of densified bamboo treated in boiling NaOH + NaSO3 solution and dried at room temperature asymptotic to a residual value of approximately 2 MPa.

This result indicates that treated samples in boiling solution accommodate its structure after the densification process faster than the other groups, and reduce internal stresses.

3.4. Image analysis

The image analysis through *ImageJ software* (Table 6) showed that the average fiber fraction for undensified groups increased after the alkali treatment, being the higher fractions obtained in room temperature solutions, which is in accordance with the removal of lignin from the bamboo structure. However, for densified samples, treated groups presented lower values in comparison to the reference one. Notably, the volume of fiber fraction of T100D100D group is similar to the undensified reference one, meaning a reduction of 10% approximately. This can be related to a reduction, in less extent, of cellulose content, which becomes apparent after densification process. This indicates that, even though the pretreatment is effective on removing lignin from the structure and facilitates the process of densification, it has a negative impact on bamboo, compromising the fiber content.

Mechanical results (presented on section 3.2) showed that the chemical pretreatment had a negative impact on mechanical resistance of densified samples, which is associated with a weaker interface between parenchyma and sclerenchyma and a reduction on fiber content due to thermal and chemical attacks. Thermal analysis, which will be discussed in detail on the next section, indicates a loss of cellulose after treatment and densification, being in accordance with the fiber fraction volume and mechanical results.

Table 6
Values of average fiber fraction for each group.

Treatment	Average Fiber Fraction
RefUN	52,13%
T25D25UN	65,98%
T25D100UN	63,29%
T100D25UN	60,92%
T100D100UN	59,71%
RefD	66,15%
T25D25D	61,64%
T25D100D	62,45%
T100D25D	54,84%
T100D100D	52,81%

The images taken from the Hitachi TM-3000 Scanning Electron Microscope (SEM) showed characteristics of the densification processes and the influence of the alkaline solution, and are presented on Fig. 15 and Fig. 16 for densified and undensified samples. Images were obtained from the inner, middle, and outer layers of the cross-section.

It is possible to observe the vascular vessels on undensified groups (Fig. 17a) and the influence of the alkali treatment on them. T25D25 treatment showed a higher efficiency on the closure of the vessels. Also, in comparison to the reference, is possible to observe a higher amount of microcracks on the bamboo structure due to extraction of lignin and degradation of the material (Fig. 17b). The samples that have gone through densification have closed voids resulting from the process and have the fiber parts (lighter region) closer to each other's (Fig. 17c).

The use of boiling solution raised the number of visible cracks and space, allowing the material to better accommodate the displacement during the densification process. However, it reduces the mechanical properties of densified bamboo, as it causes degradation of cellulose and hemicellulose in addition to lignin, and leads to a weaker bond between matrix and fibers

3.5. Chemical analysis

The FTIR spectra of bamboo is presented in Fig. 18.

The bands close to 1742 and 1249 cm-1 showed a decrease after the alkaline treatment. The band at 1742 cm-1 is attributed to C = O stretching vibration in hemicellulose in bamboo [21]. After treatment, this band is no longer observed in the samples, demonstrating the effectiveness of alkaline attack in removing hemicellulose from bamboo. Temperatures higher than 150°C can also cause a removal of hemicellulose content [7, 22], however, the decrease in intensity was more visible in treated samples, which highlights the effect of the chemical treatment.

The bands close to 1600 and 1505 are attributed to the stretching of the benzene ring and -OCH3 groups in the lignin [23]. The intense absorption band close to 1049 cm-1 is associated with the C-O/C-C stretching vibrations [24, 25]. The band close to 1249 cm-1 is attributed to the acetyl groups of lignin and presented a decrease in the intensity after the treatment with NaOH [26], which is related to the removal of lignin from the bamboo structure, with higher decrease in treatments with boiling alkali solution.

In regions close to 2900 cm-1 the band was associated with symmetric and asymmetric stretching of CH2 groups. The band at 3400 cm-1 is related to the -OH stretching vibration from the cellulose of the bamboo fiber. The band of water adsorbed on the fibers is observed in the wavenumbers close to 1639 cm-1. In all the regions related to water absorption, there was not observed significant changes, which is in accordance with the results found on water absorption test after 24 hours immersion for densified samples.

3.6. Thermogravimetric analysis

Bamboo fibers are basically composed of hemicellulose, cellulose, and lignin. Some other substances may be present as components or impurities on the surface of the fibers. The thermal decomposition of bamboo fibers can be divided into four main stages. i.e., moisture evaporation, hemicellulose decomposition, cellulose decomposition, and lignin decomposition [27].

The decomposition of hemicellulose occurs at lower temperatures, with a further decomposition of cellulose. Lignin is the component with the highest decomposition temperature and, according to some studies, represents the lowest rate of mass loss within the heating rate used [28]. Figure 19 shows the DSC curves of untreated and treated bamboo fibers.

When temperatures are lower than 200°C it is possible to observe endothermic peaks related to the evaporation of moisture present on the surface of the fibers. Cellulose decomposition can be observed at temperatures close to 350°C, with an endothermic peak appearing in all bamboo fiber samples. However, it can be noted a decrease in the peak intensity for treated groups at room temperature (T25D100D and T25D25D), which may be associated with an effective attack on bamboo cellulose by the alkaline chemical treatment. Two exothermic phenomena are observed at 275°C and 365°C, associated with the decomposition of hemicellulose and lignin, respectively. It is possible to observe a decrease in peak intensity at 365°C for T100D25 group. This result may be associated with better lignin removal when treating bamboo fiber with NaOH at 100°C and drying at 30°C [29–31].

Through DTG curves of untreated and treated bamboo (Fig. 20), is possible to observe, in the temperature range between 25 and 200°C, a small loss of mass for all groups, which was associated with the removal of moisture.

A peak close to 300°C is associated with the decomposition of hemicellulose and a peak close to 350°C is related to the decomposition of cellulose in the fibers. It is evident that in samples without alkaline treatment the peak between 300°C and 350°C is more intense than in samples treated with NaOH.

The reduction in the cellulose content of treated samples corroborate with the loss of mechanical resistance after pretreatment, indicating that the alkali treatment caused the expected removal of lignin content, but also led to a degradation on the interface between parenchyma and sclerenchyma, and removal of cellulose content.

Figure 21 shows the TG curves of untreated and treated bamboo samples. From the TG curves, the mass loss before and after the treatments are very similar, being possible to observe a greater mass loss for the untreated fiber. This result may be associated with the presence of alkalis on the surface of the treated samples that do not evaporate within the studied temperature range.

4. Conclusions

The effects of alkali treatment and drying process before densification of *Dendrocalamus asper* bamboo species was assessed and can be summarized as follows:

(1) Effect of treating bamboo using a solution of NaOH + Na2SO3, was beneficial to compressibility in densification process. It facilitates the process by removing lignin content and reducing its internal stresses.

Samples treated with a boiling solution and subsequently dried at room temperature exhibited a remarkable reduction, requiring only 40% of the stress applied to non-treated bamboo. This finding implies a significant decrease in the energy and load needed to achieve a 50% densification degree.

(2) We expected the pretreatment improves the physical performance of densified bamboo. However, for densified samples, overall untreated and treated bamboo showed similar behavior for physical properties.

(3) Three-point bending test results showed that the pre-treatment had a negative impact on modulus of rupture, limit of proportionality and elastic modulus of densified bamboo. The modulus of rupture decreased between a range of 29–46%, the limit of proportionality reduced in the order of 32–48%, and the modulus of elasticity dropped within 18–33%.

(4) Thermal analysis, FT-IR tests, and fiber volume fraction image analysis, indicated a reduction in hemicellulose and cellulose content of bamboo, in addition to the removal of lignin after alkaline treatment.

In summary, if the appliance doesn't require exceptionally high properties, it is well-suited for high production, streamlining the densification process. In summary, the advantages of subjecting bamboo to alkali solutions in an open system densification process are compromised by the detrimental effects on mechanical properties. Further research using a closed pressing system is warranted to explore the potential of these pretreatments in enhancing the physical and mechanical properties of densified bamboo.

Declarations

Acknowledgements

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Figures

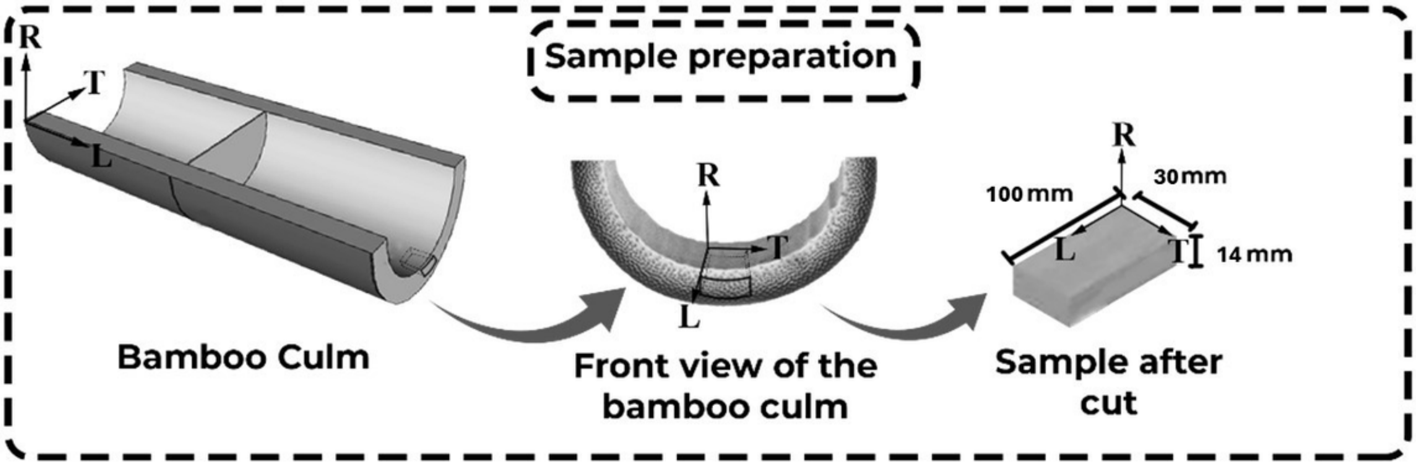


Figure 1

Sample preparation from the bamboo culm.

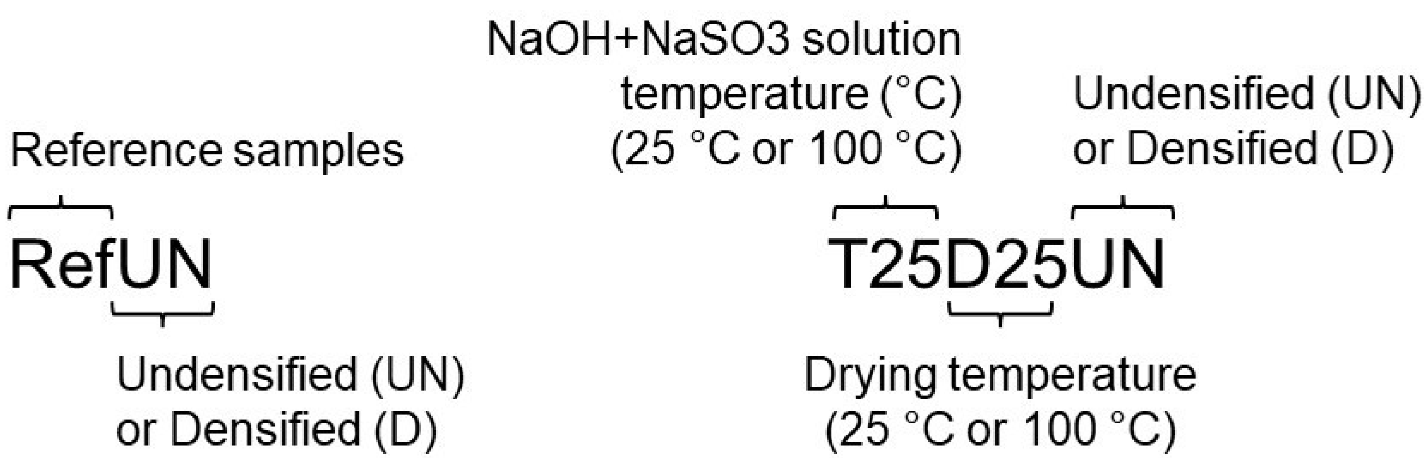


Figure 2

Sample group identification.

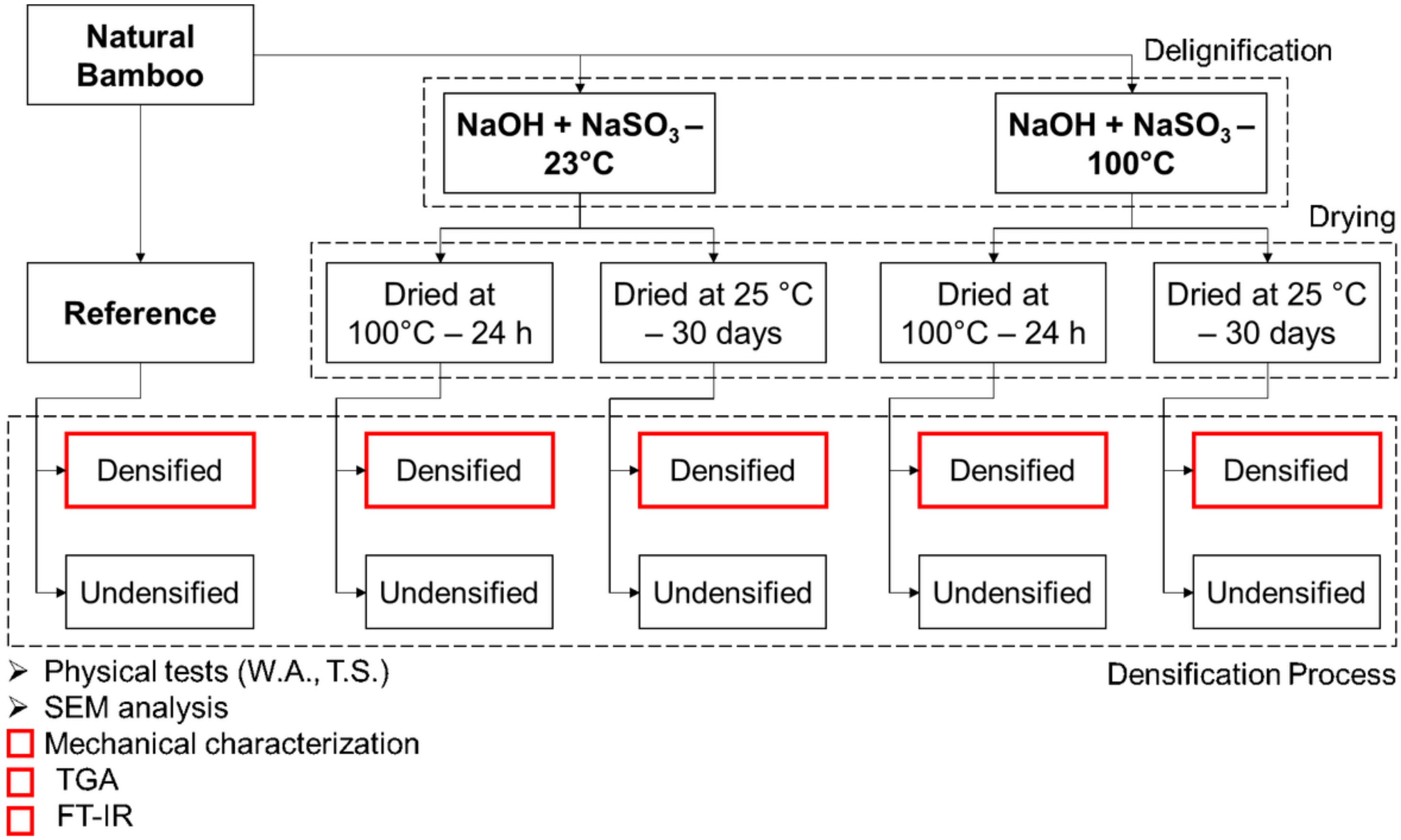


Figure 3

Fluxogram of treatment and evaluation.

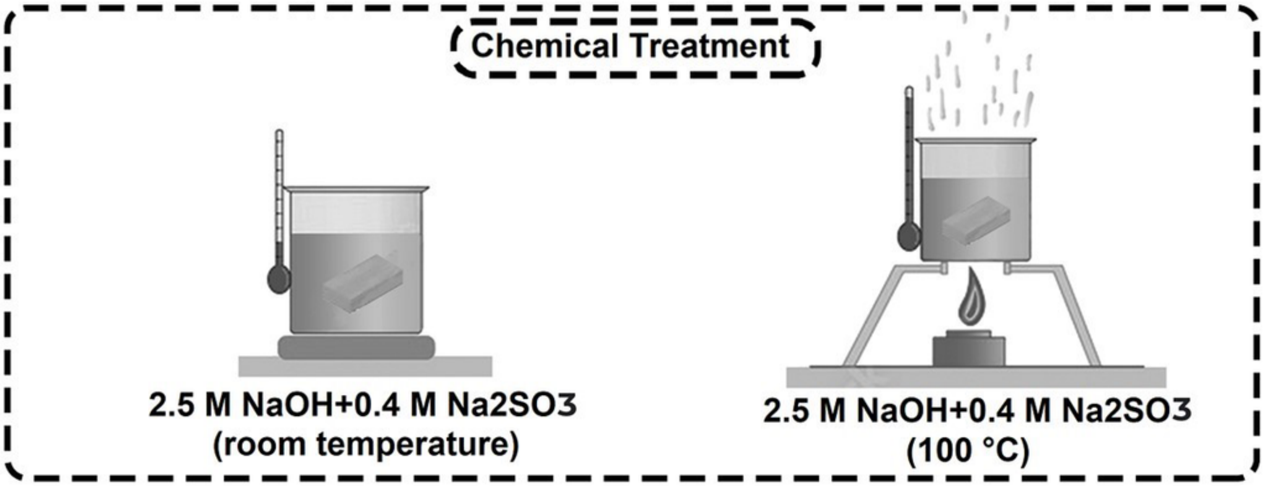


Figure 4

Scheme of delignification process.

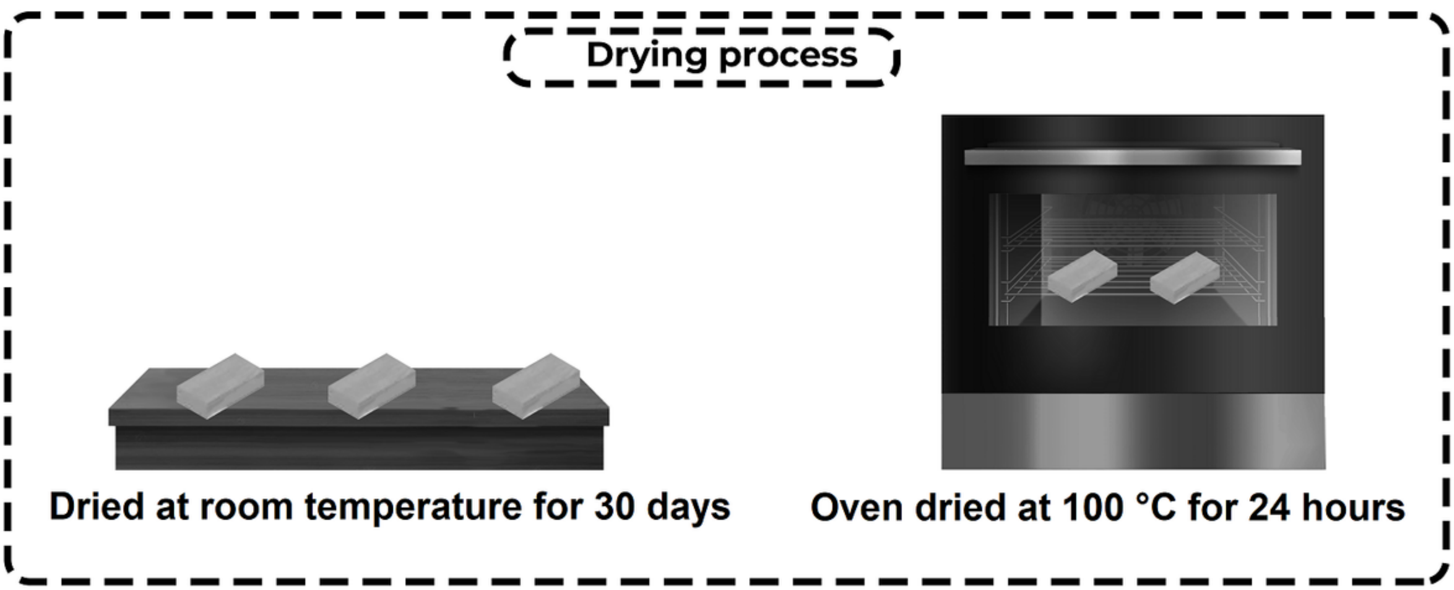


Figure 5

Scheme of drying process.

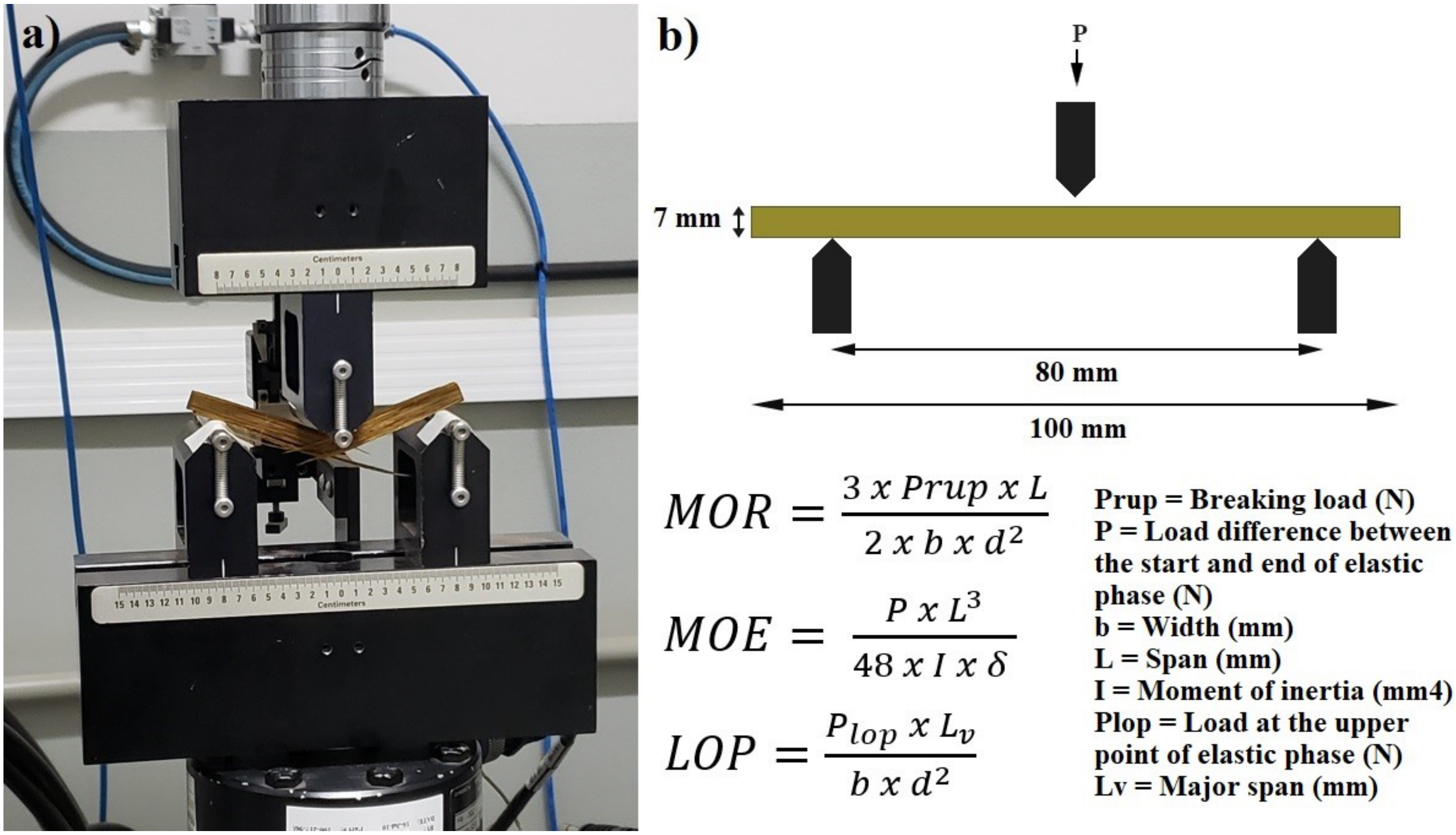
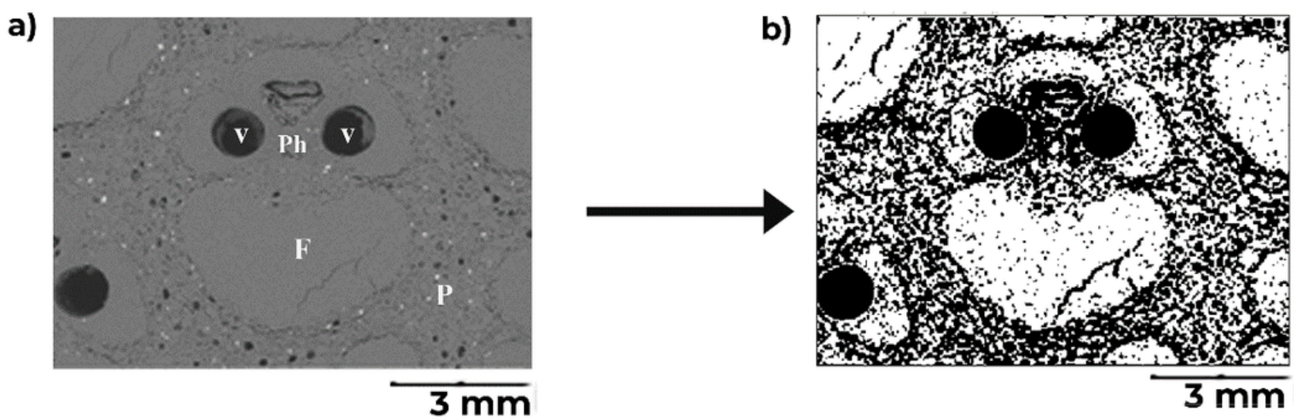


Figure 6

Bending test (a) equipment (b) scheme and formulations



V=Vessels; Ph=Phloem; F=Fiber bundles; P=Parenchyma.

Figure 7

ImageJ analysis (a) reference photo (b) grayscale image with fiber bundles isolated.

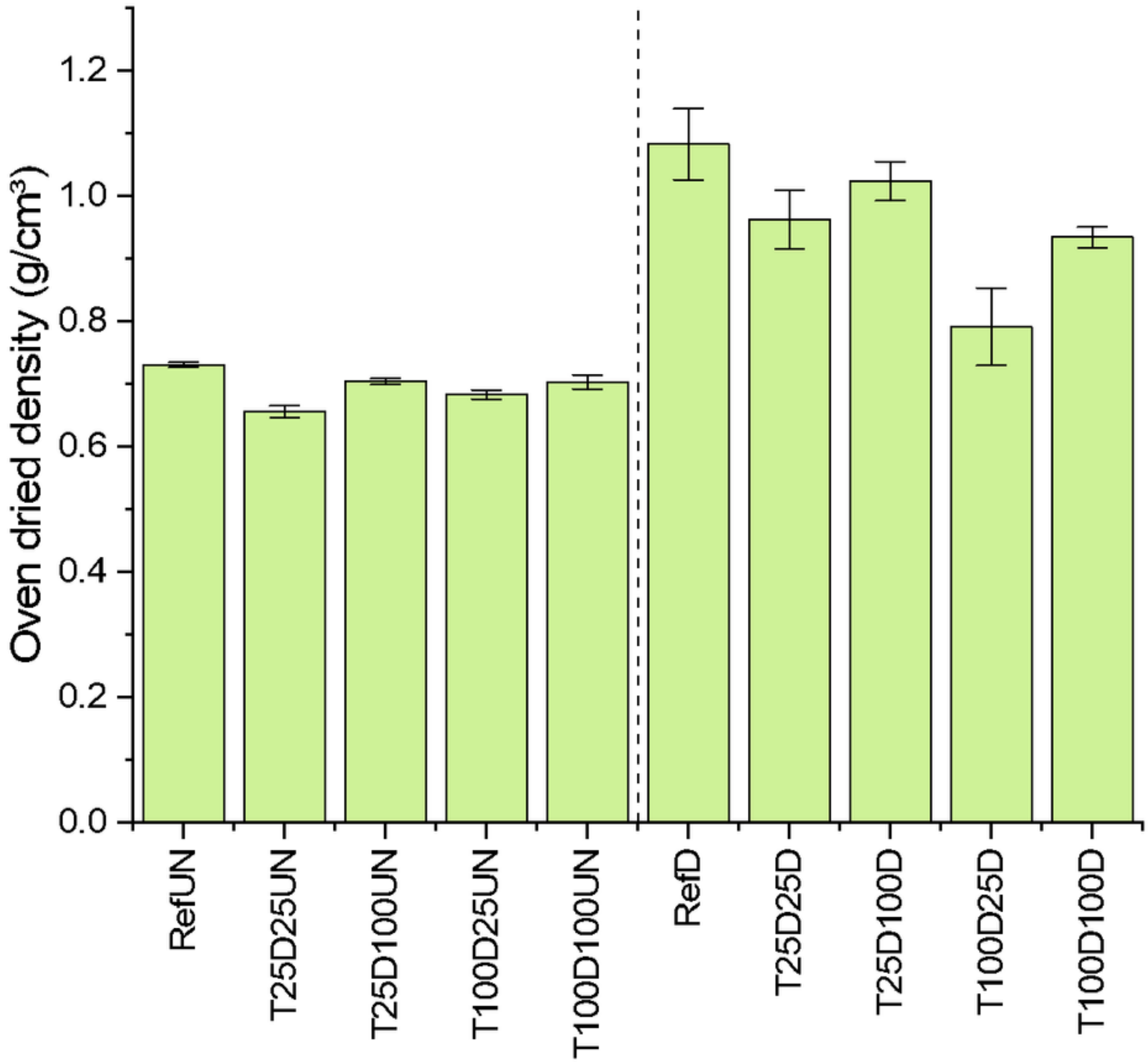


Figure 8

Bamboo oven dried density values before and after treatment.

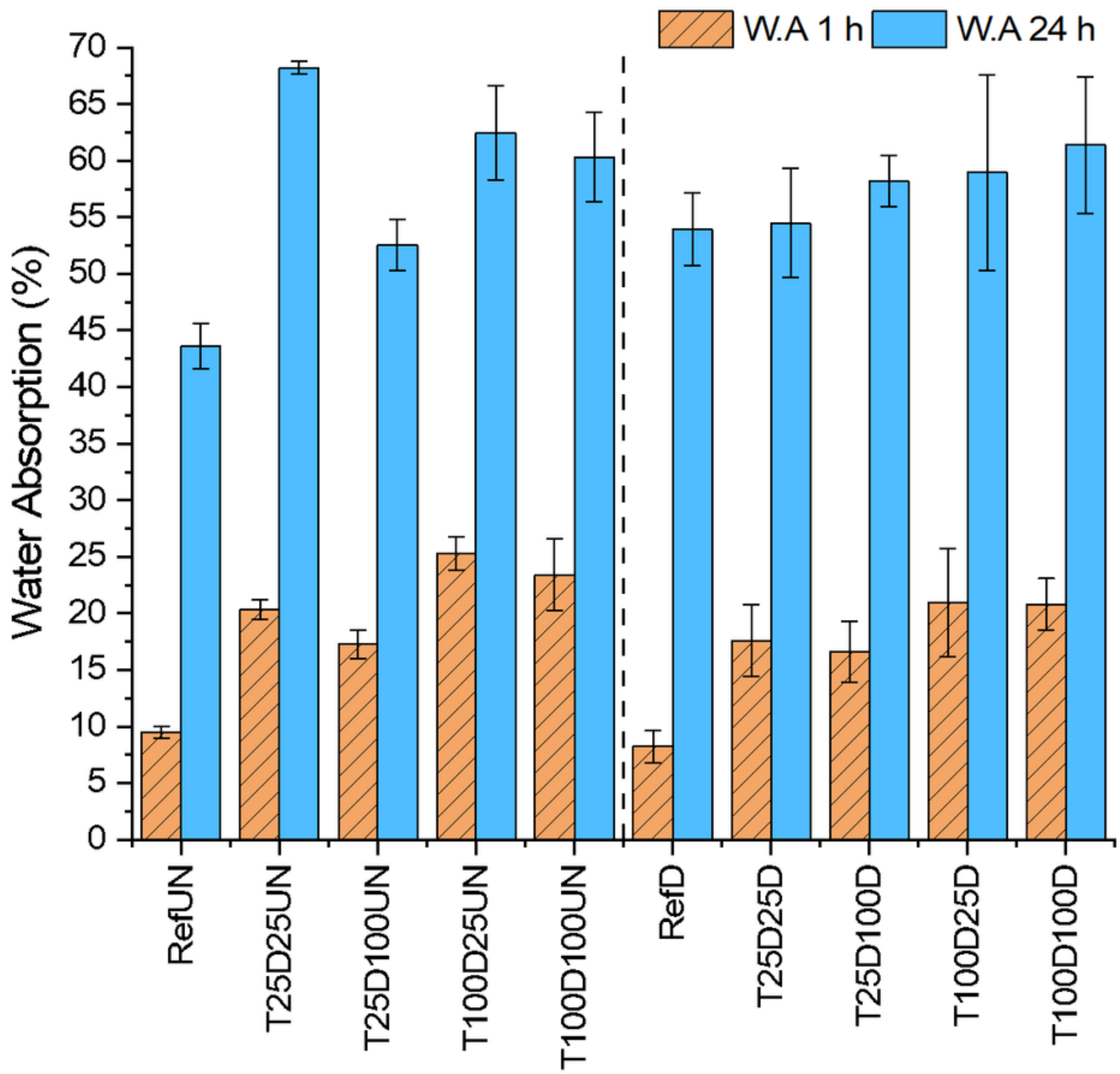


Figure 9

Bamboo water absorption values before and after treatment.

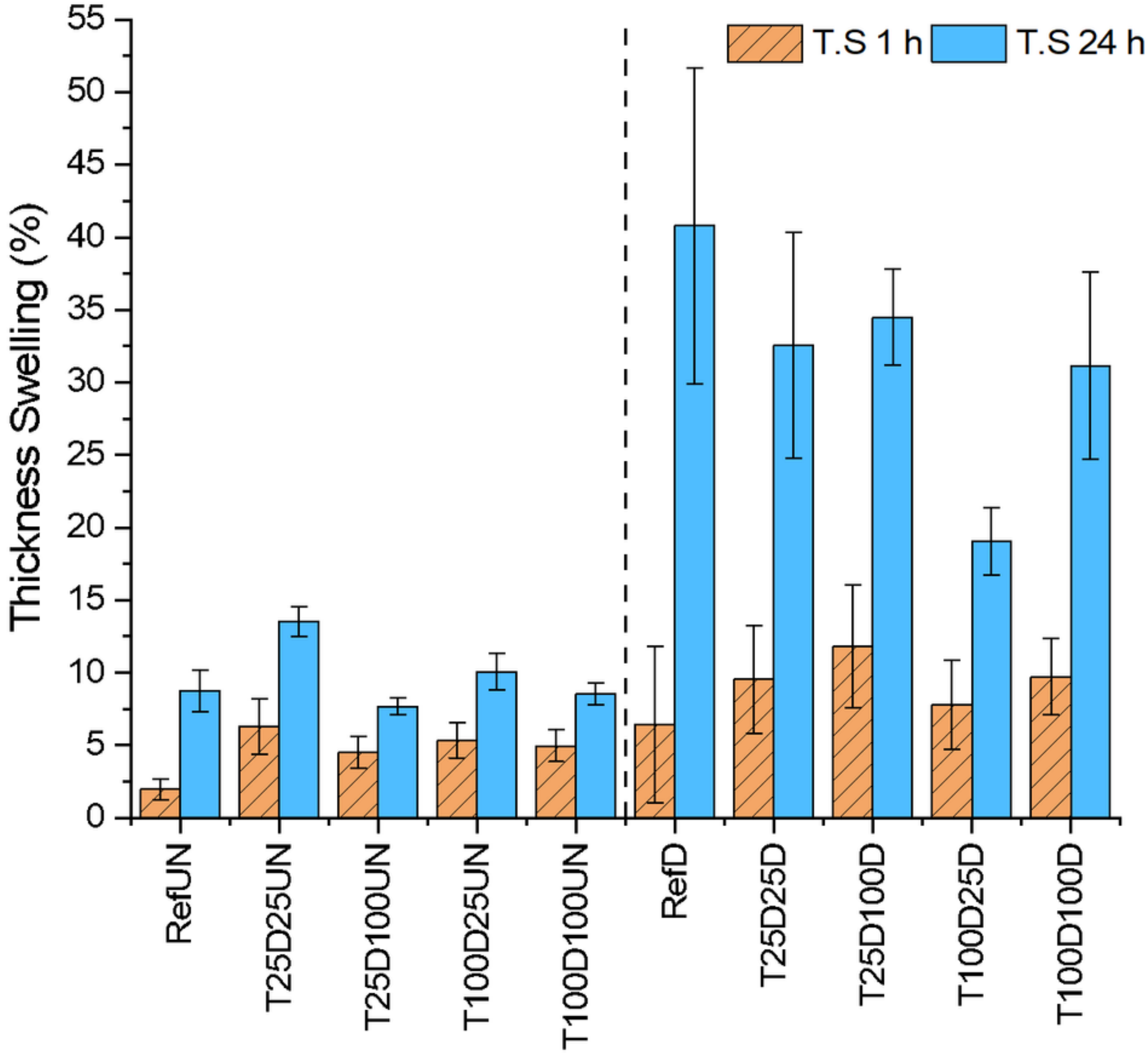


Figure 10

Bamboo thickness swelling values before and after treatment.

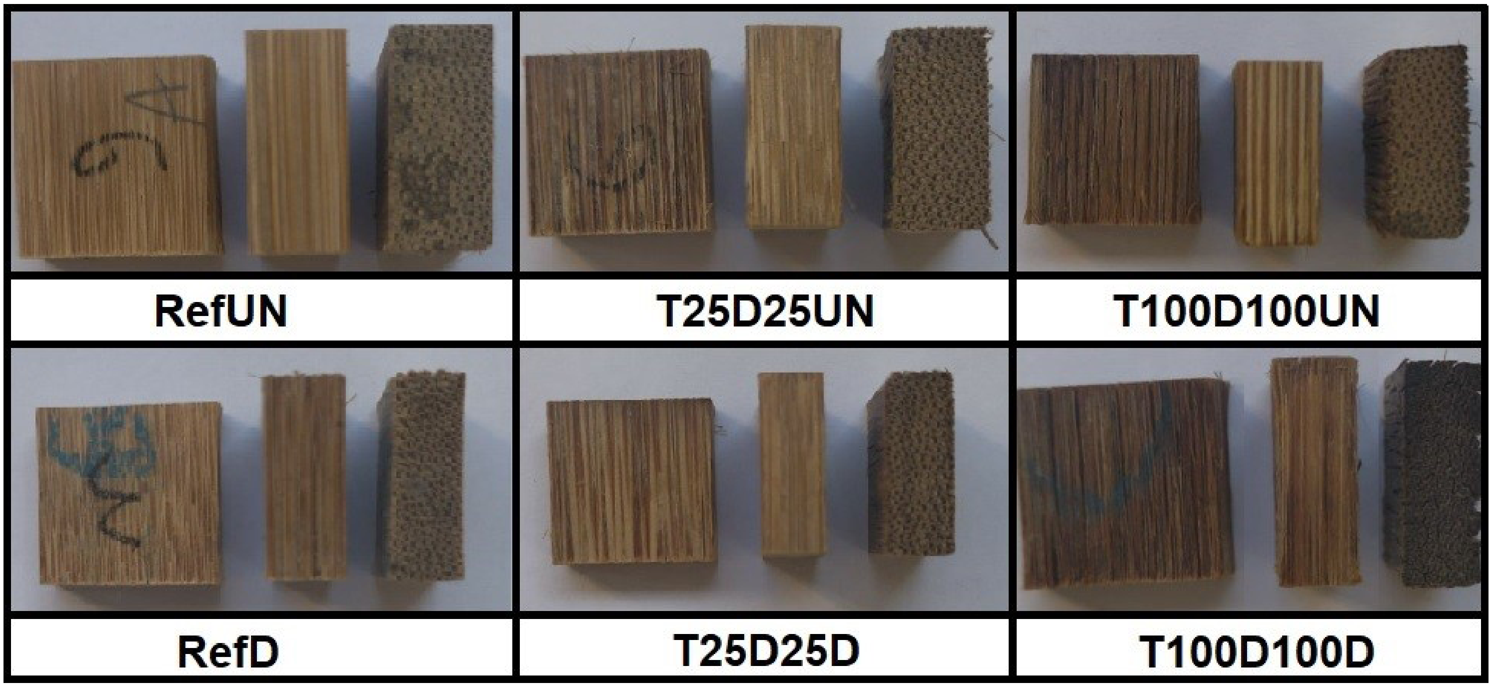


Figure 11

Samples after physical tests.

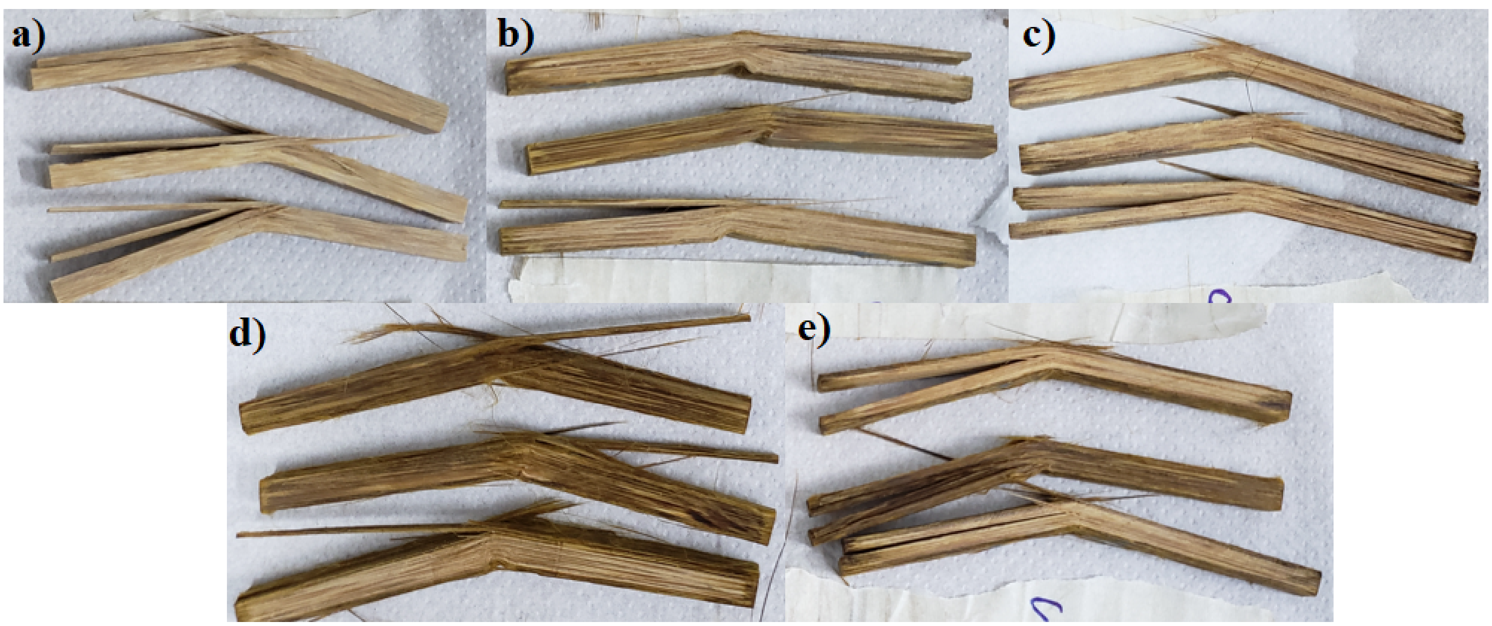


Figure 12

Failure patterns a) RefD b) T25D25D c) T25D100D d) T100D25D e) T100D100D.

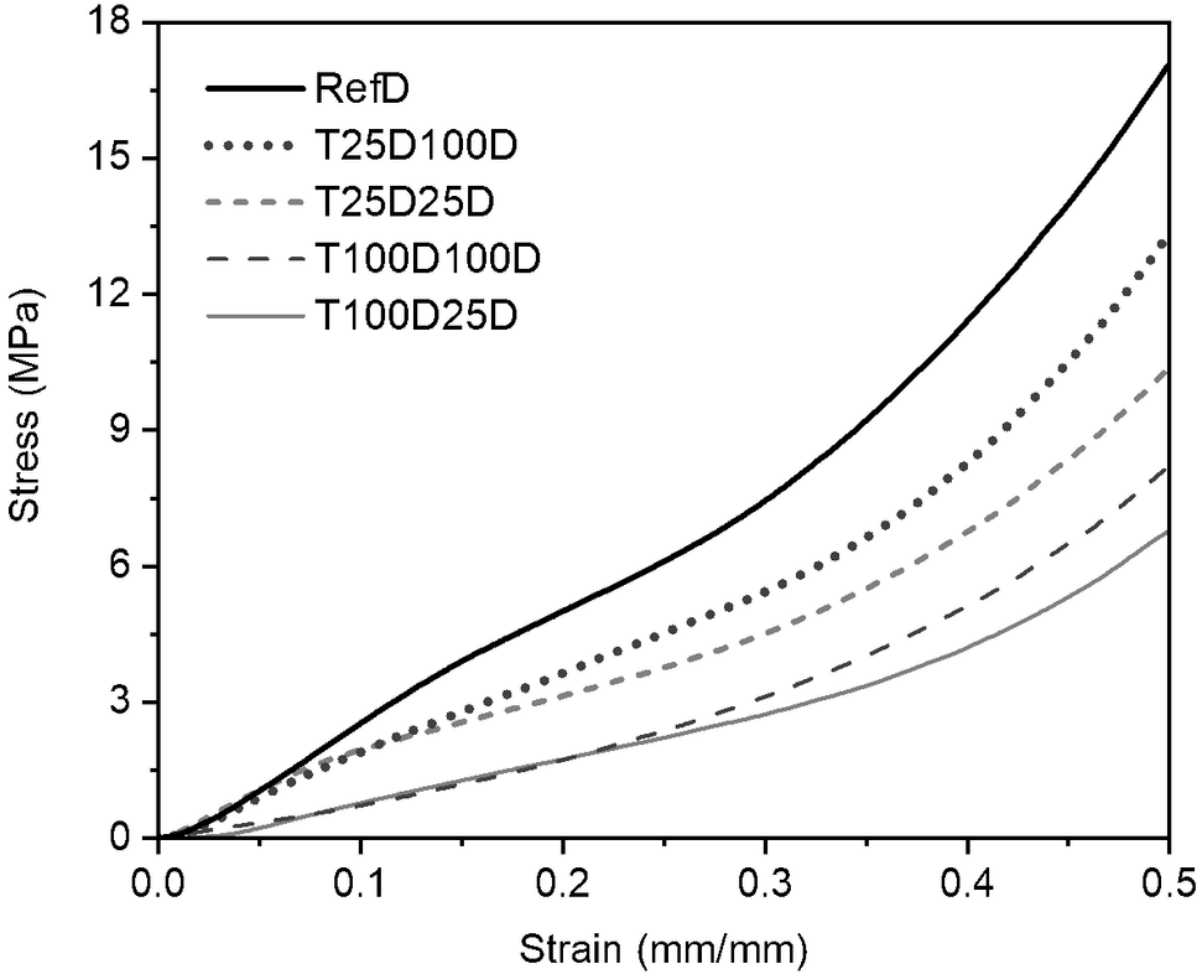


Figure 13

Stress-strain plot in the densification process.

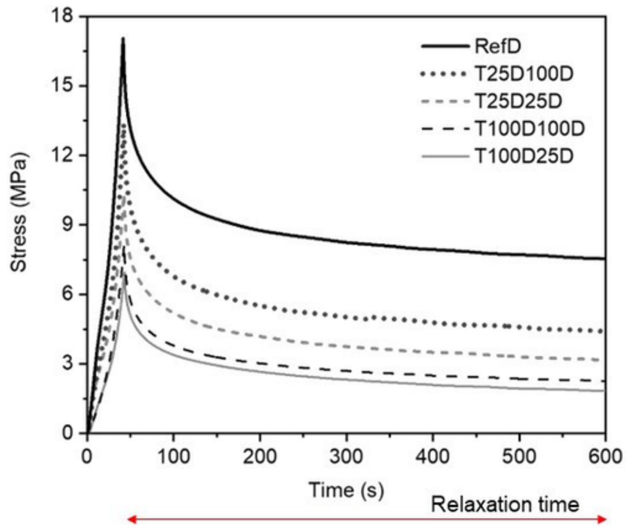


Figure 14

Relaxation curve plot in densification process.

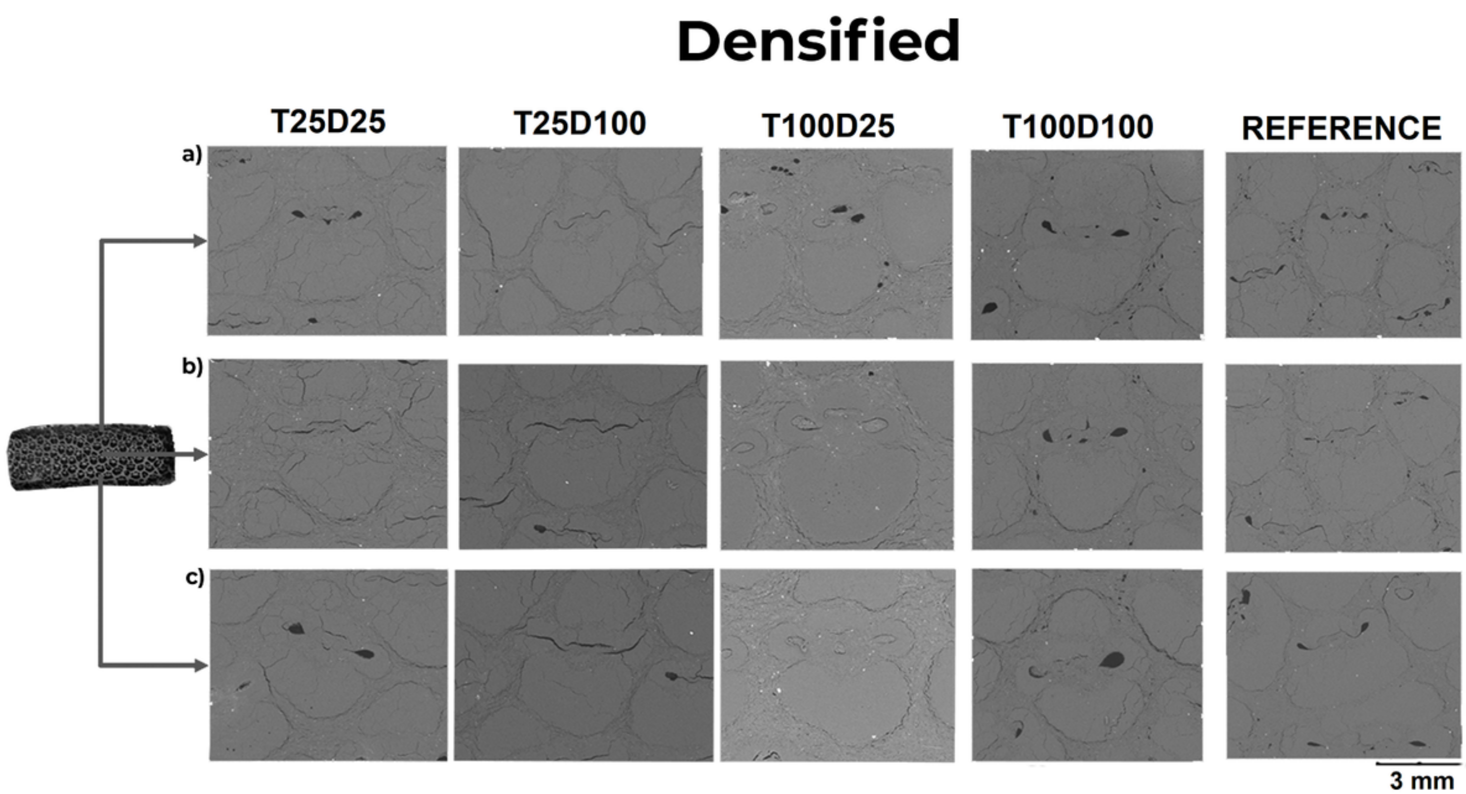


Figure 15

SEM images of densified bamboo samples. The images were extracted from the outer (a), middle (b) and inner layer (c).

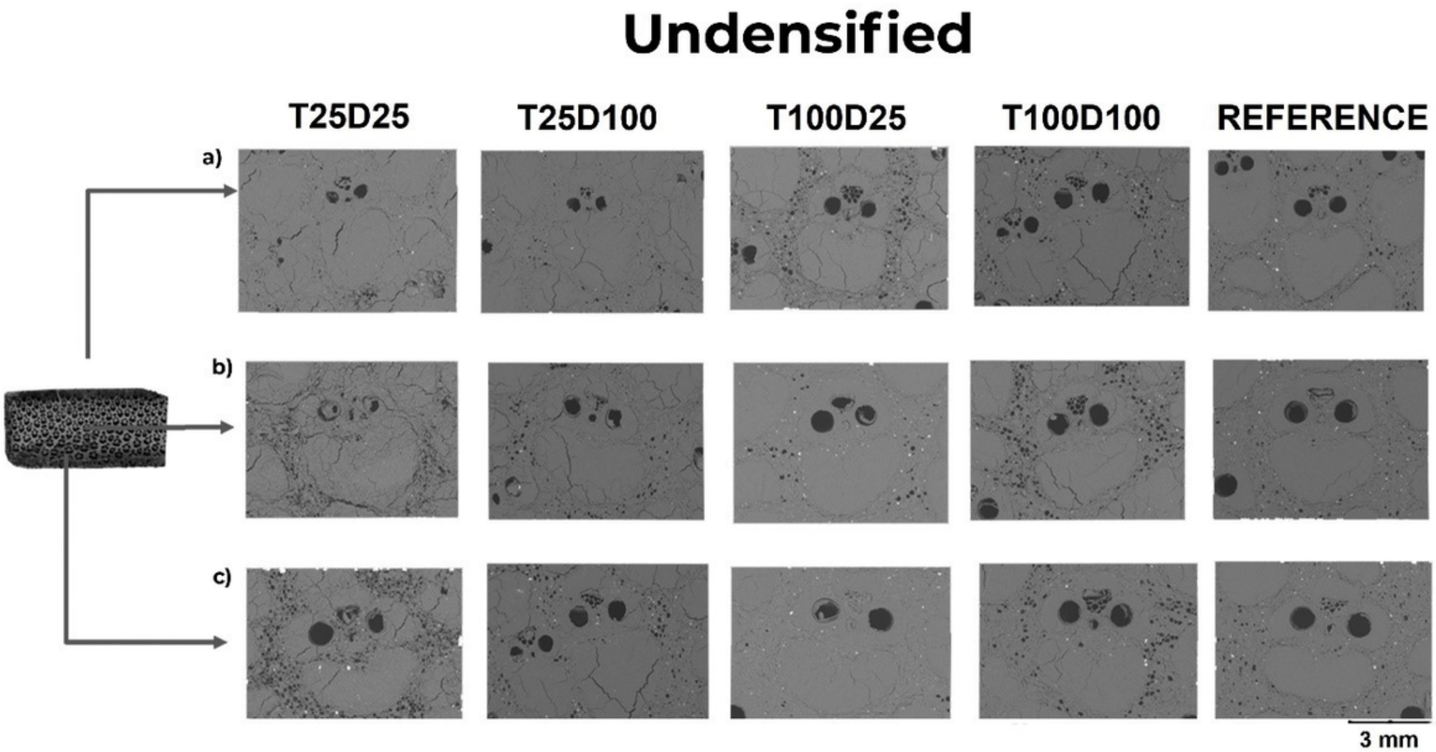


Figure 16

SEM images of undensified bamboo samples. The images were extracted from the outer (a), middle (b) and inner layer (c).

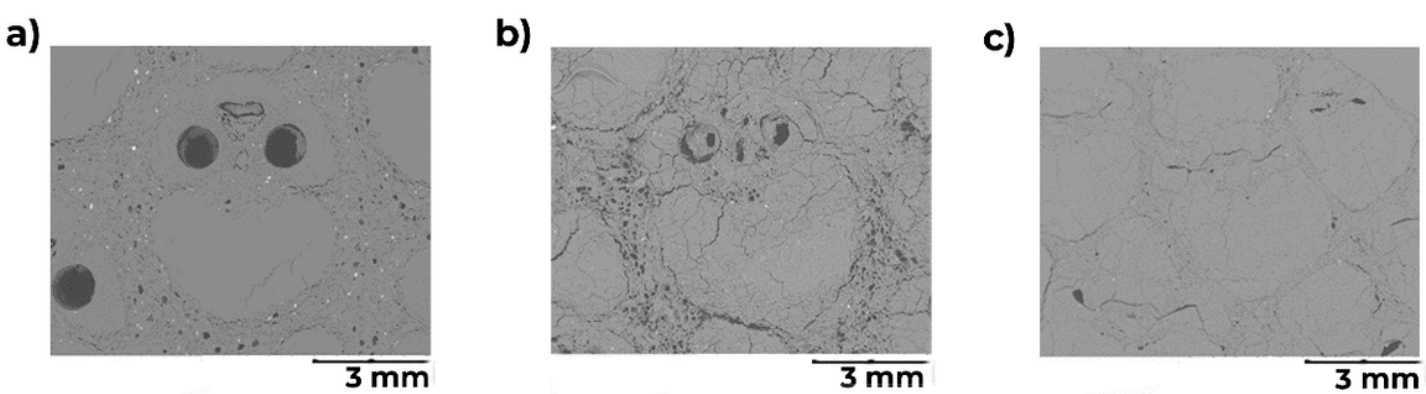


Figure 17

a) reference group without densification b) undensified sample that underwent alkaline treatment at room temperature and dried at room temperature (T25D25UN) c) densified reference group.

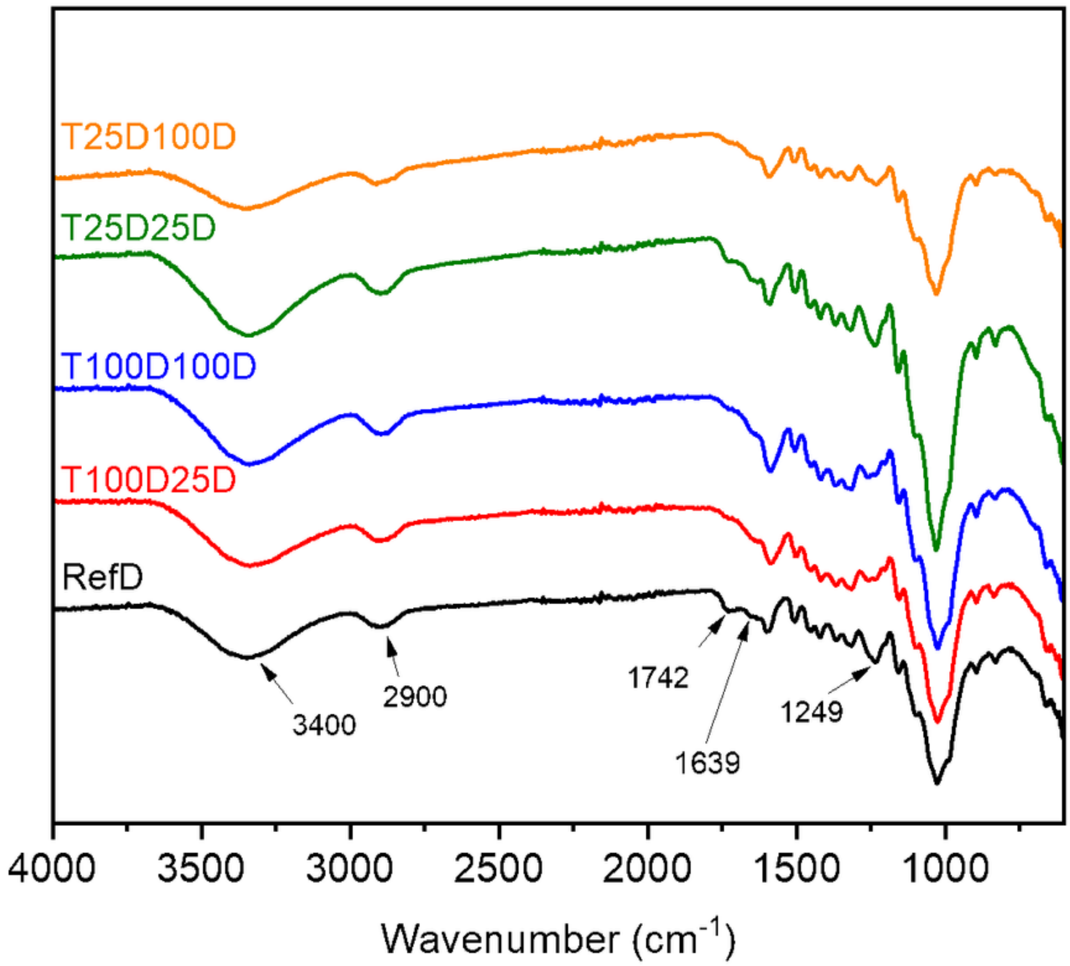


Figure 18

FT-IR spectra for densified bamboo samples.

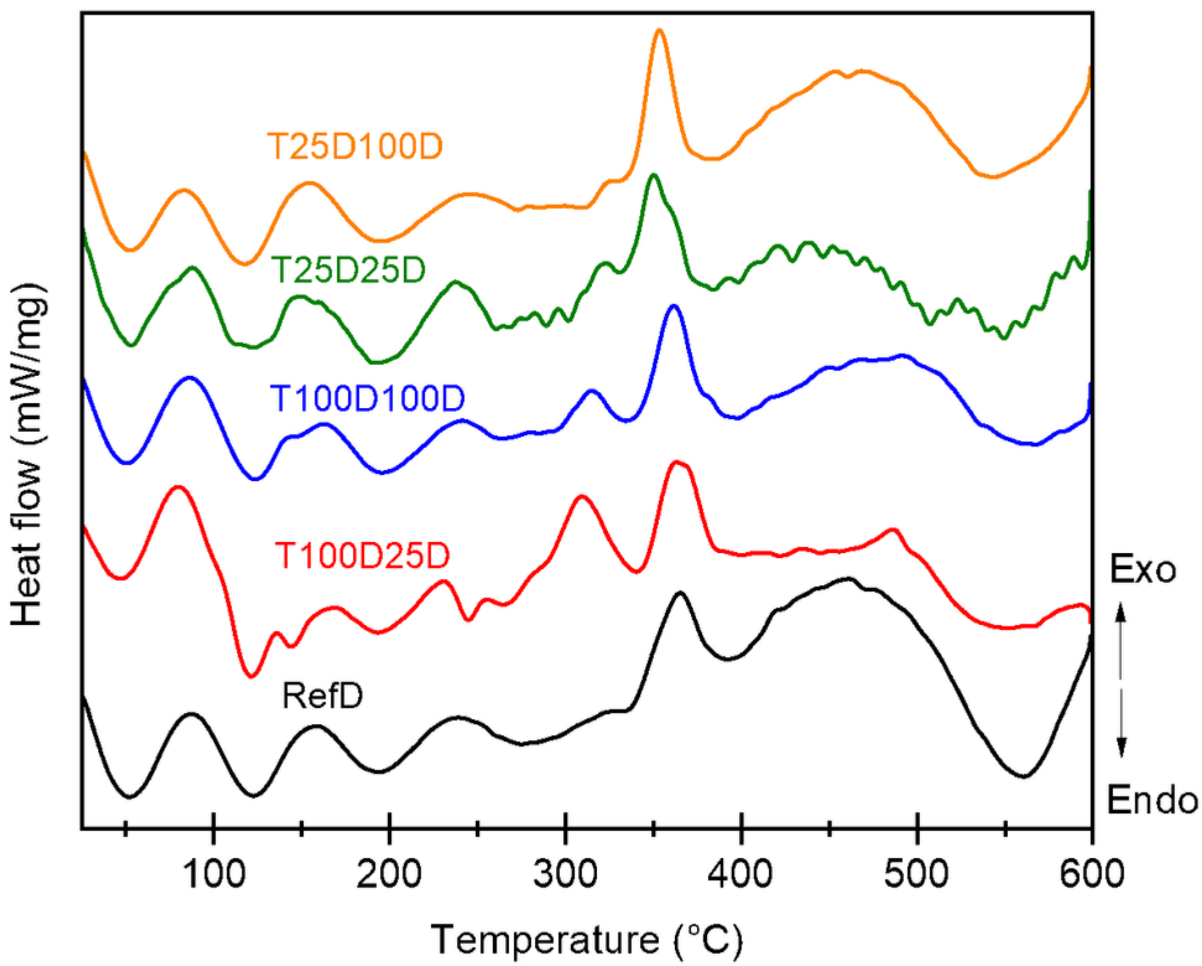


Figure 19

DSC curves of untreated and treated bamboo samples.

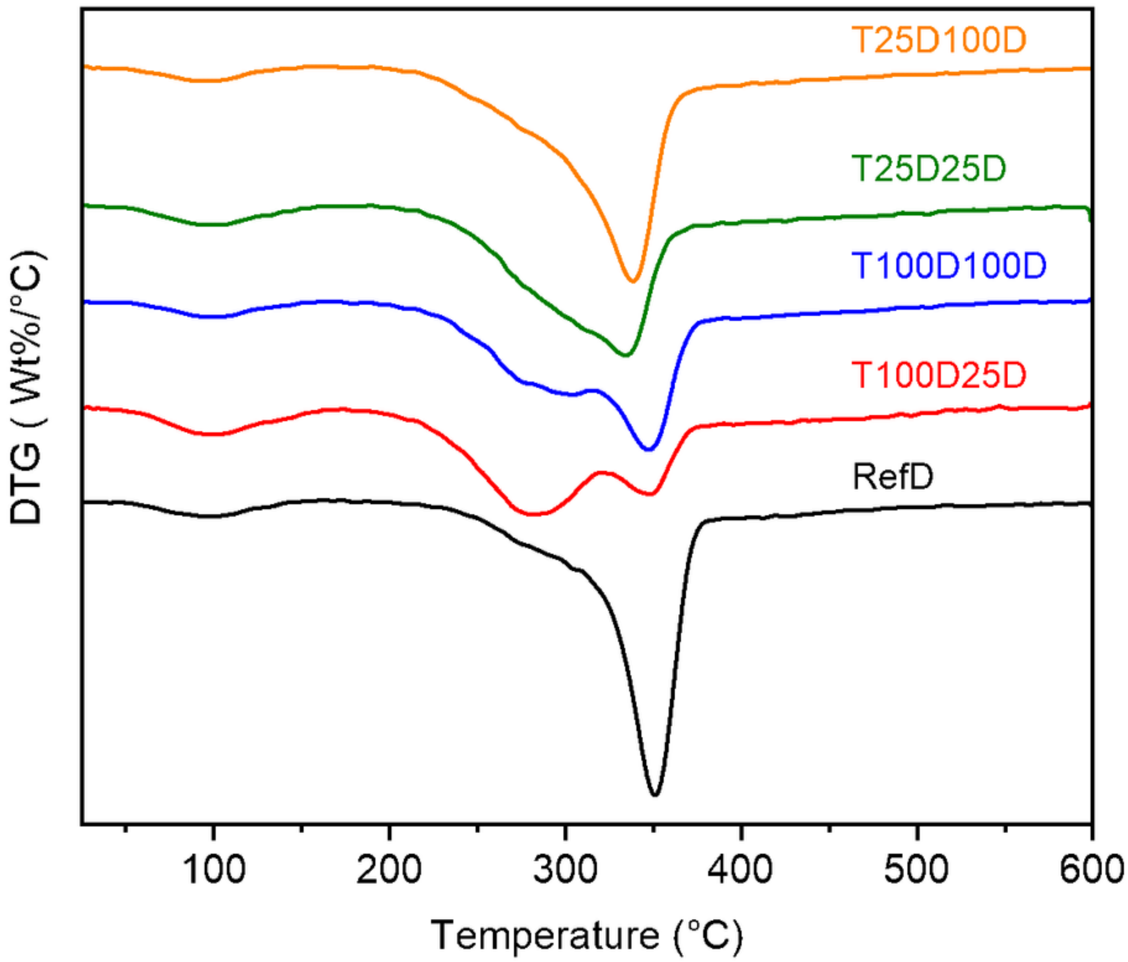


Figure 20

DTG curves of untreated and treated bamboo samples.

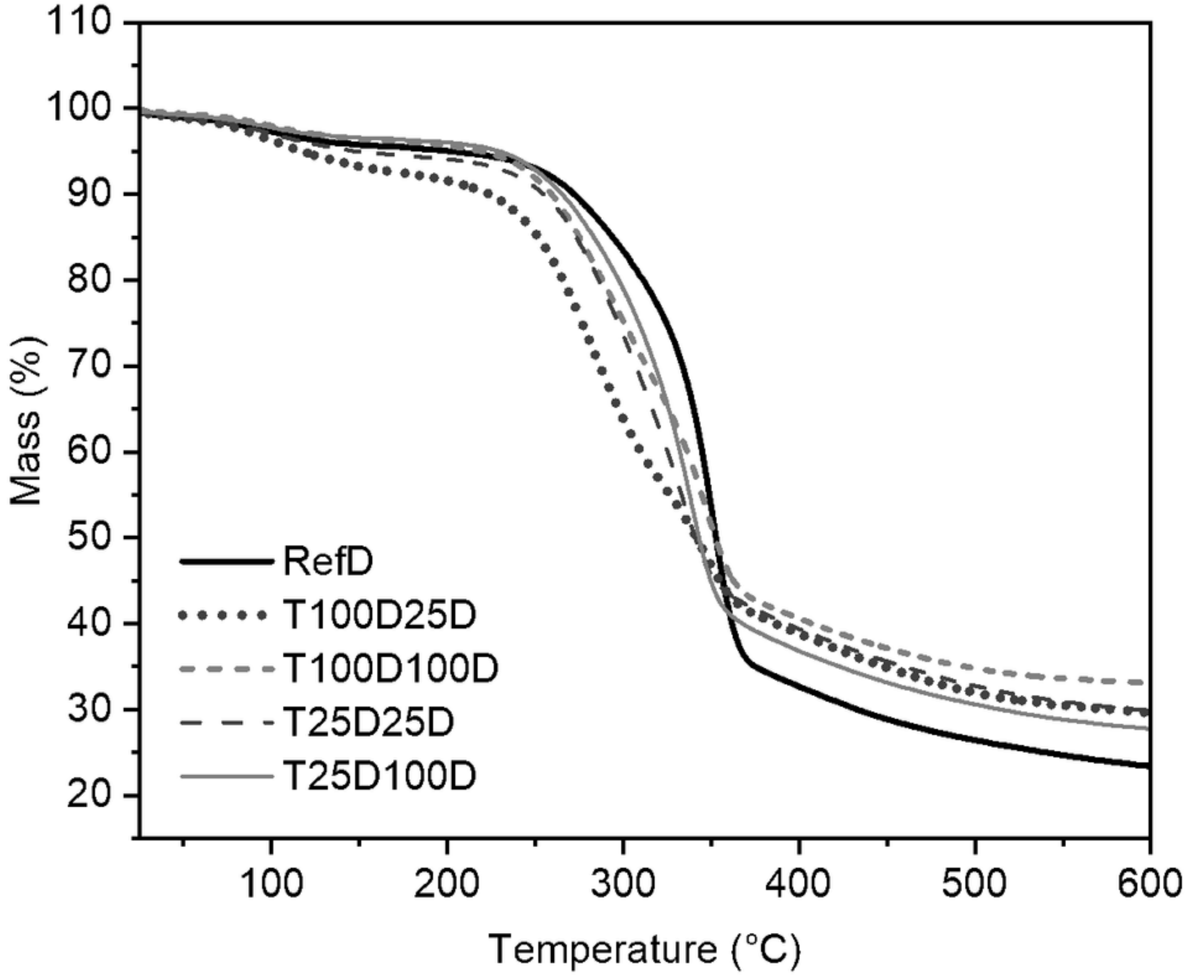


Figure 21

TG curves of untreated and treated bamboo samples.