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EFFECTS OF THERMAL TREATMENT AND WEATHERING IN THE RESISTANCE AGAINST TERMITES OF A FAST-GROWING PINE WOOD

***Ricardo Ripoll de Medeiros*[1]**

https://orcid.org/0000-0003-1474-6914

***Andrey Pereira Acosta*[2,♠]**

https://orcid.org/0000-0002-5074-3772

***Kelvin Techera Barbosa*[1]**

https://orcid.org/0000-0001-9894-703X

***Rafael de Avila Delucis*[1]**

https://orcid.org/0000-0002-3657-9216

***Rafael Beltrame*[1]**

https://orcid.org/0000-0001-6352-0052

***Darci Alberto Gatto*[1]**

https://orcid.org/0000-0002-6805-3243

ABSTRACT

Considering the limited existing literature on the combined effects of thermal treatment and weathering on the resistance of fast-growing pine wood to subterranean termites, this work deals with the resistance against subterranean termites of a thermally treated and weathered fast-growing pine wood. The pine wood was thermally treated at variable temperatures (*c.a.* 180 ºC, 200 ºC, and 220°C) for 2 h and then exposed to artificial weathering for three months. Chemical, hygroscopic, thermal, mechanical, colorimetric, biological, and morphological characteristics were evaluated. Compared to the untreated wood, as expected, the thermal treatments yielded wood parts with improved thermal, hygroscopic and colorimetric features. The thermal treatment also helped for retaining the thermal stability, volumetric hydrophobicity, color, and roughness of the pine wood exposed to the weathering. Previous changes ascribed to the weathering process did not affect the damages attributed to the termites attack, although that wood treated at 180 ºC presented an increased resistance against the termites deterioration.

Keywords: Accelerated aging, artificial weathering, biodegradation, subterranean termites, thermal treatment.

[1]Universidade Federal de Pelotas. Postgraduate Program in Materials Science and Engineering. Technological Development Center. Laboratory of physical and mechanical properties of wood. Pelotas, Brazil.

[2]Universidade Federal do Rio Grande do Sul. Postgraduate Program in Mining. Metallurgical and Materials Engineering. Technological Development Center. Porto Alegre, Brazil.

[♠]Corresponding Author: rafael.delucis@ufpel.edu.br

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INTRODUCTION

Wood is extensively utilized due to its remarkable attributes, including high mechanical strength, thermal and acoustical insulation properties, renewability, and visually appealing features. These favorable characteristics are particularly found in native Brazilian hardwoods known for their darker colors. These species are predominantly consumed in applications such as the furniture industry, musical instruments and civil construction, although they exhibit slow growth and require long cutting cycles.

Considering these factors, most the commercially available wood options exhibit fast growth and short cutting cycles. Examples of such woods include pine and eucalyptus, both of which are extensively cultivated despite being exotic species from Brazil. However, low levels of density, mechanical properties, dimensional stability, and resistance against biotic and abiotic agents are often attributed to these fast-growing woods (Herrera *et al.* 2018, Bak *et al.* 2019, Che *et al.* 2019)

In fact, when a wood part is exposed in outdoor environments, a degradation ascribed to the weathering may take place, which can be understood as a combination of biotic and abiotic factors. According to Delucis *et al*. (2017), this degradation starts by photo-initiated oxidation of chromophore groups from lignin due to ultraviolet and visible rays from the sunlight, generating free radicals, which progressively weaken the wood cell wall, leading to the depolymerization of the whole lignocellulosic structure in latter stages. These reactions also lead to the formation of several water-soluble compounds on the wood surface, like carbonyls and carboxyls, which are leached by the actions of rain and wind.

As a result, the repeated cycles of photodegradation and leaching create surface cracks, providing an entry point for xylophagous fungi to thrive. The proliferation of these fungi is contingent upon various factors, including the pH level, moisture content, and temperature of the substrate (Aramburu *et al.* 2022). Macroscopic changes in color, gloss and roughness are also commonly reported as weathering effects (Che *et al.* 2019, Kamperidou 2019).

Regarding the biotic agents, according to Afzal *et al.* (2019), subterranean termites can be considered the main harmful insects in rural regions since may lead to huge damage, especially in tropical countries. Wooden buildings located in tropical countries are prone to be attacked by subterranean termites due to the warm and humid climate (Hadi *et al.* 2016).

Therefore, fast-growing woods cannot be properly applied unless after being modified by a preservative treatment. Besides, most of the commonly applied wood treatments involve the impregnation of chemicals, although some companies devoted to manufacturing and sell of thermally treated woods have been reaching attention in certain markets, such as decks, garden furniture, frames, internal cabinets, parquet, decorative panels, and saunas (Delucis and Gatto 2014).

In recent literature, wood heat treatments have emerged as environmentally friendly and efficient methods to enhance the properties of wood, with a focus on improving dimensional stability, reducing hygroscopicity, increasing resistance to biological degradation, and promoting sustainability. These studies contribute to the understanding of surface properties and overall performance of heat-treated pine woods.

For example, Esteves *et al.* (2020) investigated the surface properties of two heat-treated pine woods after artificial weathering. Their findings demonstrated that the untreated woods darkened faster, whereas heat-treated woods maintained their original lightness. Additionally, the surface gloss decreased in the untreated woods, while both untreated and heat-treated woods exhibited increased roughness. The heat-treated woods also showed smaller levels of wettability.

Krystofiak *et al.* (2022) explored the impact of heat treatment on roughness and adhesion strength of two different woods. The study revealed that heat treatment reduced roughness in a poplar wood but increased it in a pine wood. Adhesion strength varied depending on the treatment method, with vacuum heat treatment exhibiting better performance.

Nguyen *et al.* (2019) employed an artificial neural network-based approach to predict color changes in heat-treated woods during artificial weathering. Their model accurately forecasted color changes based on exposure time, heat treatment temperature, and wood species. Besides, Herrera-Díaz *et al.* (2019) evaluated the effects of wood quality on the physical and mechanical properties of heat-treated pine wood. Wood quality influenced mild treatment, while both treatment temperatures reduced dimensional changes and maintained anisotropy. The study also indicated that mechanical properties improved, and samples treated at 210 °C exhibited stable color changes after artificial weathering.

However, there is a scarcity of studies focusing on the effects of termite attacks on thermally treated woods. Additionally, it is well-known that weathering may promote the proliferation of certain fungi, although studies regarding the infestation of termites in thermally treated woods following prior weathering are lacking (Salman *et al.* 2017).

One study conducted heat treatment on pine (*Pinus sylvestris*) and beech (*Fagus sylvatica*) woods at four different temperatures (*c.a.* 150 °C, 180 °C, 200 °C, and 220 °C) for 20 h. The treated woods underwent leaching processes and were then exposed to termites of the *Reticulitermes flavipes* species, which did not exhibit clear feeding preferences. The results showed that even after leaching, there was only a 4 % increase in deterioration for the most severe treatments, and the termite mortality rate was approximately 30 % lower compared to non-leached specimens. In the present study, a Brazilian pine wood was subjected to thermal treatments, followed by exposure to artificial weathering and subsequent biodeterioration by subterranean termites.

MATERIALS AND METHODS

Raw material selection, wood treatment, wood weathering and biological assays

Five 25 years old trees were selected in a homogeneous pine (*Pinus elliottii* Engelm.) forest located in Piratini/Brazil (31º26’53” S; 53º06’15” W). From each felled tree, a 3.5 m long baseline log was obtained at a height of 10 cm from the ground. The wood logs were transformed into 10 cm thick central planks and then subjected to outdoor drying for about three months. Prismatic sapwood parts were randomly cut according to the requirements of each characterization assay and conditioned into a climatic chamber (20 °C ± 2 °C and 65 % ± 3 % relative humidity (RH)) until reaching equilibrium moisture content. Based on the climatic condition imposed to the samples, a 12% equilibrium moisture content is expected for all of them.

These woods were then thermally treated according to the procedure described by Gallio *et al*. (2019), in which untreated samples with dimensions of 15 × 15 × 250 mm³ (R × T × L) were heated in a laboratory gravity convention oven at 180 °C, 200 °C, and 220 °C for 2 h. After that, the samples were again placed in the aforementioned climatic chamber. Artificial weathering procedures were performed on the tangential plane of the samples using a UUV-STD- SPRAY-4400 equipment (Bass brand), which had 40 W fluorescent lamps with germicidal action. This equipment can simulate sunlight, rain, and dew.

For that, we followed the procedure described by Kuka *et al*. (2020), which consists of 180 cycles of 8 h of UV radiation, 20 min of rain, and 4 h of dew, totalizing almost 2200 h (c.a. 3 months). After that, biological assays with termites were carried out following a preference feeding method described by Acosta *et al*. (2020). For that, a 1 m^3 termite nest colonized by *Coptotermes curvignathus* Holmgren termites was collected from a wooded area in Canguçu/Brazil and placed on a 5 cm thick layer of moistened sand (moisture content around 65 %) inside a plastic tank.

Afterward, ten samples (15 × 15 × 125 mm^3; R × T × L) from each group were randomly inserted in the sand around the nest and this bioassay was kept for 45 days in complete darkness. Mass loss and flexural properties were used to evaluate the effectiveness against the termites attack, in a way that a low mass loss and high flexural properties indicate a high resistance against the termites attack.

Characterization of the wood

Anatomical images were taken from 13 µm thick wood blades using an optical microscope adjusted for 25 × and a processing program called ImageJ. Based on these images, 60 wood cells were measured by each group, as recommended by Missio *et al.* (2014). Chemical groups were qualitatively evaluated in previously milled, ground (200 mesh screen) and pressed samples by Fourier-transform infrared spectroscopy (FTIR) coupled with an ATR device using a Shimadzu IRSpirit equipment.

The FTIR data were smoothed by applying a Savitzky-Golay filter (second-degree polynomial at an interval of 12). Density (ρ) and mass loss on a dry basis were measured before and after both the thermal treatments and biological termites tests. For that, we used a digital caliper with a resolution of 0,01 mm and an analytical scale with a resolution of 0,001 g. Each group consisted of seven specimens.

Thermal stability was evaluated by thermogravimetry using a Navas TGA-1000 equipment adjusted for a heating rate of 10 °C·min^{-1} and a heating ramp from 20 °C to 600 °C. For analyzing the weathered woods, a 1 mm thick surface blade was cut. Static bending tests were performed on seven specimens per group with the dimensions of 15 × 15 × 250 mm^3 (R × T × L) using an Emic DL 3000 equipment adjusted for a velocity of 0,8 mm·min^{-1}, as described in ASTM D143 (2017).

Ten samples of each group had surface roughness measured based on arithmetical mean roughness (Ra) and maximum height (Rz), using a Homis 899 equipment coupled with a 2,5 mm-diameter needle. The surface was also evaluated by optical microscopy using a RoHS equipment endowed with a resolution of 2,0 MP. Surface hydrophobicity was evaluated in terms of the contact angle using the tangential plane of three samples from each group, which was measured according to the sessile drop method, using a Kruss DSA25 goniometer adjusted to 20 µL droplet.

The data were taken from 5 s to 60 s after the water/wood contact. Volumetric hydrophobicity and dimensional stability were evaluated in terms of water-repellent efficiency (WRE; Equation 1) and anti-swelling efficiency (ASE; Equation 2), respectively, using five samples per group. The untreated samples were subjected to oven-drying at 103 °C ± 2 °C until a constant weight was achieved. Afterward, the mass and volume of the samples were measured following four cycles of drying and water immersion at 20 °C. The drying process occurred at 103 °C ± 2 °C, and the water soaking lasted for 96 h (Equation 3 and Equation 4).

$$WRE = \left(\frac{\Delta Mu - \Delta Mt}{\Delta Mu}\right) x\ 100 \quad (1)$$

$$ASE = \left(\frac{\Delta Vu - \Delta VMt}{\Delta VMu}\right) x\ 100 \quad (2)$$

$$\Delta \mathrm{V} = \frac{Vw - Vd}{Vd} x\ 100 \quad (3)$$

$$\Delta m = \frac{mw - md}{md} x\ 100 \quad (4)$$

Where: ΔV is volume variation, Vw = wet sample volume (cm^3), Vd = dried sample volume (cm^3), t = treated, u = untreated, Δm = mass variation, mw = wet sample mass (g), md1 = dried sample mass on cycle one and mdx = dried sample mass on next cycles (g).

All data were statistically analyzed using ANOVA tests at significance levels of 1 %, ensuring that the assumptions of data normality (Shapiro-Wilk test) and homogeneity of variances (Levene test) were confirmed.

RESULTS AND DISCUSSION

Effects of the thermal treatments

Figure 1 shows anatomical images taken from the studied pine woods and Table 1 shows their anatomical properties. The pine wood cell wall became approximately 50 % thinner after the thermo-treatments. However, only treatments starting at 200 ºC yielded decreases in the cell wall diameter, which is probably due to the degradation of thin segments belonging to the hemicelluloses, which begins around this temperature (Delucis *et al.* 2018).

Table 1: Anatomical properties of treated and untreated pine woods.

Treatment	Lumen diameter (µm)	Wall thickness (µm)
Untreated	17,90 b (2,29)	4,78 b (0,82)
180 ºC	14,13 a (2,52)	4,73 b (0,69)
200 ºC	12,88 a (3,10)	2,89 a (0,53)
220 ºC	14,28 a (1,80)	2,65 a (0,92)

Significant differences in means within the same column, distinct letters are used.
Standard deviations provided in parentheses.

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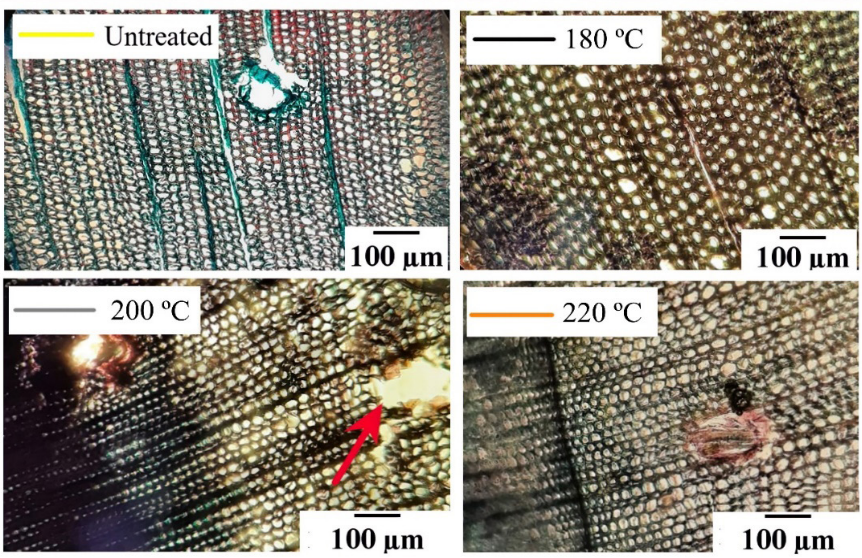


Figure 1: Anatomical images of the transverse plane of treated and untreated pine woods.

These anatomical changes attributed to thermal treatments may impart further changes in physical and chemical properties of the wood. For instance, thermal treatment can lead to decreases in wood density due to the removal of volatile components and breakdown of cell wall constituents (Lengowski *et al.* 2021), decreases in wood hygroscopicity due to the partial degradation of hydrophilic groups within the cell wall (Hill *et al.* 2021), decreases in shrinkage and swelling behavior due to structural changes in amorphous regions of hemicelluloses and lignin (Zhang *et al.* 2021), among others.

Effects of the weathering on the thermally treated woods

According to Zhang *et al.* (2015), the main chemical changes occurring in heat-treated woods can be captured by the FTIR-ATR technique based on attenuations in certain bands. Thus, changes in the main macromolecules from the wood (*c.a.* cellulose, hemicellulose and lignin) are associated with appearance, attenuation, or shift of certain bands (Pandey and Pitman 2003). Furthermore, according to Pandey and Pitman (2003), prominent bands associated with lignin may be related to the degradation of carbohydrates or lignin-related compounds.

The infrared spectra of the studied pine woods (Figure 2) demonstrated that the band located at 1030 cm^{-1}, which refers to C - O - C stretching, was slightly shifted for the treated woods in relation to the untreated one. The band at 1860 cm^{-1} is more intense for the pine wood treated at 220 ºC, which is due to the formation of carboxylic groups ascribed to the decomposition of side chains from the lignin.

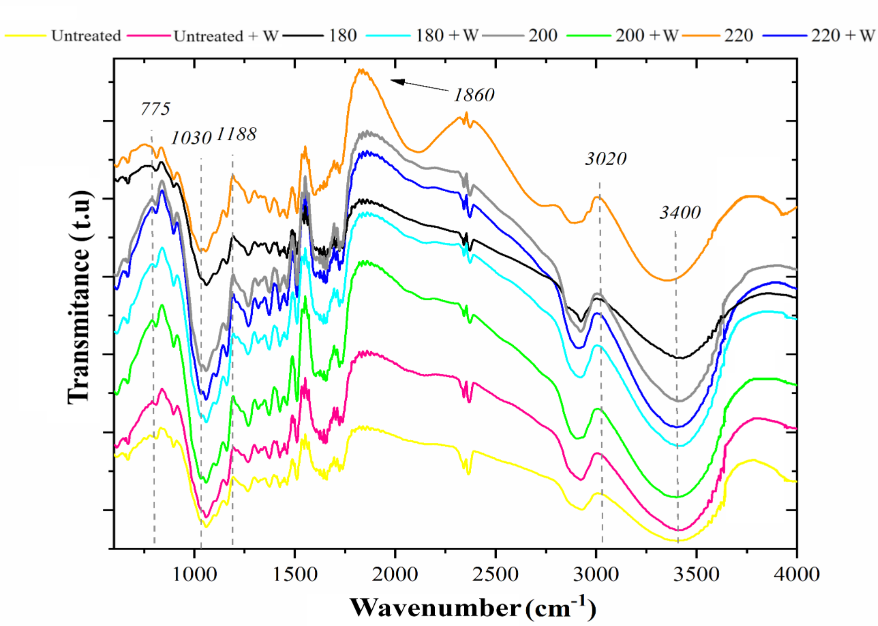


Figure 2: Infrared spectra of the studied pine woods.
+ W refers to weathered woods.

Furthermore, compared to the untreated wood, minor bands around 3400 cm^{-1} for the thermally treated woods indicate decreases in equilibrium moisture content related to increases in bulk hydrophobicity. This decreased intensity of the 3400 cm^{-1} band may be associated with the decomposition of hydroxyls from the wood cell wall. Besides that, compared to their respective untreated woods, the weathered ones showed smaller bands at 3400 cm^{-1}, which indicates a subsequent removal of hydroxyls probably due to the ultraviolet radiation applied to the wood.

The bands around 1400-1500 cm^{-1} are associated with C=C aromatic skeletal vibrations stretching of benzene rings from lignin (Özgenç *et al.* 2017). Also, increases in band intensities at 1368 cm^{-1}, 1325 cm^{-1}, 1230 cm^{-1}, 1030 cm^{-1}, and 892 cm^{-1} are associated with the removal of carbohydrates and an increase in the concentration of different chemical units from lignin (*c.a.* guaiacyl and syringyl) (Gallio *et al.* 2018). All these bands appear with greater intensity for the weathered woods, which may indicate changes in all the macromolecular compounds from the wood due to the weathering. Similar behavior was reported by Acosta *et al.* (2022), who investigated a heat-treated pine (*Pinus elliottii* Engelm.) wood.

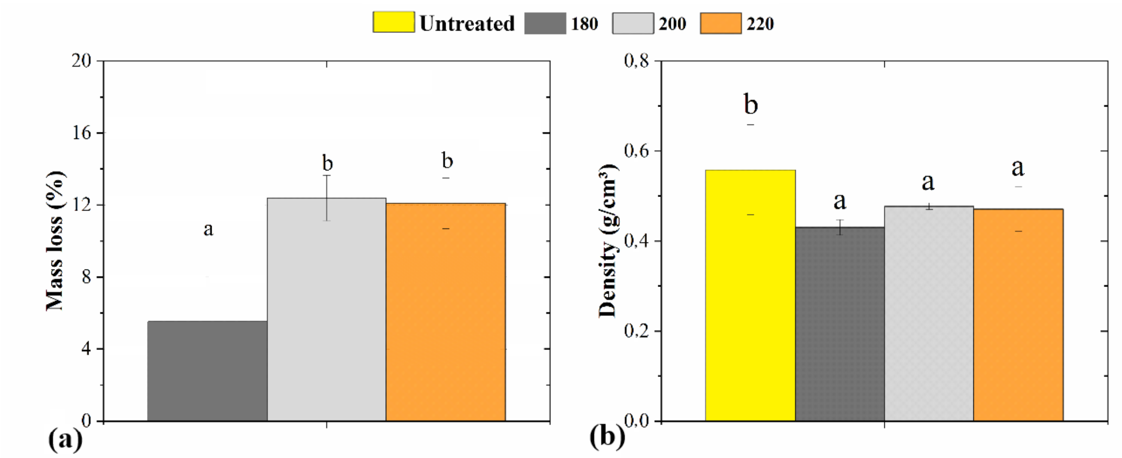


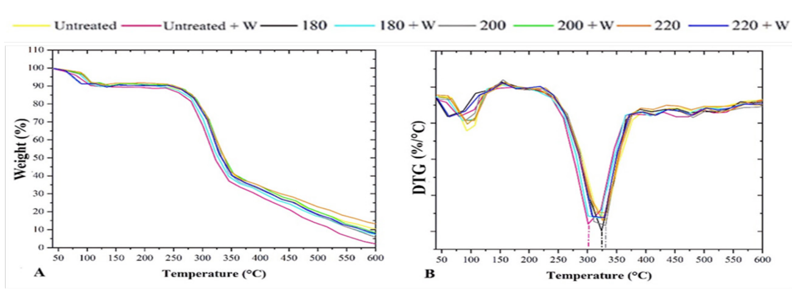
Figure 3: (a) Mass loss and (b) density of the studied pine woods. Different letters above the bars represent significantly different means.

The mass loss of the pine wood treated at 200 ºC was the highest one (Figure 3a). The opposite effect occurred with the density (Figure 3b). This relationship between the heat treatment and the decrease in density is in agreement with those verified in literature for pine woods treated in the 180 ºC - 220 ºC temperature range, which vary between 9 and 22 % (Poubel *et al.* 2013, Gallio *et al.* 2019). According to Poubel *et al.* (2013), when a wood is thermally degraded, moisture and volatile substances belonging to extractives are lost in the first stages (below 150 ºC). After that, more intense mass losses may occur above 200 ºC, which can be attributed to the decomposition of hemicelluloses (Missio *et al.* 2015, Lee *et al.* 2018).

In fact, hemicelluloses from wood are generally more susceptible to thermal degradation compared to other wood components, such as cellulose and lignin, since they have a branched and heterogeneous structure with presence of different sugar units linked with weak intermolecular forces and low crystallinity, making them easier to break down under heat. However, it is well known that the specific temperature at which hemicellulose degradation begins can vary depending on factors like wood species, hemicellulose composition, and heating conditions (Hill *et al.* 2021, Zhang *et al.* 2021).

Therefore, the limited mass loss observed after a 2-h heat treatment can be attributed to the relatively short duration of exposure. Thus, it is expected that severe thermal treatments carried out at elevated temperatures and extended treatment durations will facilitate a greater breakdown and volatilization of hemicellulose-related groups (He *et al.* 2023).

The obtained TG curves are presented in Figure 4 and Table 2. The thermal degradation profile can be divided into two distinct regions. Region I encompasses an initial moisture evaporation stage at approximately 30 ºC and extends to the degradation of amorphous portions of the polysaccharides, which takes place at around 130 ºC. On the other hand, region II encompasses the entire range of structural degradation occurring between 150 ºC and 450 ºC, which refers to both polysaccharides and lignin (Ding *et al.* 2016).



Group	$T_{2\%}$	$T_{5\%}$	$T_{50\%}$	Residue after 600°C
Untreated	85	90	340	10
Untreated + W	60	80	323	3
180	85	92	335	9
180 + W	75	88	330	8
200	70	93	340	8
200 + W	60	90	338	9
220	90	93	342	14
220 + W	65	75	335	8

Figure 4: (a) TG curves and (b) their derivatives for the studied pine woods. + W refers to weathered samples.

Table 2: Main thermal events for the studied pine woods.

Treatment	$T_{2\%}$	$T_{5\%}$	$T_{50\%}$	Residue after 600 °C
Untreated	85	90	340	10
Untreated + W	60	80	323	3
180 °C	85	92	335	9
180 °C + W	75	88	330	8
200 °C	70	93	340	8
200 °C + W	60	90	338	9
220 °C	90	93	342	14
220 °C + W	65	75	335	8

+ W refers to eathered samples

The TG curves of the investigated wood samples exhibited comparable shapes, suggesting that the changes induced by both heat treatments and weathering were not so remarkable. Therefore, the thermal treatment may not have penetrated deeply into the wood samples, resulting in localized effects rather than overall changes in the wood's thermal stability. The heat may primarily affect the surface layers of the wood, while the internal regions remain relatively unaffected (Hill *et al.* 2021). This limited penetration can contribute to the observed similarity in the thermal stability of the thermally treated and untreated wood samples.

Also, it can be highlighted that the thermal degradation curve of each thermally treated wood closely overlaid that of its corresponding untreated wood, indicating that the thermal treatment did not significantly alter the overall degradation behavior of the wood. In fact, overall weathering effects can result in the degradation of the wood's surface layers, which may lead to the removal or alteration of more thermally unstable components (Kymäläinen *et al.* 2022). Consequently, the remaining wood material may exhibit thermal stability similar to that of the unaged sample (Hill *et al.* 2022).

On the other hand, the thermal degradation events (main thermo-degradation peaks shown in the DTG curves) of the weathered and non-weathered woods clearly occurred in different temperature ranges. The first main thermo-degradation peak shifted towards the right after the weathering process, which is probably due to a drying process or perhaps degradation of hydroxyls and, consequently, a decrease of equilibrium moisture content caused by the UV radiation (Popescu *et al.* 2011). Regarding the region II, the peaks of the weathered samples shifted toward the left in relation to their respective non-weathered woods. This is probably due to the oxidation of chromophore groups from lignin, which is commonly attributed to the action of UV rays on wood surfaces since this temperature range (300 ºC - 350 ºC) is associated with cleavage of aromatic groups from lignin (Popescu *et al.* 2011).

Regarding the surface color (Figure 5), the heat treatments yielded decreases in L* and h, which were accompanied by increases in a*. Besides that, both b* and C* remained almost unchanged (that is, with slight increases or decreases depending on the treatment). These changes in colorimetric parameters indicate a darkening of the natural color of the pine wood, which is known by its yellow shades. In terms of the total color variation (ΔE), the higher the treatment temperature was, the higher the ΔE was. Therefore, compared to the untreated wood, the thermal treatments at 180 ºC, 200 ºC, and 220 ºC yielded ΔE values of 16,49; 28,12 and 34,84 respectively.

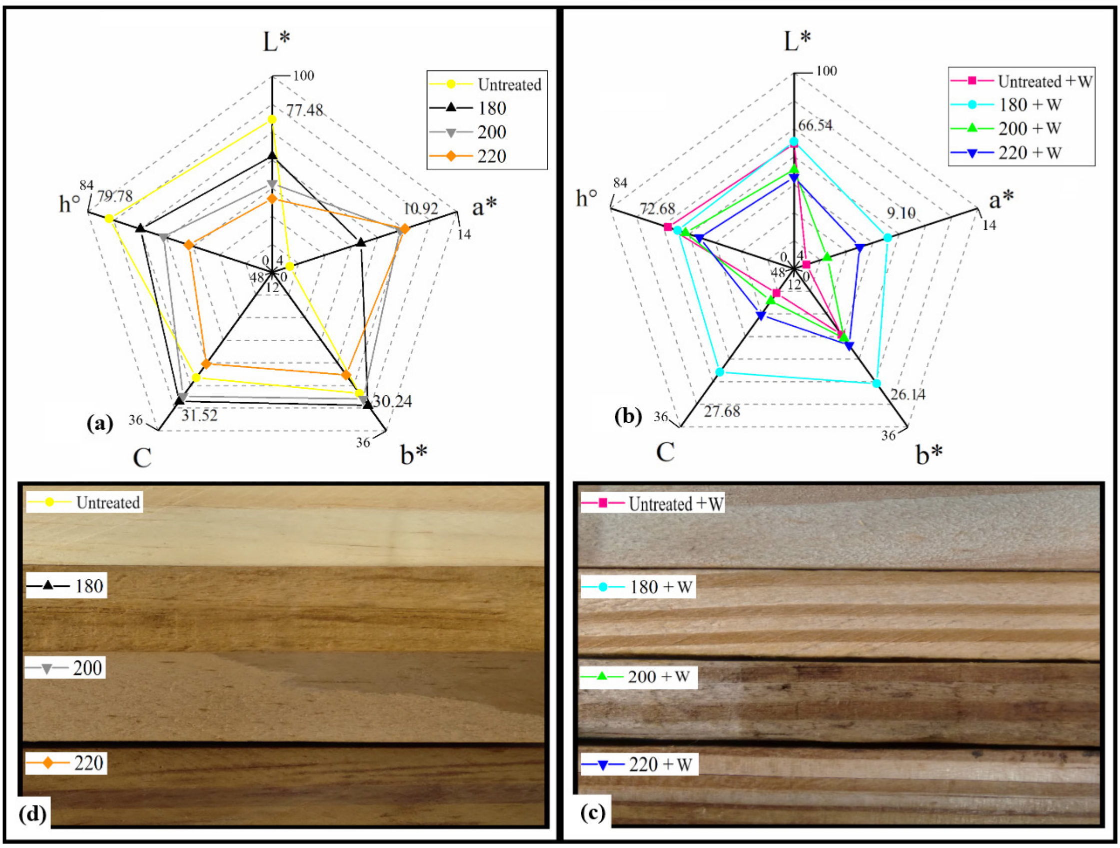


Figure 5: (a) – (b) Colorimetric parameters and (c) – (d) photographs of the radial planes of the studied pine woods.
+ W refers to weathered samples.

The darkening on wood surfaces attributed to heat action is due to changes in double bonds from some extractives (namely fatty acids, terpenes, phenols, and so on) (Frybort *et al.* 2014). According to Mattos *et al.* (2016), the extractive content of Brazilian pine wood is approximately 6 %, and the predominant compounds found in these extracts were primarily fatty acids, with n-hexadecanoic acid being the main compound. These low-molecular-weight compounds may migrate to outside wood, becoming a resinous layer, which also leads to increases in surface energy (de Peres *et al.* 2020).

The weathering-induced increases in L* and h were accompanied by decreases in a*, b* e C* for all the studied woods. This combination of changes in colorimetric parameters is associated with fading and greying of the color (Delucis *et al*. 2019). Furthermore, according to Delucis *et al*. (2017), changes in L* and a* due to weathering are related to oxidations mechanisms in lignin and extractives, respectively. In terms of ΔE values, the higher the treatment temperature was, the higher the color retention was. Therefore, in relation to each unexposed wood, those weathered woods treated at 180 °C, 200 ºC, and 220 ºC showed ΔE values of 14,75; 10,36 and 6,42 respectively. On the other hand, the untreated woods underwent an ΔE value of 17,35 attributed to the weathering, which confirms that the previous thermal treatments provided pine wood with effective retardation against the action of weathering.

In general, compared to untreated pine woods, thermally treated ones may present a higher retention of their original color after the weathering process due to the degradation of their cell wall as per Figure 1 and due to their reduced extract content related to the migration of extractive compounds to outside wood (Lovaglio *et al.* 2022), greater crystallinity of para-crystalline polysaccharides in wood, since in heat-treated wood there are fewer amorphous zones susceptible to degradation by UV radiation (Pratiwi *et al.* 2019), higher dimensional stability since the moisture content also may impact on wood color (Peng *et al.* 2021), enhanced decay resistance since fungi attack is also possible during a weathering decay (Jirouš-rajković and Miklecić 2021), among other.

The thermal treatments yielded decreases in the surface roughness (both Ra and Rz presented in Figure 6) above 200 ºC, which was not seen for that wood treated at 180 ºC. These changes can be attributed to the decomposition of thin segments from the wood surface and even impurities, which brings a smooth wood surface, as can be seen in the optical micrographs shown in Figure 6c.

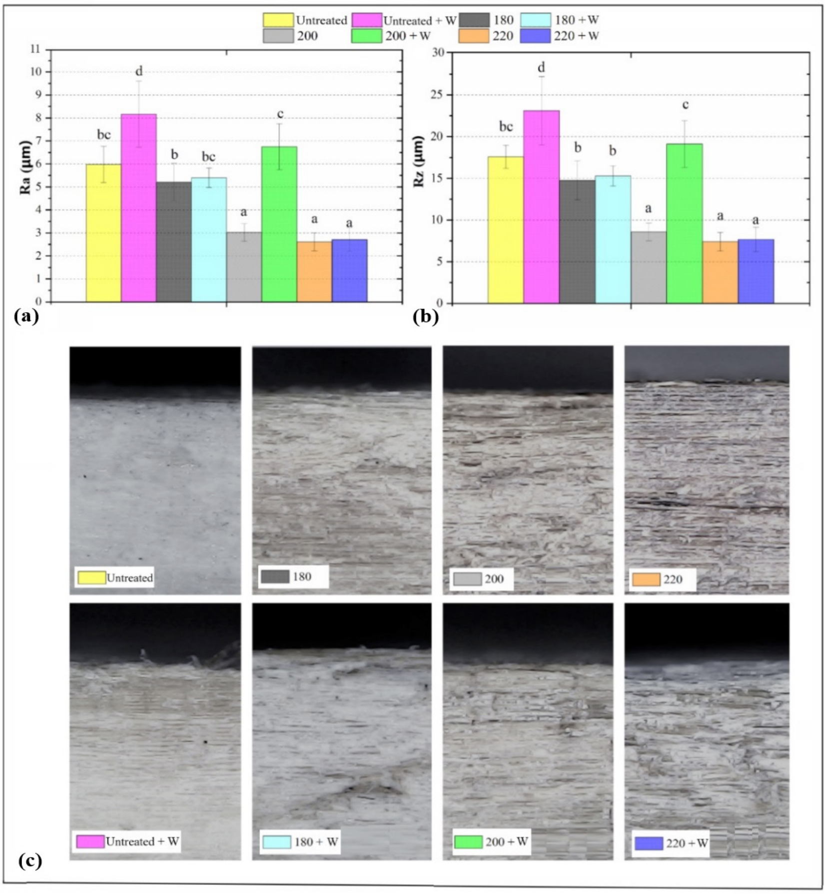


Figure 6: (a) Ra, (b) Rz, and (c) optical micrographs of the studied pine woods.
+ W refers to weathered samples.
Different letters above the bars represent significantly different means.

Regarding the weathering, those woods treated at 180 ºC and 220 ºC presented resistant wood surfaces, which did not undergo changes in surface roughness as weathering effects. On the other hand, the untreated woods underwent an increase in surface roughness due to the weathering, which can be ascribed to surface cracks, photodegraded soluble substances, among other aforementioned weathering effects. This increase in surface roughness may be detrimental to wood bonds (with other materials), which demands a suitable wetting (Laina *et al.* 2017).

Figure 7 shows the means of WRE, ASE, and contact angle results, as well as images taken from the droplets after 10 s of wetting (Figure 7d). As expected, all of the thermal treatments yielded positive WRE and ASE means, which indicates that they were effective to confer increases in bulk hydrophobicity and dimensional stability. In this sense, there was no discernible effect attributed to the treatment temperature.

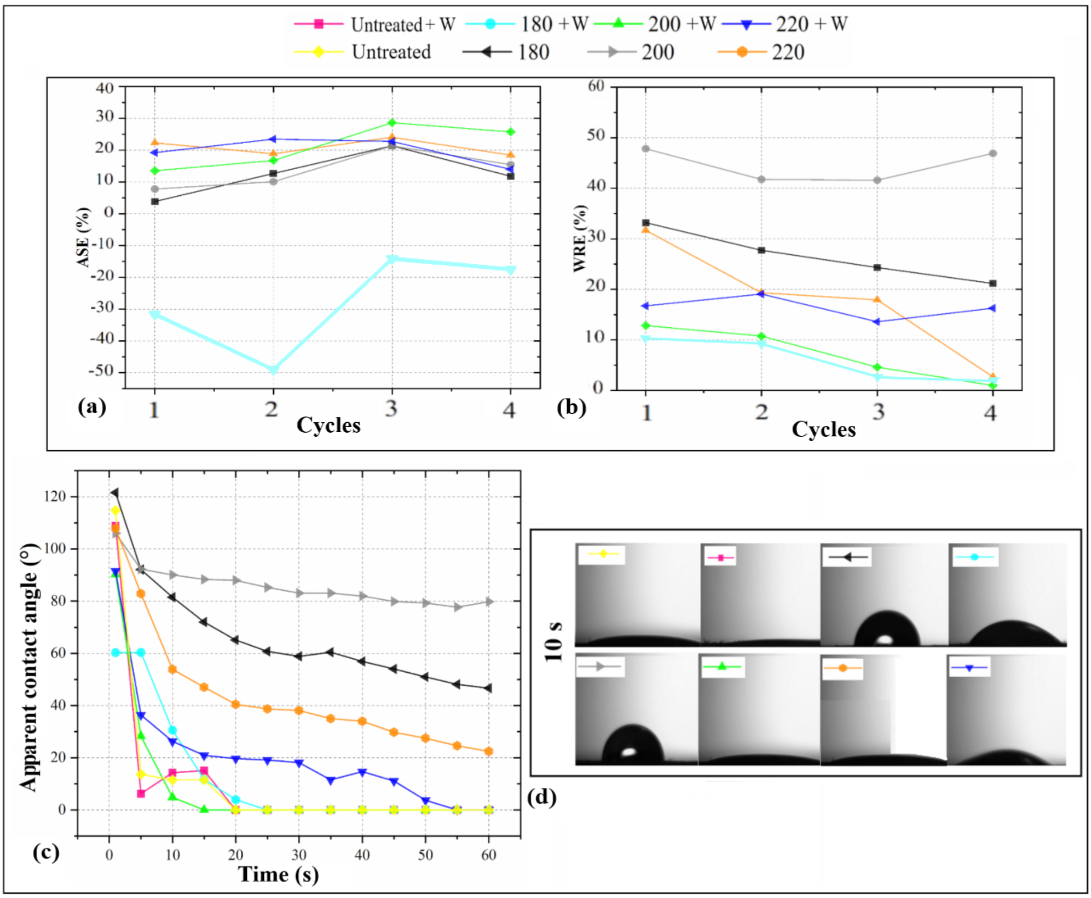


Figure 7: (a) ASE, (b) WRE, (c) contact angle, and (d) images of droplets after 10 s of wetting for the studied pine woods.

+ W refers to weathered samples.

In general, weathering caused an increase in surface and bulk hydrophilicity, although dimensional stability was not affected in most cases. Compared to the untreated pine wood, those woods treated at temperatures above 200 ºC presented higher surface hydrophilicities, which were retained for the weathered pine woods treated at this temperature range. These surface effects were not found for that wood treated at 180 ºC. Similar increases in ASE and WRE means were found in the literature and normally ascribed to the degradation of amorphous segments from wood polysaccharides (Missio *et al.* 2016).

Effects of the termites attack in the weathered thermally treated woods

Regarding the mass losses attributed to the termites attack (Figure 8), pine woods treated at 180 ºC showed the smallest averages, which indicates a significant effect of this treatment condition in preventing termite degradation. This effective protection brought by the thermal treatment at 180 ºC is probably related to the aforementioned migration of extractive to outside wood. Besides that, those woods treated above 200 ºC may undergo structural losses related to the decomposition of hemicelluloses and celluloses (Missio *et al*. 2016, Delucis *et al*. 2018), which seems to be detrimental in relation to the termites attack. Pine wood treated at both 200 ºC and 220 ºC did not differ significantly from untreated wood in terms of mass loss attributed to termite degradation, which was also reported in the literature.

In fact, heat treatments usually do not provide enough protection against termite attacks (Salman *et al.* 2017). According to Boonstra *et al*. (2006), chemicals are not added during a wood thermal treatment and even those chemical compounds formed due to the wood decomposition (such as acetic acid and carbon dioxide) are not toxic against termites. In terms of resistance against the termites attack, any studied wood was affected by the previous weathering, which is probably due to the weathering mechanism focused on the wood surface, as well as the chemical compounds formed due to the weathering, which are not considered toxic to termites. A similar study by Sivrikaya *et al*. (2015) dealt with five woods, namely pine (*Pinus sylvestris* L.), oriental spruce (*Picea orientalis* (L.) *Peterm.)*, ash (*Fraxinus spp* L.), iroko (*Chlorophora excels* (Welw.) Benth.), and tali (*Erythrophleum ivorense* A. Chev.), treated at two different temperatures (180 ºC and 210 °C) and also reported some mass losses above 10 %.

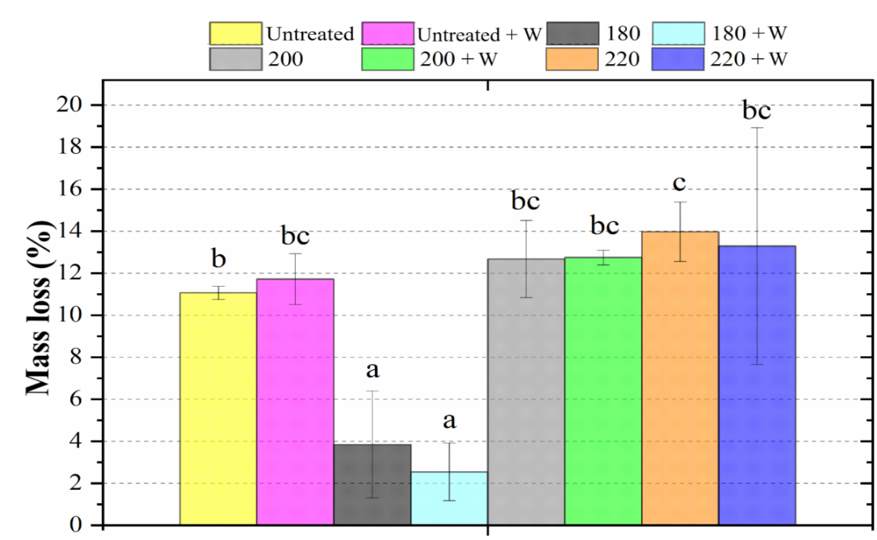


Figure 8: Mass losses ascribed to the termites damage for the studied pine woods.
+ W refers to weathered samples.
Different letters above the bars represent significantly different means.

Regarding stiffness (MOE) and strength (MOR) (Figure 9a and Figure 9b), no significant differences were observed attributable to the heat treatments or the weathering process. The preservation of mechanical properties following the heat treatments is considered a positive outcome since thermal treatment often leads to a decrease in mechanical properties compared to untreated wood (Gallio *et al.* 2019).

While heating exposure can depolymerize some cellulose and lignin chains, resulting in mechanical property losses (Tomak *et al.* 2014), the unchanged mechanical properties observed in this study can be explained by the increase in crystalline segments of wood polysaccharides relative to their amorphous chains, which are more susceptible to thermal decomposition (Boonstra *et al.* 2006). Similarly, the weathering process did not cause significant loss of mechanical properties, likely due to its superficial nature as an abiotic degradation mechanism simulated in this study, involving temperature, water, and ultraviolet radiation.

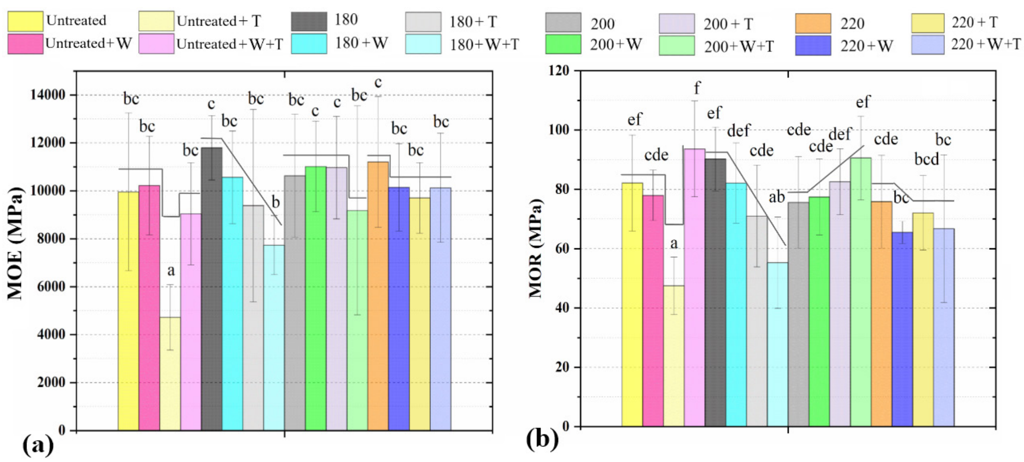


Figure 9: Modulus of elasticity ((a) MOE) and modulus of rupture ((b) MOR) of the studied pine woods. + W and + T refer to weathered and biodeteriored samples. Different letters above the bars represent significantly different means.

In terms of termite attack on the pine woods, most of the samples did not show significant decreases in mechanical properties, except for the untreated wood's MOE and MOR and the MOR of the pine wood treated at 180 °C. This indicates that thermal treatments above 200 °C were effective in protecting the pine wood against termite attack. Therefore, despite mass losses exceeding 10 % in these woods, their mechanical properties remained unaffected. Additionally, the termites exhibited a preference for feeding on the untreated pine woods, which aligns with the obtained results. Existing literature reports that no-preference feeding tests with thermally treated pine woods result in complete sample destruction, likely due to the moistened sand providing a favorable environment for termite development (Esteves and Pereira 2009).

Furthermore, it appears that the previous weathering had no significant effect on termite damage, except for the MOR of the pine wood treated at 180 °C and the untreated wood. In the former case, the pine wood treated at 180 °C and subsequently weathered exhibited a lower MOR than its non-weathered counterpart. This could be attributed to the heterogeneous effects of heating, primarily concentrated on the wood surface, with the treated layer possibly degrading and leaching during the weathering tests (Yildiz *et al.* 2013).

Consequently, the wood located in deeper layers may remain partly untreated and susceptible to termite attack. In the latter case, the untreated pine wood exposed to weathering demonstrated a higher MOR than its weathered counterpart, potentially due to a reduction in equilibrium moisture content caused by previous weathering degradation.

CONCLUSIONS

Heat treatments performed at temperatures above 200 ºC have been found to cause reductions in lumen diameter and cell wall thickness in wood. These changes can be attributed to the breakdown of hydroxyl groups present in amorphous polysaccharides like cellulose and hemicelluloses. These anatomical and chemical alterations result in a significant increase in weight loss, along with a decrease in surface roughness and hydrophobicity.

However, the bulk density, mechanical properties, and thermal stability of the wood remain stable. As expected, the thermal treatments also lead to increased volumetric hydrophobicity and enhanced dimensional stability. Moreover, treatments above 200 ºC have proven effective in reducing surface effects associated with weathering, such as color greying, increased roughness, and heightened surface hydrophilicity.

Interestingly, these weathering-induced surface effects do not impact the termite resistance of pine wood heat-treated above 180 ºC. This suggests that heat-treated wood exposed to outdoor environments remains susceptible to degradation by subterranean termites.

Conversely, pine wood treated at 180 ºC exhibits higher resistance to deterioration by termites. This enhanced resistance appears to be related to balanced chemical changes, including the migration of extractives to the wood's exterior and the preservation of polysaccharides at this intermediate treatment temperature.

Authorship contributions

R. R. M.: Writing – review & editing, Project administration, Methodology, Investigation, Visualization. A. P. A.: Writing – review & editing, Methodology, Project administration, Formal analysis. K. T. B.: Writing – review & editing, Methodology.

R. A. D: Writing – original draft, Supervision; Data curation; Conceptualization. R. B.: Funding acquisition, Resources. D. A. G.: Funding acquisition, Resources.

All authors have read and agreed to the published version of the manuscript.

REFERENCES

Acosta, A.P.; Diaz, R.H.; Amico, S.C.; Beltrame, R.; Barbosa, K.T.; Delucis, R.A.; Gatto, D.A. 2022. Effect of the temperature of the heat treatment of pine wood on subsequent in situ polymerization with poly(methyl methacrylate). *Biofuels, Bioproducts and Biorefining* 17(3): 499-509. https://doi.org/10.1002/bbb.2451

Acosta, A.P.; Labidi, J.; Barbosa, K.T.; Cruz, N.; Delucis, R.A.; Gatto, D.A. 2020. Termite resistance of a fast-growing pine wood treated by in situ polymerization of three different precursors. *Forests* 11(8): e865. https://doi.org/10.3390/f11080865

Afzal, I.; Shinwari, Z.K.; Sikandar, S.; Shahzad, S. 2019. Plant beneficial endophytic bacteria: Mechanisms, diversity, host range and genetic determinants. *Microbiological Research* 221: 36-49. https://doi.org/10.1016/j.micres.2019.02.001

Aramburu, A.B.; Guidoti, A.B.; Schneider, D.M.; Cruz, N.D.; de Avila-Delucis, R. 2022. Colour of polyurethane foams filled with wood and wood derivatives exposed to two xylophagous fungi. *Journal of Cellular Plastics* 58(3): 541-553. https://doi.org/10.1177/0021955X221074608

ASTM D143. 2017. Standard Test Methods for Small Clear Specimens of Timber. ASTM International. https://www.astm.org/d0143-94.html

Bak, M.; Molnár, F.; Németh, R. 2019. Improvement of dimensional stability of wood by silica nanoparticles. *Wood Material Science & Engineering* 14(1): 48-58. https://doi.org/10.1080/17480272.2018.1528568

Boonstra, M.J.; Rijsdijk, J.F.; Sander, C.; Kegel, E.; Tjeerdsma, B.; Militz, H.; Van-Acker, J.; Stevens, M. 2006. Microstructural and physical aspects of heat treated wood. Part 1. Softwoods. *Maderas. Ciencia y Tecnología* 8(3): 193-208. https://revistas.ubiobio.cl/index.php/MCT/article/view/1469

Che, W.; Xiao, Z.; Wang, Z.; Nguyen, T.T.; Xie, Y. 2019. Enhanced Weathering Resistance of Radiata Pine Wood by Treatment with an Aqueous Styrene/Acrylic Acid Copolymer Dispersion. *Journal of Wood Chemistry and Technology* 39(6): 421-435. https://doi.org/10.1080/02773813.2019.1636824

de Peres, M.L.; de Avila-Delucis, R.; Beltrame, R.; Gatto, D.A. 2020. Hydrothermal treatments to promote surface inactivation and increased flexibility in three hardwoods. *Maderas. Ciencia y Tecnología* 22(4): 439-446. http://dx.doi.org/10.4067/S0718-221X2020005000402

Delucis, R. de A.; Magalhães, W.L.E.; Petzhold, C.L.; Amico, S.C. 2018. Thermal and combustion features of rigid polyurethane biofoams filled with four forest-based wastes. *Polymer Composites* 39 (S3): E1770-E1777. https://doi.org/10.1002/pc.24784

Delucis, R.D.A.; Diaz, R.H.; Amico, S.C.; Labidi, J.; Gatto, D.A. 2017. Comparative study of weathering behavior of four fast-growing eucalyptus species. *Cellulose Chemistry and Technology* 51(9-10): 889-898. https://www.cellulosechemtechnol.ro/pdf/CCT9-10(2017)/p.889-898.pdf

Delucis, R.D.A.; Gatto, D.A. 2014. Flexural properties of four fast-growing eucalypts woods deteriorated by three different field tests. *Acta Scientiarum - Technology* 39(1): 39-44. https://doi.org/10.4025/actascitechnol.v39i1.27067

Delucis, R.D.A.; Beltrame, R.; Gatto, D.A. 2019. Discolouration of heat-treated fast-growing eucalyptus wood exposed to natural weathering. *Cellulose Chemistry and Technology* 53(7-8): 635-641. https://10.35812/CelluloseChemTechnol.2019.53.62

Ding, Y.; Ezekoye, O.A.; Lu, S.; Wang, C. 2016. Thermal degradation of beech wood with thermogravimetry/Fourier transform infrared analysis. *Energy Conversion and Management* 120: 370-377. https://doi.org/10.1016/j.enconman.2016.05.007

Esteves, B.M.; Herrera, R.; Santos, J.; Carvalho, L.; Nunes, L.; Ferreira, J.; Domingos, I.J.; Cruz-Lopes, L. 2020. Artificial Weathering of Heat-treated Pines from the Iberian Peninsula. *BioResources* 15(4): 9642-9655. https://bioresources.cnr.ncsu.edu/resources/artificial-weathering-of-heat-treated-pines-from-the-iberian-peninsula/

Esteves, B.M.; Pereira, H.M. 2009. Wood modification by heat treatment: A review. *BioResources* 4(1): 370-404. https://bioresources.cnr.ncsu.edu/BioRes_04/BioRes_04_1_0370_Esteves_P_Wood_Mod_Heat_Treatment_Rev_367.pdf

Frybort, S.; Obersriebnig, M.; Müller, U.; Gindl-Altmutter, W.; Konnerth, J. 2014. Variability in surface polarity of wood by means of AFM adhesion force mapping. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 457: 82-87. https://doi.org/10.1016/j.colsurfa.2014.05.055

Gallio, E.; Zanatta, P.; Cruz, N.D.; Zanol, G.S.; Schulz, H.R.; Gatto, D.A. 2019. Influence of thermal rectification and furfurylation treatments on technological properties of a conifer. *Materia* 24(3). https://doi.org/10.1590/S1517-707620190003.0739

Gallio, E.; Zanatta, P.; Gatto, D.A.; Beltrame, R. 2018. Fourier transform infrared spectroscopy in treated woods deteriorated by a white rot. *Maderas. Ciencia y Tecnología* 20(3): 479-488. http://dx.doi.org/10.4067/S0718-221X2018005031701

Hadi, Y.S.; Massijaya, M.Y.; Arinana, A. 2016. Subterranean termite resistance of polystyrene-treatedwood from three tropicalwood species. *Insects* 7(3): 6-11. https://doi.org/10.3390/insects7030037

He, L.; Zhang, T.; Zhao, X.; Zhao, Y.; Xu, K.; He, Z.; Yi, S. 2023. Synergistic effect of tung oil and heat treatment on surface characteristics and dimensional stability of wood. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 665: 131233. https://doi.org/10.1016/j.colsurfa.2023.131233

Herrera, R.; Sandak, J.; Robles, E.; Krystofiak, T.; Labidi, J. 2018. Weathering resistance of thermally modified wood finished with coatings of diverse formulations. *Progress in Organic Coatings* 119: 145-154. https://doi.org/10.1016/j.porgcoat.2018.02.015

Herrera-Díaz, R.; Sepúlveda-Villarroel, V.; Torres-Mella, J.; Salvo-Sepúlveda, L.; Llano-Ponte, R.; Salinas-Lira, C.; Peredo, M.; Ananías, R.A. 2019. Influence of the wood quality and treatment temperature on the physical and mechanical properties of thermally modified radiata pine. *European Journal of Wood and Wood Products* 77(4): 661-671. https://doi.org/10.1007/s00107-019-01424-9

Hill, C.; Altgen, M.; Rautkari, L. 2021. Thermal modification of wood - a review : chemical changes and hygroscopicity. *Journal of Materials Science* 56 (11): 6581-6614. https://doi.org/10.1007/s10853-020-05722-z

Hill, C.; Kymalainen, M.; Rautkari, L. 2022. Review of the use of solid wood as an external cladding material in the built environment. *Journal of Materials Science* 57:9031-9076. https://doi.org/10.1007/s10853-022-07211-x

Jirouš-Rajković, V.; Miklecić, J. 2021. Enhancing Weathering Resistance of Wood - A Review. *Polymers* 13(12): e1980. https://doi.org/10.3390/polym13121980

Kamperidou, V. 2019. The biological durability of thermally-and chemically-modified black pine and poplarwood against basidiomycetes and mold action. *Forests* 10(12):e1111. https://doi.org/10.3390/f10121111

Krystofiak, T.; Can, A.; Lis, B., 2022. Investigation of Roughness and Adhesion Strength Properties of Pine and Poplar Wood Heat Treated in Air and under Vacuum after Artificial Aging. *Coatings* 12(12): e1910. https://doi.org/10.3390/coatings12121910

Kuka, E.; Andersons, B.; Cirule, D.; Andersone, I.; Kajaks, J.; Militz, H.; Bicke, S. 2020. Weathering properties of wood-plastic composites based on heat-treated wood and polypropylene. *Composites Part A: Applied Science and Manufacturing* 139: e106102. https://doi.org/10.1016/j.compositesa.2020.106102

Kymäläinen, M.; Lourençon, T.V.; Lillqvist, K. 2022. Natural weathering of soft - and hardwoods modified by contact and flame charring methods. *European Journal of Wood and Wood Products* 80: 1309-1320. https://doi.org/10.1007/s00107-022-01864-w

Laina, R.; Sanz-Lobera, A.; Villasante, A.; López-Espí, P.; Martínez-Rojas, J.A.; Alpuente, J.; Sánchez-Montero, R.; Vignote, S. 2017. Effect of the anatomical structure, wood properties and machining conditions on surface roughness of wood. *Maderas. Ciencia y Tecnología* 19(2): 203-212. http://dx.doi.org/10.4067/S0718-221X2017005000018

Lee, S.H.; Ashaari, Z.; Lum, W.C.; Abdul Halip, J.; Ang, A.F.; Tan, L.P.; Chin, K.L.; Md-Tahir, P. 2018. Thermal treatment of wood using vegetable oils: A review. *Construction and Building Materials* 181: 408-419. https://doi.org/10.1016/j.conbuildmat.2018.06.058

Lengowski, E.C.; Bonfati Junior, E.A.; Nisgoski, S.; Muñiz, G.I.B.; Klock, U. 2021. Properties of thermally modified teakwood. *Maderas. Ciencia y Tecnología* (23): 1-16. http://dx.doi.org/10.4067/s0718-221x2021000100410

Lovaglio, T.; Auria, M.D.; Gindl-altmutter, W.; Giudice, V.L.; Langerame, F.; Salvi, A.M.; Todaro, L. 2022. Thermal Modification and Alkyl Ketene Dimer Effects on the Surface Protection of Deodar Cedar (*Cedrus deodara* Roxb .) Wood. *Forest* 13(10): e1551. https://doi.org/10.3390/f13101551

Mattos, B.D.; Lourençon, T.V.; Gatto, D.A.; Serrano, L.; Labidi, J. 2016. Chemical characterization of wood and extractives of fast-growing *Schizolobium parahyba* and *Pinus taeda*. *Wood Material Science & Engineering* 11(4): 209-216. https://doi.org/10.1080/17480272.2014.970574

Missio, A.L.; Bayer, F.M.; Gatto, D.A.; Cademartori, P.H.G. 2014. Sampling sufficiency of the anatomical characteristics of Brazilian hardwood using the resampling method. *Acta Scientiarum. Technology* 36 (3): 413-420. https://doi.org/10.4025/actascitechnol.v36i3.20335

Missio, A.L.; Mattos, B.D.; De Cademartori, P.H.G.; Gatto, D.A. 2016. Effects of Two-Step Freezing-Heat Treatments on Japanese Raisintree (*Hovenia dulcis* Thunb.) Wood Properties. *Journal of Wood Chemistry and Technology* 36(1): 16-26. https://doi.org/10.1080/02773813.2015.1039544

Missio, A.L.; Mattos, B.D.; Cademartori, P.H.G.; Pertuzzatti, A.; Conte, B.; Gatto, D.A. 2015. Thermochemical and physical properties of two fast-growing eucalypt woods subjected to two-step freeze-heat treatments. *Thermochimica Acta* 615: 15-22. https://doi.org/10.1016/j.tca.2015.07.005

Nguyen, T.T.; Nguyen, T.H.; Ji, X.; Yuan, B.; Mai, H.; Khoa, T.; Lanh, T. Guo, M. 2019. Prediction of the color change of heat - treated wood during artificial weathering by artificial neural network. *European Journal of Wood and Wood Products* 77(6): 1107-1116. https://doi.org/10.1007/s00107-019-01449-0

Özgenç, Ö.; Durmaz, S.; Boyaci, I.H.; Eksi-Kocak, H. 2017. Determination of chemical changes in heat-treated wood using ATR-FTIR and FT Raman spectrometry. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 171: 395-400. https://doi.org/10.1016/j.saa.2016.08.026

Pandey, K.K.; Pitman, A.J. 2003. FTIR studies of the changes in wood chemistry following decay by brown-rot and white-rot fungi. *International Biodeterioration & Biodegradation* 52(3): 151-160. https://doi.org/10.1016/S0964-8305(03)00052-0

Peng, Y.; Wang, Y.; Zhang, R.; Wang, W.; Cao, J. 2021. Industrial Crops & Products Improvement of wood against UV weathering and decay by using plant origin substances : Tannin acid and tung oil. *Industrial Crops and Products* 168: e113606. https://doi.org/10.1016/j.indcrop.2021.113606

Popescu, C.M.; Spiridon, I.; Tibirna, C.M.; Vasile, C. 2011. A thermogravimetric study of structural changes of lime wood (Tilia cordata Mill.) induced by exposure to simulated accelerated UV/Vis-light. *Journal of Photochemistry and Photobiology A: Chemistry* 217(1): 207-212. https://doi.org/10.1016/j.jphotochem.2010.10.010

Poubel, D.; Garcia, R.A.; Dos-Santos, W.A.; Oliveira, G.L.; Abreu, H.S. 2013. Efeito da termorretificação nas propriedades físicas e químicas da madeira de *Pinus caribaea*. *Cerne* 19(3): 391-398. https://doi.org/10.1590/S0104-77602013000300005

Pratiwi, L.A.; Darmawan, W.; Priadi, T.; George B.; Merlin, A.; Gérardin, C.; Dumarçay, S.; Gérardin, P. 2019. Characterization of thermally modified short and long rotation teaks and the effects on coatings performance. *Maderas. Ciencia y Tecnología* 21(2): 209-222. http://dx.doi.org/10.4067/S0718-221X2019005000208

Salman, S.; Thévenon, M.F.; Pétrissans, A.; Dumarçay, S.; Candelier, K.; Gérardin, P. 2017. Improvement of the durability of heat-treated wood against termites. *Maderas. Ciencia y Tecnología* 19(3): 317-328. http://dx.doi.org/10.4067/S0718-221X2017005000027

Sivrikaya, H.; Can, A.; De-Troya, T.; Conde, M. 2015. Comparative biological resistance of differently thermal modified wood species against decay fungi, *Reticulitermes grassei* and *Hylotrupes bajulus*. *Maderas. Ciencia y Tecnología* 17(3): 559-570. http://dx.doi.org/10.4067/S0718-221X2015005000050

Tomak, E.D.; Ustaomer, D.; Yildiz, S.; Pesman, E. 2014. Changes in surface and mechanical properties of heat treated wood during natural weathering. *Measurement* 53: 30-39. https://doi.org/10.1016/j.measurement.2014.03.018

Yildiz, S.; Tomak, E.D.; Yildiz, U.C.; Ustaomer, D. 2013. Effect of artificial weathering on the properties of heat treated wood. *Polymer Degradation and Stability* 98 (8): 1419-1427. https://doi.org/10.1016/j.polymdegradstab.2013.05.004

Zhang, X.; Wang, F.; Keer, L. 2015. Influence of Surface Modification on the Microstructure and Thermo-Mechanical Properties of Bamboo Fibers. *Materials* 8(10): 6597-6608. https://doi.org/10.3390/ma8105327

Zhang, Y.; Yu, Y.; Lu, Y.; Yu, W.; Wang, S. 2021. Effects of heat treatment on surface physicochemical properties and sorption behavior of bamboo (*Phyllostachys edulis*). *Construction and Building Materials* 282: e122683. https://doi.org/10.1016/j.conbuildmat.2021.122683