DOI: 10.4067/s0718-221x2021000100410

PROPERTIES OF THERMALLY MODIFIED TEAKWOOD

Elaine Cristina Lengowski^{1,*} https://orcid.org/0000-0002-7336-7626



Eraldo Antonio Bonfatti Júnior²

https://orcid.org/0000-0002-2730-7681

Silvana Nisgoski²

https://orcid.org/0000-0001-9595-9131

Graciela Inês Bolzon de Muñiz²

https://orcid.org/0000-0003-4417-0178

Umberto Klock²

https://orcid.org/0000-0003-3946-3320

ABSTRACT

Thermal modification is a treatment that seeks to improve the properties of wood and reduce the heterogeneity in its color. The objective of this work was to evaluate the effect of thermal treatment on the anatomical, chemical, physical, mechanical, colorimetric, and thermal stability properties of teakwood. For this, teakwood samples were treated by an industrial autoclave at final cycle temperature of 160 °C. The reduction of cell wall thickness, the formation of cross-fissures and the crystallization of the wax inside the pores were observed in the anatomical structure. Chemically, the extractives evaporated and the polysaccharides ruptured, of which hemicellulose was the most affected. The heat treatment promoted lower equilibrium moisture, reducing the hygroscopicity and improving the dimensional stability of the wood. Considering the mechanical properties, the rupture modulus and the longitudinal and tangential hardness decreased after the heat treatment. The color of the wood changed significantly, from pink to dark brown. The treated wood had higher thermal stability, with greater weight loss at higher temperatures than the untreated wood.

Keywords: Colorimetry, cell wall thickness, thermogravimetry, *Tectona grandis*, wood properties, wood mechanical properties, wood hygroscopicity, wood modification.

¹Federal University of Mato Grosso, Faculty of Forestry Engineering, Cuiabá, Mato Grosso, Brazil.

²Federal University of Paraná, Department of Forest Engineering and Technology, Curitiba, Paraná, Brazil.

 $\label{eq:corresponding} Corresponding author: elainelengowski@gmail.com$

Received:11.04.2019 Accepted:14.10.2020

INTRODUCTION

Tectona grandis, commonly known as teak, grows naturally in Southeast Asia and is one of the most valuable tropical species in the international market (Niamké *et al.* 2011, Nocetti *et al.* 2011, Niamké *et al.* 2014, Pratiwi *et al.* 2019). Besides its natural occurrence, teak is planted in many tropical regions of the Americas and Africa (Kokutse *et al.* 2004). In Brazil, there are approximately 93,957 hectares planted of teak (IBÁ 2019), and mostly are concentrated mostly in Midwest, especially in the state of Mato Grosso (FAMATO 2013).

Teakwood is appreciated for its moderate basic density, high mechanical strength, texture, aesthetics, color, workability, dimensional stability, and natural durability (Kokutse *et al.* 2006, Derkyi *et al.* 2009). It can be used for many purposes, both internal and external, including home building, shipbuilding, furniture manufacture, poles, and sculptures (Niamké *et al.* 2011, Niamké *et al.* 2014).

Teakwood is porous with distinct growth rings marked by lines of marginal parenchyma, and its sapwood has a yellowish color and brown heartwood. The quality of teak wood is mainly linked to the heartwood region (Lemos *et al.* 2019), since high natural durability and high dimensional stability, characteristics due to the presence of some substances, such as caucho, a species of latex responsible for the reduction water absorption, and tectoquinone, a natural preservative contained in the cells of the wood (Kokutse *et al.* 2006).

In the *T. grandis* species, the sapwood presents inferior wood quality than heartwood (Lemos *et al.* 2019), the heterogeneous and yellowish color pattern in the sapwood reduces its acceptance in the market (Mononen *et al.* 2002). As a solution, it is common to apply heat treatment in teakwood to reduce the differences observed in coloring (Bonfatti Júnior and Lengowski 2018).

The modification of wood consists of processes to improve its properties, producing a new material. In this context, thermal modification stands out: since it does not use any chemicals, it does not present a greater environmental liability than wood without thermal modification (Hill 2006).

The thermal modification of wood is conducted using controlled heating at relatively high temperatures of 150 °C to 260 °C (Grinins *et al.* 2016). This treatment is used to improve dimensional stability, reduce hygroscopicity, and modify and standardize staining. However, as adverse result in wood, the mechanical properties decrease (Esteves and Pereira 2009), flammability increases (Čekovská *et al.* 2017), mass is lost (Esteves and Pereira 2009) and chemical components are modified and broken (Weiland and Guyonnet 2003, Shi *et al.* 2018).

To understand the effects of thermal modification technique beyond color changes, this article compares the anatomical, chemical, physical, mechanical, colorimetric, and thermal stability properties of thermally treated teakwood with the characteristics of the untreated teakwood.

MATERIAL AND METHODS

Wood

Boards of teakwood (*Tectona grandis* L. f.), untreated and thermally treated, were donated by TW Brazil company, the wood came from 25-years-old commercial plantations in Mato Grosso state, but the heat treatment station is in Ponta Grossa, Paraná state, Brazil. The thermal modification was performed by the VAP HolzSysteme® process, applying heat of 160 °C in a saturated steam atmosphere with efficient elimination of oxygen. The treatment was performed in five stages: an initial heating ramp with duration up to constant temperature (110 °C), 25 minutes at this temperature; a second ramp with duration until the final temperature (160 °C); 45 minutes at maximum temperature; and natural cooling. The total duration of the process was about 16 hours, carried out in two 8-hours heating-cooling cycles, with mass loss not exceeding 12%. Five boards per treatment were analyzed.

Anatomical and surface analysis

For the general description of the anatomical characteristics, samples with dimensions of 1,5cm x 1,5 cm x 2,0 cm were collected from the boards. These samples were submitted to boiling for softening and then histological sections in the transverse, tangential and radial directions were cut in a sliding microtome, with a thickness of 28 μ m. The anatomical description of the wood, following the standards established by International Association of Wood Anatomists (Wheeler *et al.* 1989), was carried out with an Olympus CX 40 microscope (Tokyo, Japan, Olympus Corporation).

Scanning electron microscopy (SEM) was used for surface description of the untreated and thermally modified samples, with a PHILIPS XL-30 microscope after the samples were covered with a thin layer of gold in a vacuum chamber.

Chemical constituents

The wood sampling and preparation for chemical analysis were carried out in accordance with the Technical Association of the Pulp and Paper Industry T 257 sp-14 standard (TAPPI 2014) in three samples per treatment. At this point we determined total extractive content following T 204 cm-17standard (TAPPI 2017) and insoluble lignin content following T 222 om-15 standard (TAPPI 2015). Holocellulose content was calculated by Equation 1.

Holocellulose content = 100 - total extractive content -insoluble lignin content (1)

Physical and mechanical properties

The wood's basic density was determined in accordance with ASTMD-2395-17 (2017). To analyze the effect of the thermal modification on the dimensional stability, the radial, tangential and volumetric shrinkage were tested following ASTM D-143-14 (2014), and the anisotropy of shrinkage was calculated by the ratio of tangential shrinkage divided by radial shrinkage.

The wood samples were air-conditioned in a climatic chamber with 12% relative air humidity. After this, the moisture was determined following ASTM D-143-14 (2014) and the result was used as a measure of hygroscopicity of untreated and thermally modified wood.

Finally, to analyze the effect on the mechanical properties, static bending and hardness (longitudinal, radial and tangential) were tested following ASTM D-143-14(2014).

Color measurements

Wood color was measured with a Konica Minolta CM-5 spectrophotometer coupled to a computer, with adjustment to a D65 light source and 10° observation angle. The reflectance data were obtained with a spectral range from 400 nm to 750 nm. Ten spectra were collected per board, directly on the radial/tangential surface. A total of 200 spectra were obtained, 50 for each treatment, and analysis was performed of all spectra.

The following color parameters were measured and calculated, following the ASTM D-2244-16 (2016): lightness (L*), green-red coordinate (a*), blue-yellow coordinate (b*), color saturation (C*), hue angle (h) and the color difference between the two kinds of produced pulps (ΔE).

Thermal analysis

The thermogravimetric characterization (TGA) was performed with a Netzsch TGA 209 under N_2 atmosphere with a heating rate of 20 °C·min⁻¹ to maximum temperature of 900 °C.

Statistical analysis

Analysis of variance (ANOVA) was applied to identify differences between natural and thermally modified wood. The significance level (α) was 5%, considering the null hypothesis (H0) of equivalence between the means and alternative hypothesis (H1) of non-equivalence. F-critical greater than the F value involves accepting H0, rejecting it otherwise. To validate the ANOVA model, Shapiro-Wilk and the Bartlett's tests were used to verify the normality of the distribution and the homogeneity between variances, respectively, both at 5% significance.

RESULTS AND DISCUSSION

Anatomical and surface analysis

Teakwood presented distinct growth rings. The rings were porous, with numerous large pores in the initial zone of the growth layers, with simple perforation plates and alternate intervessel pits. Tyloses, gums and other deposits were present in heartwood vessels. Fibers had simple, septate and non-septate scoring. The axial parenchyma was composed of marginal or seemingly marginal vasicentric bands. All cells of the rays were procumbent, with presence of silica (Figure 1).



Figure 1: Microscopic photos of the anatomical aspects of teakwood. (a) = Transversal section; (b) = Radial section; (c) = Tangential section.

The anatomical structure of the wood did not change significantly (Figure 2). There was a decrease in the thickness of the walls and the formation of cracks in the cross section (Figure 2b). In the radial section, the presence of the substances inside the crystallized pores can be observed in the treated wood (Figure 2d).

There was formation of many cracks due to the rupture of the wall and breaking of links between fibrils. These cracks result from the high vapor pressure generated by resistance to water movement when the wood is subjected to heating, since this species has pores obstructed by gums and tyloses. Cell walls ruptured perpendicular to the direction of the fiber, resulting in transverse ruptures and contributing to the abrupt fracture in bending tests of treated wood (Boonstra *et al.*2006a).



Figure 2: Scanning electron microscopy images of the morphological aspects before and after treatment of teakwood. (a) = Transverse section of the wood without heat treatment; (b) = Transverse section of wood with heat treatment; (c) = Radial section of the wood without heat treatment; (d) = Radial section of wood with heat treatment; (e) = Tangential section of the wood without heat treatment; (f) = Tangential section of wood with heat treatment.

Anatomically, the modifications depend on the conditions of the process used and the peculiarities of the species (Esteves and Pereira 2009, Boonstra *et al.*2006a, Shi*et al.*2018). When heat treating *Picea abies* between 180 °C to 200 °C, Fengel (1966) found cracks in the middle lamella and layer S1, and visible changes in the walls, as well as dissolved substances deposited in the cell cavities. In turn, Boonstra *et al.*(2006b), studying the thermal treatment of hardwoods, concluded that *Populus* sp. was sensitive to vessel collapse and to some deformations in the libriform fibers near the vessels, *Betula* sp. Wood presented some radial cracks, and *Fagus* sp. wood presented the two types of mentioned damage.

Chemical constituents

The thermal treatment altered the chemical composition of the wood significantly, degrading extractive and cell wall compounds. The total extractives content and insoluble lignin content were greater in the treated teakwood, but the thermal treatment caused a drop in holocellulose content (Table 1).

Treatment	Total extractives (%)	Insoluble lignin (%)	Holocellulose (%)
UTW	11,03* (11,22)	25,75* (17,98)	61,22* (9,89)
TTW	16,39* (28,48)	32,56* (9,80)	49,07* (14,48)

 Table 1: Chemical constituents of wood samples.

UTM = untreated teakwood; TTU = treated teakwood; ns = no significant difference by the F-test at 5 % confidence; * significant difference by the F-test at 5 % confidence. Values between parentheses are the coefficients of variation of the samples.

When analyzing the chemical constituents of the teakwood Chagas *et al.* (2014) and Pratiwi *et al.* (2019) found lower extractives content (4,76% and 7,41%), higher insoluble lignin content (30,43% and 32,57%) and holocellulose content (64,01% and 67,42%) to the values of the untreated teakwood in the present study.

After the heat treatment at 220 °C for 20 h Pratiwi *et al.* (2019) found a mean holocellulose reduction of 15,18% and total extractives of 21,32%, while an increase in lignin content of 31,3% occurred. While in this work an increase in total extractive content (48,59%) and lignin (26,44%) and a reduction in holocellulose content of 19,84% were found. Chemical changes due to heating depend on the duration, temperature and type of the treatment, with temperature being the main factor (Esteves and Pereira 2009). Lengowski *et al.* (2018), studying the wood of *Pinus taeda* and *Eucalyptus grandis*, observed an increase in extractives content and reduction of holocellulose content for both species, but only for *E. grandis* was there a significant increase in lignin content.

The most extractives disappear or degrade during the heat treatment, especially the more volatile ones. However, due to degradation of the structural components of the cell walls, new compounds that can be extracted from the wood are created, causing the extractives content to increase substantially with the loss of weight (Esteves *et al.* 2008, Esteves and Pereira 2009).

Hemicellulose is the most affected fraction due to its amorphous structure and low molecular weight (Poncsák *et al.* 2006, Hamada *et al.* 2017, Shi*et al.* 2018), thus responsible for the drop in holocellulose content. Degradation of the hemicelluloses begins by deacetylation, and the resulting formation of acetic acid acts as a catalyst for depolymerization, further increasing the polymer breakdown, leading to the formation of formaldehyde, furfural and other aldehydes (Nuopponen *et al.* 2005). The degradation of pentoses and hexoses formed the furfural and hydroxymethylfurfural products (Nuopponen *et al.* 2005). At the same time as these reactions occur, the hemicelluloses undergo dehydration reactions, with decrease of the hydroxyl groups (Weiland and Guyonnet 2003).

The loss in resistance of the cell wall observed in Figure 2b may also have occurred due to the elimination of part of the hemicellulose, which acts as a binding element between cellulose and lignin.

Cellulose is less affected by thermal treatments, probably due to its semi-crystalline nature (Esteves and Pereira 2009). However, as the temperature increases, the amorphous regions are degraded (Lengowski *et al.* 2013), causing an increase in the cellulose crystallinity, which decreases in the accessibility to hydroxyl groups by water molecules (Bhuiyan and Hirai 2005, Boonstra and Tjeerdsma 2006). This may be one of the causes of the reduction of the equilibrium moisture content.

The percentage increase of lignin occurs because this polymer degrades at temperatures higher than the polysaccharides (Esteves *et al.* 2008). The cleavage of the ether linkages, especially β -O-4, leads to the formation of free phenolic hydroxyl groups and α - and β -carbonyl groups (Nuopponen *et al.* 2005), which are

responsible for crosslinking through the formation of methyl groups (Nuopponen *et al.* 2005, Tjeerdsma and Militz 2005). With the reduction of the methoxyl content, new reactive regions in the aromatic ring can lead to new condensation reactions (Wikberg and Maunu 2004).

Physical and mechanical analysis

For equilibrium moisture with the environment, a significant drop was observed after the heat treatment. No significant variation was observed in the physical properties of basic density, longitudinal contraction, and radial contraction after thermal modification. However, the equilibrium moisture, volumetric contraction, tangential contraction and contraction anisotropy were reduced (Table 2).

Treatment	SG (kg m^{-3})	EM (%)	VS (%)	LS (%)	RS (%)	TS (%)	AS
UTW	480 ^{ns}	15,21*	6,07*	0,71 ^{ns}	1,89 ^{ns}	3,57*	1,88*
	(1,15)	(1,84)	(9,19)	(9,19)	(9,23)	(9,99)	(3,22)
TTW	470^{ns}	8,76*	4,22*	$0,53^{ns}$	$1,73^{ns}$	2,01*	1,15*
	(1,24)	(2,87)	(8,81)	(8,81)	(7,48)	(17,77)	(15,7)

Table 2: Physical properties of wood.

UTM = untreated teakwood; TTU = untreated teakwood; SG = specific gravity; EM = equilibrium moisture; VS = volumetric shrinkage; LS = longitudinal shrinkage; RS = radial shrinkage; TS = tangential shrinkage; AC = anisotropy of shrinkage; ns = no significant difference by the F-test at 5 % confidence; * significant difference by the F-test at 5 % confidence. Values between

parentheses are the coefficients of variation of the samples.

According to Lima *et al.* (2009) and Motta *et al.* (2010), the average density values of teakwood are between 670 kg/m³ to 550 kg/m³. Moya *et al.* (2009) found a wide variation for density of this species in different years, ranging from 550 kg/m³ to 875 kg/m³. Our results are below the values mentioned above, but they are in line with those reported by Gonçalvez *et al.* (2007), who found values for teakwood of Brazilian origin between 400 kg/m³ to 470 kg/m³.

A reduction of the basic density of the wood is usually observed after heat treatment (Boonstra *et al.* 2007, Korkut 2008, Esteves and Pereira 2009, Ozsahin and Murat 2017). This was not observed for teakwood under our treatment conditions, since there was no significant difference in the basic density of treated and untreated wood.

Because it is an organic material, wood tends to absorb water and balance with the moisture of the environment. As the water vapor occupies the empty spaces between the cells of the wood, causing the dimensions of the cell walls to increase, and as a consequence the wood increases in dimension. These changes in dimension are anisotropic and are greatest in the tangential direction than radial direction, and least in the longitudinal direction (Hill 2006).

The reduction of equilibrium moisture was 42,40 % in relation to wood without treatment. The reason for the decrease in equilibrium moisture is that less water is absorbed by the cell walls after the heat treatment, as a result of the decrease of the hydroxyl groups present in the hemicelluloses and in the amorphous regions of the cellulose. The inaccessibility of hydroxyl groups occurs due to increased crystallinity of cellulose with the heat treatment (Wikberg and Maunu 2004, Bhuiyan and Hirai 2005, Boonstra and Tjeerdsma 2006) and consequent decrease in the wood hydrophilic carbohydrates (Santos *et al.* 2014). This fact was demonstrated by Lengowski *et al.* (2013) who found, while modifying the cellulose crystallinity, that treatments with higher temperatures caused an increase in the crystalline index, indicating the removal of amorphous regions that are highly hygroscopic. The decrease in equilibrium moisture is also influenced by polycondensation and lignin crosslinking reactions (Repellin and Guyonnet 2005, Tjeerdsma and Militz 2005, Boonstra and Tjeerdsma 2006, Esteves *et al.* 2008).

The mean values for volumetric contraction of teakwood range from 6,31 % to 5,23%; 0,34% for longitudinal contraction, 1,75 % to 1,88% for radial contraction, and 3,49 % to 4,25% for tangential contraction, while the anisotropy coefficient is on the order of 1,99 to 2,27 (Bonduelle *et al.* 2015, Dias *et al.* 2018). The contractions found in the present work are close to those reported in the literature, but the anisotropy coefficient

is higher.

There was a significant variation in the tangential contraction, causing a reduction of 77,86%. The most important index to evaluate the dimensional stability of wood is the coefficient of anisotropy, defined as the ratio between tangential and radial contractions (RS/TS) (Durlo and Marchiori 1992). According to those authors' classification, the anisotropy coefficient of the untreated wood was normal wood ($1,5 \le AC \le 2,0$) and wood after heat treatment has excellent workability ($1,2 \le AC \le 1,5$).

The increase in dimensional stability of thermally treated wood is due to the decrease in the hygroscopicity because of the chemical changes that occur. Tjeerdsma *et al.* (1998) observed that one of the probable reasons for the improvement of the dimensional stability is the loss of the methyl radicals of the guaiacyl and syringyl units of lignin, which leads to an increase in the proportion of phenolic groups. These chemical changes lead to greater reactivity of lignin, with the formation of several crosslinks, responsible for increasing dimensional stability. As the crosslinking increases, the molecule becomes less elastic and the cellulose microfibrils have less possibility to expand and absorb water, which explains the decrease in the equilibrium moisture and the improvement in the dimensional stability.

Not all mechanical properties were influenced by the heat treatment. For MOR, there was a significant drop in the property, from 69,39 MPa to 32,31 MPa, whereas there was no statistical difference in MOE. For longitudinal and tangential hardness, significant declines were observed, while in the radial direction this property did not change significantly (Table 3).

The mechanical properties most affected by the heat treatment are MOR in flexural strength and impact flexion tests (Esteves and Pereira 2009). The reduction of these properties is related to the changes in the chemical structures of the wood (Yildiz *et al.* 2005). However, thermal treatments can increase the modulus of elasticity (Esteves and Pereira 2009).

Traatmont	Static ber	nding (MPa)	Hardness (N)			
Treatment	MOR	MOE	Longitudinal	Radial	Tangential	
UTW	69,39*	7202,17 ^{ns}	4921,47*	4575,00 ^{ns}	4178,81*	
	(17,79)	(15,15)	(6,27)	(13,46)	(6,82)	
TTW	32,31*	7505,77 ^{ns}	2355,46*	2019,48 ^{ns}	2024,97*	
	(35,61)	(5,23)	(6,33)	(22,69)	(12,19)	

UTM = untreated teakwood; TTU = treated teakwood; MOR = modulus of rupture; MOE = modulus of elasticity; ns = no significant difference by the F-test at 5 % confidence; * significant difference by the F-test at 5 % confidence.

Values between parentheses are the coefficients of variation of the samples.

The mechanical properties most affected by the heat treatment are MOR in flexural strength and impact flexion tests (Esteves and Pereira 2009). The reduction of these properties is related to the changes in the chemical structures of the wood (Yildiz *et al.* 2005). However, thermal treatments can increase the modulus of elasticity (Esteves and Pereira 2009).

There are two theories that explain the increase of the MOE. The first one affirms that the high temperature increases the crosslinks of lignin, improving the rigidity around cellulose microfibrils and the resistance of the lamella media (Gunduz *et al.* 2009). The second theory states that the increase in MOE is due to the increase in cellulose crystallinity and the reduction of equilibrium moisture (Esteves and Pereira 2009). In the present study, the thermal treatment provoked a 50% reduction in MOR without significant increase of MOE.

The undesirable effect of thermal modifications the degradation of some mechanical properties, since the wood becomes more brittle with the deterioration of the amorphous polysaccharides (Esteves and Pereira 2009), causing a decrease in hardness (Unsal *et al.* 2003, Korkut 2008, Modes *et al.* 2017). In the present work, significant declines of hardness occurred in the longitudinal and tangential section.

Color measurements

The heat treatment caused significant reductions in the blue-yellow color coordinate (b *), luminosity (L), color saturation (C *) and hue angle (h *), but there was no significant change in the red-green chromatic coordinate (a *) (Table 4). The total color variation (ΔE) was 24.11.

For the untreated teakwood, the parameters L, a* and b* were classified as pink color and for the treated wood the parameters were in the dark brown pattern (Camargos and Gonçalez 2001).

Treatment	L	a*	b*	C*	h*
	59,77*	9,59 ^{ns}	24,33*	26,17*	68,38*
UTW	(5,74)	(8,70)	(7,46)	(5,60)	(3,99)
	38,10*	9,81 ^{ns}	15,97*	18,87*	58,03*
TTW	(11,10)	(14,54)	(24,43)	(21,72)	(4,64)

 Table 4: Colorimetric parameters of wood.

UTM = untreated teakwood; TTU = treated teakwood; L = brightness; a * = chromatic coordinate (green - red); b * = chromatic coordinate (blue - yellow); C * = color saturation; h * = hue angle; ns = non-significant difference by the F-test at 5 % confidence; * significant difference by the F-test at 5 % confidence. Values between parentheses are the coefficients of variation of the samples.

After the heat treatment, a significant reduction of 59.1% in the luminance (L) was observed. This darkening has been described in similar studies of teakwood (Lopes *et al.* 2014, Méndez-Mejías and Moya 2016) and of other species (Esteves and Pereira 2009, Santos *et al.* 2014, Bonfatti Júnior and Lengowski 2018, Lengowski *et al.* 2018, Cetera *et al.* 2019). This loss of luminosity is caused by the chemical compounds resulting from the thermal degradation of hemicelluloses (Esteves and Pereira 2009). The decrease in the b* coordinate means that the heat treated wood has lower color saturation (C *) than the wood without heat treatment (Santos *et al.* 2014), and the hue angle (h *) declines since this parameter is calculated as a function of the coordinates a * and b * (ASTM 2016).

The total color change (ΔE) was 23,84, considered very appreciable according to the classification proposed by Hikita *et al.* (2001), making the wood classification change from the pink color standard to the brown color of according to the wood color groups proposed by Camargos and Gonçalez (2001). These color changes in wood are attributed to the formation of colored compounds after the chemical reactions caused by the heat treatment (Chen *et al.* 2014, Lengowski *et al.* 2018, Cetera *et al.* 2019), as well as phenols (Cetera *et al.* 2019) and quinones (Tjeerdsma *et al.* 1998). Pratiwi *et al.* (2019) emphasizes a lower photodegradation in the color stability after the heat treatment of teakwood, this improvement being justified due to the increase of the lignin content formed by condensation during the heat treatment (Ayadi *et al.* 2013).

Thermal analysis



Figure 3: Weight loos of wood.

The thermal degradation of the wood can be divided into three temperature ranges. The first region (100 °C to 200 °C) is related to loss of water and extractives, as well as changes in chemical bonds; the second region (200 °C to 400 °C), where the greatest decomposition of the macromolecular constituents of wood occurs; and the third region (>400 °C), where the complete degradation of the wood components occurs. A reduction in the initial temperature of the thermal degradation bands after the heat treatment of the wood was observed (Figure 3).

For treated teakwood, there was a lower initial weight loss (up to 200 °C). In the range of 200 °C to 300 °C, a lower weight loss was also observed for treated wood in relation to the control sample. In the range of 300 °C to 350 °C, there was greater degradation of the wood without treatment, while in the range of 350 °C to 400 °C treated wood presented the greater degradation. The lowest weight loss for the untreated sample was also observed for the other degradation bands (500 °C to 700 °C). Residual weight was high at 16,29% for the control sample and 13,08% for treated wood (Table 5).

	Mass loss (%) at different temperature ranges (°C)								Residual
Treatment	25-	100-	200-	300-	350-	400-	500-	600-	weight
	100	200	300	350	400	500	600	700	(%)
UTW	6,14	2,55	11,22	30,53	13,29	8,35	7,1	4,53	16,29
TTW	4,11	2,26	5,34	12,79	38,53	8,28	8,65	6,96	13,08

Table 5: Weight loss and residual weight of thermally treated teakwood wood.

UTM = untreated teakwood; TTU = treated teakwood.

The untreated sample had greater weight loss compared to the treated sample during the initial heating (25°C to 100 °C). This temperature range is responsible for the evaporation of bound water in the cell wall, which is why the treated wood has less weight loss, since this modification makes the material less hydrophilic, and therefore less able to retain water.

Between 100 °C to 200 °C, the temperature range where changes occur in the chemical bonds of the con-

stituents of the wood and evaporation of extractives, there was low weight loss for both samples. Silva *et al.* (2019) and Pereira *et al.* (2013) also observed a small weight loss in this temperature range when investigating wood of *Eucalyptus* spp. by thermogravimetry.

The degradation of the hemicelluloses begins at 200 °C (Sjöström 1981) and occurs up to 300°C (Poletto *et al.* 2012). Therefore, this temperature range is associated with loss of hemicelluloses and beginning of cellulose degradation. The lower weight loss for treated wood in this temperature range compared to untreated wood can be attributed to the previous degradation of the hemicelluloses and amorphous cellulose caused by the heat treatment.

In the range of 277 °C to 397 °C, multiple stages of decomposition occur, such as dehydration and the formation of volatile components of cellulose (Ming *et al.* 2005, Wang *et al.* 2007). The loss of cellulose mass occurs after the degradation of hemicellulose, since the energy required for depolymerization of the cellulose chains is higher because it is semi-crystalline (Chaouch *et al.* 2012).

In both samples, the highest degradation occurred between 300 °C to 400 °C, a range that characterizes cellulose degradation. Faster weight loss was observed between 200 °C to 350 °C for wood without heat treatment. The possible cause of this difference is the high extractives content of the studied species and partial loss of these with the heat treatment. Wood with higher extractives content had accelerated thermal degradation compared to wood with lower extractive content (Poletto *et al.* 2012), due to the volatility of these compounds (Mészáros *et al.* 2007).

In the range of 350 °C to 400 °C, larger weight loss occurred for treated wood. This can be attributed to the predominance of crystalline cellulose after thermal treatment, where amorphous regions have already been partially eliminated, since the more organized the cellulose structure is, the more thermally stable wood is (Poletto *et al.* 2012).

Although it is the most thermally stable polymer, lignin does not have a specific degradation temperature, with rupture starting at 200 °C and continuing to 900 °C (Sjöström 1981, Wang *et al.* 2007, Pereira *et al.* 2013). The thermal resistance of lignin is linked to the type of precursor, where guaiacyl lignin is the most resistant to cleavage at high temperatures (Poletto *et al.* 2012).

CONCLUSIONS

The results of this study indicate that the heat treatment caused reduction of cell wall thickness, the formation of cross-fissures and the crystallization of the wax inside the pores. The volatilization of extractives and rupture of polysaccharides occurred, in which the hemicellulose was the macromolecular chemical component most affected. The equilibrium moisture, volumetric contraction, tangential contraction, contraction anisotropy, rupture modulus and longitudinal and tangential hardness were reduced after the heat treatment. The color previously classified as pink changed to dark brown. The thermal stability of the wood was improved by the heat treatment, which resulted in different behaviors between samples. In the untreated wood, the largest weight losses occurred between 25 °C to 300 °C and 400 °C to 500 °C, while after the heat treatment, the larg-est weight losses occurred between 350 °C to 400 °C and 500 °C to 700 °C. Thermal treatment can be used in teakwood to improve physical properties and modify its colorimetric and thermal properties, adding value to this wood species.

REFERENCES

Ayadi, N.; Lejeune, F.; Charrier, F.; Charrier, B.; Merlin, A. 2013. Color stability of heat-treated wood during artificial weathering. *Holz Roh Werkst* 61(3): 221-226. https://doi.org/10.1007/s00107-003-0389-2

ASTM. 2014. Standard Test Methods for Small Clear Specimens of Timber. ASTM D-143-14. 2014. West Conshohocken, PA, USA. http://www.astm.org/cgi-bin/resolver.cgi?D143-14

ASTM. 2016. Standard practice for calculation of color tolerances and color differences from instrumentally measured color coordinates. ASTM D-2244-16.2016. West Conshohocken, PA, USA. http://www.astm.org/cgi-bin/resolver.cgi?D2244-16

ASTM. 2017. Standard Test Methods for Density and Specific Gravity (Relative Density) of Wood and Wood-Based Materials. ASTM D-2395-17. 2017. West Conshohocken, PA, USA. http://www.astm.org/cgi-bin/resolver.cgi?D2395-17

Bonfatti Júnior, E.A.; Lengowski, E.C. 2018. Colorimetry applied to wood science and technology. *Pesquisa Florestal Brasileira* 38: 1-13. e201601394. https://doi.org/10.4336/2018.pfb.38e201601394

Bhuiyan, T.; Hirai, N. 2005. Study of crystalline behavior of heat-treated wood cellulose during treatments in water. *J Wood Sci* 51(1): 42-47. https://doi.org/10.1007/s10086-003-0615-x

Bonduelle, G.M.; Iwakiri, S.; Trianoski, R.; Prata, J.G.; Rocha, V.Y. 2015. Analysis of wood density and shrinkage of *Tectona grandis* wood in axial and radial direction of the tree trunk. *Floresta* 45(4): 671-680. http://dx.doi.org/10.5380/rf.v45i4.31991

Boonstra, M.J.; Van Acker, J.; Tjeerdsma, B.F.; Kegel, E.V. 2007. Strength properties of thermally modified softwoods and its relation to polymeric structural wood constituents. *Ann For Sci* 64(7): 679-690. https://doi.org/10.1051/forest:2007048

Boonstra, M.J.; Tjeerdsma, B. 2006. Chemical analysis of heat-treated softwoods. *Holz Roh Werkst* 64: 204-211. https://doi.org/10.1007/s00107-005-0078-4

Boonstra, M.J.; Rijsdijk, J.F.; Sander, C.; Kegel, E.V.; Tjeerdsma, B.; Militz, H.; Acker, J.V.; Stevens, M. 2006a. Microstructural and Physical aspects of heat-treated wood. Part 1. Softwoods. *Maderas-Cienc Tecnol* 8(3): 193-208.

Boonstra, M.J.; Rijsdijk, J.F.; Sander, C.; Kegel, E.V.; Tjeerdsma, B.; Militz, H.; Acker, J.V.; Stevens, M. 2006b Microstructural and physical aspects of heat treated wood. Part 2. Hardwoods. *Maderas-Cienc Tecnol* 8(3): 209-217. https://doi.org/10.4067/S0718-221X2006000300007

Camargos, J.A.A.; Gonçalez, J.C. 2001. A colorimetria aplicada como instrumento na elaboração de uma tabela de cores de madeira. *Brasil Florestal* 71: 30-41. https://core.ac.uk/download/pdf/33542076.pdf

Čekovská, H.; Gaff, M.; Makovická Osvaldová, L.M.; Kačík, F.; Kaplan, L.; Kubš, J. 2017. *Tectona-grandis* Linn. and its fire characteristics affected by its thermal modification of wood. *BioResources* 12(2): 2805-2817.https://bioresources.cnr.ncsu.edu/resources/tectona-grandis-linn-and-its-fire-characteristics-affect-ed-by-its-thermal-modification-of-wood/

Cetera, P.; Russo, D.; Milella, L.; Todaro, L. 2019. Thermo-treatment affects *Quercuscerris* L. wood properties and the antioxidant activity and chemical composition of its by-product extracts. *Ind Crops Prod* 130: 380-388. https://doi.org/10.1016/j.indcrop.2018.12.099

Chagas, S.F.; Evangelista, W.V.; Silva, J.C.; Macedo, A.M.; Carvalho, L. 2014. Properties of teakwood of different ages coming from thinning. *Brazilian Journal of Wood Science* 5(2): 138-150. http://dx.doi.org/10.12953/2177-6830.v05n02a08

Chaouch, M.; Dumarçay, S.; Pétrissans, A.; Pétrissans, M.; Gérardin, P. 2012. Effect of heat treatment intensity on some conferred properties of different European softwood and hardwood species. *Wood Sci Technol* 47(4): 663-673. https://doi.org/10.1007/s00226-013-0533-z

Chen, Y.; Tshabalala, M.A.; Gao, J.; Stark, N.M.; Fan, Y. 2014. Color and surface chemistry changes of extracted wood flour after heating at 120 °C. *Wood Sci Technol* 48 (1): 137-150. https://doi.org/10.1007/s00226-013-0582-3

Derkyi, N.S.A.; Bailleres, H.; Chaix, G.; Thevenon, M.F.; Oteng-Amoako, A.A.; Adu-Bredu, S. 2009. Colour variation in teak (*Tectona grandis*) wood from plantations across the ecological zones of Ghana. *Ghana Journal of Forestry* 25: 40-48. https://doi.org/10.4314/gjf.v25i1.60698 Dias, A.C.C.; Marchesan, R.; Almeida, V.C.; Monteiro, T.C.; Moraes, C.B. 2018. Relationship between basic density and shrinkage in teca wood. *Braz J Wood Sci* 9(1): 37-44. http://dx.doi.org/10.12953/2177-6830/rcm.v9n1p37-44

Durlo, M.A.; Marchiori, J.N.C. 1992. Wood technology: retractability. Série Técnica, 10. CEPEF: Santa Maria, Brazil

Esteves, B.M.; Graça, J.; Pereira, H.M. 2008. Extractive composition and summative chemical analysis of thermally treated eucalypt wood. *Holzforschung* 62(3): 344-351. https://doi.org/10.1515/HF.2008.057

Esteves, B.M.; Pereira, H.M. 2009. Wood modification by heat treatment: A Review. *BioResources* 4(1): 370-404. https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_04_1_%23%23%23%23_Esteves P_Wood_Mod_Heat_Treatment

FAMATO. 2013. Diagnosis of Planted Forests in the State of Mato Grosso. IMEA: Brazil.

Fengel, D. 1966. On the changes of the wood and its components within the temperature range up to 200°C - Part 2. *Holz Roh Werkst* 24:98-109.

Gonçalvez, M.P.M.; Coffler, R.; Carvalho, A.M.; Garcia, R.A. 2007. Radial variation of basic density and fiber length of the wood of *Tectona grandis* L. *Floram* 14(1): 70-75. https://www.floram.org/article/588e2217e710ab87018b464c

Grinins, J.; Irbe, I.; Andersons, B.; Andersone, I.; Meija A.; Janberga, A.; Pavlovics, G.; Sansonetti, E. 2016. Thermo-hydro treated (THT) birch plywood with improved service properties. *International Wood Products Journal* 7(4): 181-187. https://doi.org/10.1080/20426445.2016.1212963

Gunduz, G.; Aydemir, D.; Karakas, G. 2009. The effects of thermal treatment on the mechanical properties of wild Pear (*Pyrus elaeagnifolia* Pall.) wood and changes in physical properties. *Mater Des* 30(10): 4391-4395.https://doi.org/10.1016/j.matdes.2009.04.005

Hamada, J.; Pétrissans, A.; Mothe, F.; Ruelle, J.; Pétrissans, M.; Gérardin, P. 2017. Intraspecific variation of european oak wood thermal stability according to radial position. *Wood Sci Technol* 51(4): 785-794. https://doi.org/10.1007/s00226-017-0910-0

Hill, C. 2006. *Wood Modification: Chemical, Thermal and Other Processes*. Wiley: New York, NY, USA. https://doi.org/10.1002/0470021748

Hikita, Y.; Toyoda, T.; Azuma, M. 2001. Weathering testing of timber - discoloration. In *High performance utilization of wood for outdoor uses: report on research project*. Grant-in-Aid for Scientific Research. Inamura, Y (Ed.), Press-Net: Kyoto, Japan. p. 27-32.

IBÁ. 2019. Report 2019. IBÁ: Sao Paulo, Brazil. https://iba.org/datafiles/publicacoes/relatorios/iba-relatorioanual2019.pdf

Kokutse, A.D.; Bailleres, H.; Stokes, A.; Kokou, K. 2004. Proportion and quality of heartwood in togolese teak (*Tectona grandis* L.f.). *Forest Ecol Manag* 189(1-2): 37-48. https://doi.org/10.1016/j.foreco.2003.07.041

Kokutse, A.D.; Stokes, A.; Baillères, H.; Kokou, K.; Baudasse, C. 2006. Decay resistance of Togolese teak (*Tectona grandis* L. f) heartwood and relationship with colour. *Trees* 20(3): 219-223. https://doi.org/10.1007/s00468-005-0028-0

Korkut, S. 2008. The effects of heat treatment on some technological properties in Uludag fir (*Abies born-muellerinana* Mattf.) wood. *Build Environ* 43(4): 422-428. https://doi.org/10.1016/j.buildenv.2007.01.004

Lemos, J.A.S.; Mendes, M.C.S.; Madi, J.P.S.; Pereira, B.L.C.; Oliveira, A.C. 2019. Influence of the propagation method on the production and quality of *Tectona grandis* wood. *Advances in Forestry Science* 6(3): 761-765. http://dx.doi.org/10.34062/afs.v6i3.8183

Lengowski, E.C.; Muniz, G.I.B.; Klock, U.; Nisgoski, S. 2018. Potential use of NIR and visible spectroscopy to analyze chemical properties of thermally treated wood. *Maderas-Cienc Tecnol* 20(4): 627-640.

http://dx.doi.org/10.4067/S0718-221X2018005041001

Lengowski, E.C.; Muniz, G.I.B.; Nisgoski, S.; Magalhães, W.L.E. 2013. Cellulose acquirement evaluation methods with diferente degrees of crystallinity. *Sci For* 41(98): 185-194. https://www.ipef.br/publicacoes/ scientia/nr98/cap04.pdf

Lima, I.L.; Florsheim, S.M.B.; Longui, E.L. 2009. Influence of spacing on some physical properties of *Tectona grandis* Linn. f. *Cerne* 15(2): 244-250. http://cerne.ufla.br/site/index.php/CERNE/article/view/209

Lopes, J.O.; Garcia, R.A.; Nascimento, A.M.; Latorraca, J.V.F. 2014. Physical properties of heat-treated teak wood. *Floram* 21(4): 569-577. http://dx.doi.org/10.1590/2179-8087.040213

Méndez-Mejías, L.D.; Moya, R. 2016. Effects on density, shrinking, color changing and chemical surface analysis through FTIR of *Tectona grandis* thermo-treated. *Sci For* 44(122): 811- 820. http://dx.doi.org/10.18671/scifor.v44n112.03

Mészáros, E.; Jakab, E.; Várhegyi, G. 2007. TG/MS, PyGC/MS and THM-GC/MS study of the composition and thermal behavior of extractive components of *Robinia pseudoacacia*. *J Anal Appl Pyrol* 79(1-2): 61-70. https://doi.org/10.1016/j.jaap.2006.12.007

Ming, G.; Biaocan, L.; Shou Sheng, Y.; Min, Z. 2005. Flame retardance of wood treated with guanidine compounds characterized by thermal degradation behavior. *J Anal Appl Pyrol* 73(1): 151-156. https://doi.org/10.1016/j.jaap.2005.01.006

Modes, K.S.; Santini, E.J.; Vivian, M.A.; Haselein, C.R. 2017. Effect of heat treatment on mechanical properties of *Pinus taeda* and *Eucalyptus grandis* woods. *Cienc Florest* 27(1): 291-302. https://doi.org/10.5902/1980509826467

Mononen, K.; Alvila, L.; Pakkanen, T. 2002. CIELab measurements to determine the role of felling season, log storage and kiln drying on coloration of silver Birch wood. *Scandinavian Journal Forest Research* 17(2): 179-191. https://doi.org/10.1080/028275802753626827

Motta, J.P.; Alves, R.C.; Paes, J.B. 2010. Effect of heat treatment on the static flexural strength of wood *Tectona grandis* L.f. In II Simpósio de Ciência e Tecnologia da Madeira do Rio de Janeiro. Rio de Janeiro, Brazil.

Moya, R.; Berrocal, A.; Serrano, JR.; Tomazello, M. 2009. Variación radial de la anatomía, densidad y durabilidad de la Madera de teca (*Tectona grandis*) procedente de dos calidades de sitio y dos regiones climáticas de Costa Rica. *Inv Agrar-Sist Rec F* 18(2): 119-131

Niamké, F.B.; Amusant, N.; Charpentier, JP.; Chaix, G.; Baissac, Y.; Boutahar, N.; JayAllmand, C. 2011. Relationships between biochemical attributes (non-structural carbohydrates and phenolics) and natural durability against fungi in dry teakwood (*Tectona grandis* L. f.). *Ann Forest Sci* 68(1): 201-211. https://doi.org/10.1007/s13595-011-0021-2

Niamké, F.B.; Amusant, N.; Kadio, A.A.; Thevenon, MF.; Nourissier, S.; Adima, A.A.; Chaixh, G. 2014. Rapid prediction of phenolic compounds as chemical markers for the natural durability of teak (*Tectona grandis* Linn f.) heartwood by near infrared spectroscopy. *J Near Infrared Spec* 22(1): 35-43. https://doi.org/10.1255/jnirs.1091

Nocetti, M.; Rozenberg, P.; Chaix, G.; Macchioni, N. 2011. Provenance effect on the ring structure of teak (*Tectona grandis* L. f.) wood by X-ray microdensitometry. *Ann Forest Sci* 68(8): 1375-1383. https://doi.org/10.1007/s13595-011-0145-4

Nuopponen, M.; Vuorinen, T.; Jamsä, S.; Viitaniemi, P. 2005. Thermal modifications in softwood studied by FT-IR and UV resonance Raman spectroscopies. *J Wood Chem Technol* 24(1): 13-26. https://doi.org/10.1081/WCT-120035941

Ozsahin, S.; Murat, M. 2017. Prediction of equilibrium moisture content and

specific gravity of heat treated wood by artificial neural networks. *Eur J Wood Wood Prod* 76(2): 563-572. https://doi.org/10.1007/s00107-017-1219-2

Pereira, B.L.C.; Carneiro, A.C.O.; Carvalho, A.M.M.L.; Trugilho, P.F.; Melo, I.C.N.A.; Oliveira, A.C. 2013. Study of thermal degradation of *Eucalyptus* wood by thermogravimetry and calorimetry. *Rev* Árvore 37(3): 567-576. https://doi.org/10.1590/S0100-67622013000300020

Poletto, M.; Zattera, A.J.; Santana, R.M.C. 2012. Thermal decomposition of wood: kinetics and degradation mechanisms. *Bioresour Technol* 126: 7-12. https://doi.org/10.1016/j.biortech.2012.08.133

Poncsák, S.; Kocaefe, D.; Bouazara, M.; Pichette, A. 2006. Effect of high temperature treatment on the mechanical properties of birch (*Betula papyrifera*). *Wood Sci Technol* 40(8): 647-663. https://doi.org/10.1007/s00226-006-0082-9

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-Cienc Tecnol* 21(2):209-222. http://dx.doi.org/10.4067/S0718-221X2019005000208

Repellin, V.; Guyonnet, R. 2005. Evaluation of heat-treated wood swelling by differential scanning calorimetry in relation to chemical composition. *Holzforschung* 59(1): 28-34. https://doi.org/10.1515/HF.2005.005

Santos, D.V.B.; Moura, L.F.; Brito, J.O. 2014. Effect of heat treatment on color, weight loss, specific gravity and equilibrium moisture content of two low market valued tropical woods. *Wood Res* 59(2): 253-264.

Shi, J.; Lu, Y.; Zhang, Y.; Cai, L.; Shi, S. 2018. Effect of thermal treatment with water, H₂SO₄ and NaOH aqueous solution on color, cell wall and chemical structure of poplar wood. *Sci Rep* 8(1): 17735. https://doi.org/10.1038/s41598-018-36086-9

Silva, E.J.; Cremonez, V.G.; Nisgoski, S. 2019. Color change and thermogravimetric analysis of thermally treated *Eucalyptus grandis* wood. *Brazilian Journal of Wood Science* 10(1): 39-47. https://doi. org/10.12953/2177-6830/rcm.v10n1p39-47

Sjöström, E. 1981. Wood Chemistry fundamentals and applications. Academic Press: New York, NY, USA.

TAPPI. 2014. Sampling and preparing wood for analysis. TAPPI T 257 sp-14. 2014. Atlanta, GA, USA: TAPPI Press. https://www.tappi.org/content/sarg/t257.pdf

TAPPI. 2015. Acid-insoluble lignin in wood and pulp. TAPPI T 222 om-15. 2015. Atlanta, GA, USA: TAPPI Press. https://www.tappi.org/content/SARG/T222.pdf

TAPPI. 2017. Solvent extractives of wood and pulp. TAPPI T 204 cm-17. 2017. Atlanta, GA, USA: TAPPI Press.

Tjeerdsma, B.; Boonstra, M.; Pizzi, A.; Tekely, P.; Militz, H. 1998. Characterization of thermally modified wood: molecular reasons for wood performance improvement. *Holz Roh Werkst* 56: 149-153 https://doi.org/10.1007/s001070050287

Tjeerdsma, B.; Militz, H. 2005. Chemical changes in hydroheat wood: FTIR analysis of combined hydroheat and dry heat-treated wood. *Holz Roh Werkst* 63(2): 102-111. http://dx.doi.org/10.4067/S0718-221X2013005000020

Unsal, O.; Korkut, S.; Atik, C. 2003. The effect of heat treatment on some properties and colour in eucalyptus (*Eucalyptus camaldulensis* Dehn.) wood. *Maderas-Cienc Tecnol* 5(2): 145-152. http://dx.doi.org/10.4067/S0718-221X2003000200006

Wang, S.; Liu, Q.; Luo, Z.; Wen, L.; Cen, K. 2007. Mechanism study on cellulose pyrolysis using thermogravimetric analysis coupled with infrared spectroscopy. *Frontiers of Energy and Power Engineering*

in China 4(1): 413-419. https://doi.org/10.1007/s11708-007-0060-8

Weiland, J.; Guyonnet, R. 2003. Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy. *Holz Roh Werkst* 61(3): 216-220. https://doi.org/10.1007/s00107-003-0364-y

Wheeler, E.; Baas, P.; Gasson, P. 1989. IAWA list of microscopic features for hardwood identification. *IAWA Bulletin* 10(3): 219-332. https://doi.org/10.1002/fedr.19901011106

Wikberg, H.; Maunu, S.L. 2004. Characterization of thermally modified hard and softwoods by ¹³C CP-MAS NMR. *Carbohydr Polym* 4(7): 461-466. https://doi.org/10.1016/j.carbpol.2004.08.008

Yildiz, U.C.; Yildiz, S.; Gezer, E.D. 2005. Mechanical and chemical behavior of beech wood modified by heat. *Wood Fiber Sci* 37(3): 456-461. https://wfs.swst.org/index.php/wfs/article/view/2034