INFRARED SPECTROSCOPY OF THE SURFACE OF THERMALLY-MODIFIED TEAK JUVENILE WOOD

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ABSTRACT

During the thermal modification of the wood there is a decreasing gradient of temperature from the surface to its interior, therefore, the most severe chemical modifications occur on the surface. These chemical modifications directly affect the quality and durability of adhesives and coating. Therefore, this study investigated the chemical modification of the surface of thermally-modified teak juvenile wood. Heartwood and sapwood samples were treated at 180 and 200ºC. Chemical analyses were performed by Fourier transform infrared spectroscopy (FTIR) in reflectance mode with a microscope. Spectra showed an increase in cellulose crystallinity and a decrease in relative contents of hydroxyl groups, lignin and extractives – especially quinones, waxes and oils – following thermal modification. Extractive content of the heartwood was relatively higher than that of sapwood. Heartwood was more susceptible to thermal degradation than sapwood.

Keywords: Cellulose crystallinity, chemical modification, heat treatment, quinone derivatives, *Tectona grandis*.

INTRODUCTION

Thermal modification provides desirable properties to wood such as increased resistance to fungal degradation (Weiland and Guyonnet 2003), greater dimensional stability (Syrjäne 2001) and change on the original colour (Lopes *et al*. 2014). It is an alternative method to the use of chemical preservatives in which wood is heated to temperatures ranging from 160 to 250ºC, usually near to 200ºC, for variable processing time depending on the intrinsic characteristics of the wood species and the desired properties for the final product. Although the treatment causes physical and chemical modifications in the cellular structure of the wood, the chemical modifications are the most important because of their impact to the properties of the thermally-modified material. For example, on thermally-modified wood occurs conversion of hydroxyl (OH) groups in cross-ether bonds between the polymers of the cell wall; extractive volatilization and migration to the surfaces (Christiansen 1994); reaction of depolymerization of hemicelluloses; degradation of the amorphous region of cellulose; increasing in cellulose crystallinity with a decrease of the free OH groups (Boonstra and Tjeerdsma 2006); and condensation and crosslinking between lignin and the products resulting from thermal degradation (Tjeerdsma and Militz 2005) which reduce the hygroscopicity. Hence, during thermal modification of wood are initiated various hydrolysis, oxidation and mass transfer reactions resulting in a modified structure (Popescu and Popescu 2013). The reduction in free OH groups has a positive impact on the

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wood resistance to water penetration, resulting in a more hydrophobic and dimensionally stable material (Weiland and Guyonnet 2003, Rousset *et al*. 2004, Wikberg and Maunu 2004). Thermal modification can also degrade the anatomical structure of wood (Awoyemi and Jones 2011) and increase its porosity (Nunes *et al*. 2016). Awoyemi and Jones (2011) observed a degradation in the bordered pits of the tracheids of *Thuja plicata* wood following thermal modification. Nunes *et al*. (2016) observed a higher adhesive penetration in the thermally-modified *Eucallyptus pellita* and *Corymbia citriodora* woods compared to unmodified wood due to increased porosity. All these modifications can also affect the quality and durability of adhesives and coatings applied to wood surfaces.

The teak wood has a high commercial value due to the excellent physical and mechanical properties. However, teak wood from Brazilian plantations has peculiar characteristics such as high proportion of juvenile wood (short cutting cycle - 25 years) (Shimizu *et al*. *2*007) and higher proportion of sapwood, which has physical, chemical and aesthetic characteristics (color and design) different from those of heartwood. The composition and content of extractives are different between heartwood and sapwood. In teak wood are found various quinone derivatives, some present in heartwood and sapwood such as 2-hydroxymethyl; and other exclusively in heartwood such as anthraquinone, 1,4-naphthoquinone, anthraquinone-2-carboxylic acid and lapachol (Niamké *et al*. 2011). Teak sapwood has high concentration of starch, sucrose, glucose and fructose and low concentrations of H1 (hydroxycinnamic acid derivative) and tectoquinone (Niamké *et al*. 2011). The largest natural durability of the heartwood compared to that of sapwood could be explained by the higher concentration of 2-hydroxymethyl anthraquinone, tectoquinone (Moreira *et al*. 2006, Niamké *et al*. 2011, Nidavani and Mahalaksmi 2014) and lapachol (Nidavani and Mahalaksmi 2014), which have phenolic nature. The lapachol is one of the most studied naphthoquinones in the fields of chemistry and pharmacology due to its therapeutic applications such as anti-inflammatory, antimalarial, antiseptic, antitumor, antiviral, antibactericidal and fungicidal (Hussain *et al*. 2007). The teak wood also presents caoutchouc in the cell wall and lumen, which are responsible for the hydrophobicity and antioxidant properties of the wood (Yamamoto *et al*. 1998). Heartwood contains higher caoutchouc concentration than sapwood, giving it lower permeability (Yamamoto *et al*. 1998). The amount of extractives also depends of the tree age. Haupt *et al.* (2003) found higher extractives amount in teak heartwood from fast-grown plantation trees (29 years-old) than from natural stands (100 years-old).

Thermal modification could provide greater durability and dimensional stability to the teak sapwood besides standardizes the color of wood pieces containing heartwood and sapwood (Lopes *et al*. 2014). The chemical modifications of lignocellulosic materials following thermal modification have been evaluated by several spectroscopic methods among them the Fourier transformed infrared (FTIR) spectroscopy stands out for providing quickly and effectively information on the composition of the functional groups (Li *et al*. 2015). However, the FTIR analysis of thermally-modified wood are usually held for sapwood (Fabiyi and Ogunleye 2015), whose composition is less complex than heartwood. Furthermore, several studies evaluate the chemical modification of thermally-modified wood by FTIR spectroscopy (Li *et al*. 2015) potassium bromide pellet (KBr) method, which does not allow assessing the condition of the wood surface. During the thermal modification have a decreasing gradient of temperature from surfaces to the interior of the wood, therefore the surface modifications are more severe than the inner part, emphasizing the importance of evaluating the surface condition using FTIR spectroscopy in the reflectance mode. In this context, this study investigated the chemical modification of the surface of teak juvenile wood following thermal modification by FTIR spectroscopy in the reflectance mode using a microscope.

MATERIAL AND METHODS

Material and thermal modification

Teak (*Tectona grandis* L. f.) wood samples with nominal dimensions of 150 mm x 75 mm x 20 mm were obtained from six trees of 12 years old. The material was separated in heartwood and sapwood, air dried and conditioned at 20°C and 65% relative humidity (RH) in a climate chamber until constant weight.

The thermal modification was carried out in an electric laboratorial muffle furnace from Linn Elektro Therm, with dimensions of 600 mm x 600 mm x 700 mm equipped with a system of temperature and time control. The treatment was conducted in four steps at two different temperatures: 180 and 200ºC. The four steps were: (1) heating up to 100ºC for 2 h; (2) increase of temperature from 100ºC to final temperature (180 or 200ºC) for 30 min; (3) treatment time in the selected temperature for 2 h and 30 min; and (4) cooling for approximately 1 h. The initial moisture content of the samples was approximately 8-10% (based on the oven-dry of the wood). After thermal modification, samples were conditioned at 20ºC and 65% RH until constant weight.
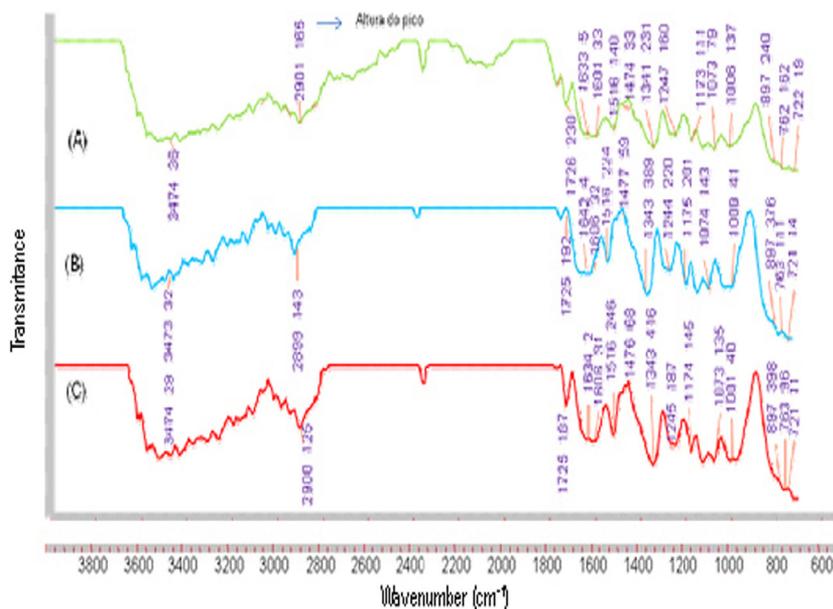
FTIR spectroscopy

The chemical structure of the surfaces of unmodified and thermally-modified heartwood and sapwood was analyzed by FTIR spectroscopy in the reflectance mode using a microscope coupled to a VARIAN 640-IR spectrometer. Infrared measurements were performed at a resolution of 4 cm^{-1}, 128 scans and spectral range between 4000-400 cm^{-1}. The FTIR spectra were obtained from the wood surfaces without prior preparation, baseline-corrected and normalized afterwards.

RESULTS AND DISCUSSION

The FTIR spectra of the surface of unmodified and thermally-modified heartwood and sapwood are shown in Figure 1 and Figure 2. Table 1 summarizes the FTIR band assignments of the unmodified and thermally-modified heartwood and sapwood. The effect of thermal modification on teak heartwood and sapwood surfaces was evaluated by the peaks corresponding to the lignin, polysaccharides (cellulose and hemicelluloses) and extractives, specifically quinones and oils.
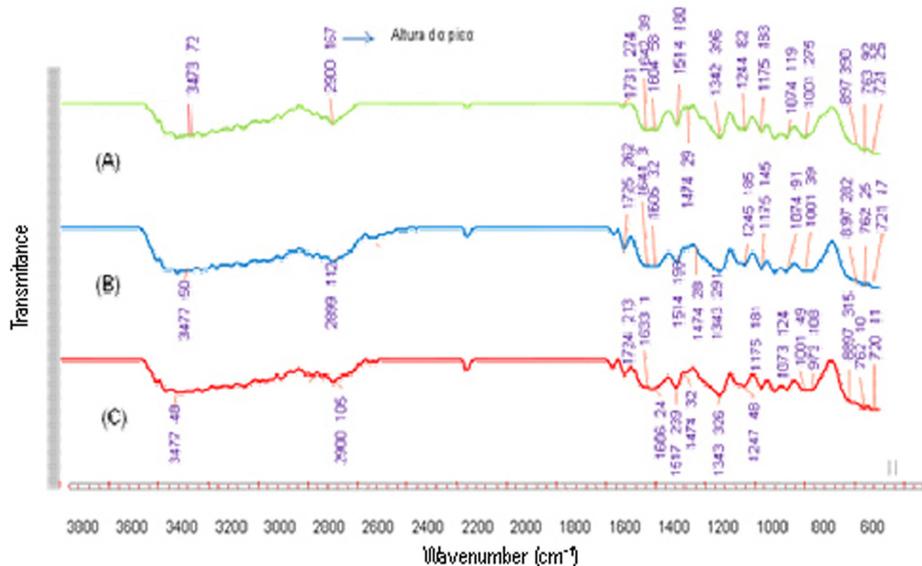
Figure 1. FTIR spectra of teak heartwood. A: unmodified wood. B and C: thermally-modified woods at 180 and 200ºC, respectively.

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Figure 2. FTIR spectra of teak sapwood. A: unmodified wood. B and C: thermally-modified woods at 180 and 200ºC, respectively.

Table 1. Summary of FTIR spectroscopy band assignments of unmodified and thermally-modified teak heartwood and sapwood.

Wavenumber (cm^{-1})	Band assignment	Polymer
≈ 3470	O-H stretching	Polymers[1]
≈ 2900, ≈ 2943	CH-sp^3 stretching	Polymers[2]
≈ 1725	C=O stretching of carbonyl, carboxyl and acetyl groups; and of xylans	Oils[3]; cellulose and hemicelluloses[4-5]
≈ 1640	Conjugation of C=O with two aromatic rings	Quinones[3]
≈ 1514	Aromatic skeletal vibration (C=C) of lignin, guaiacyl> syringyl	Lignin[1]
≈ 1474	C-H deformation in lignin and carbohydrates; CH$_2$ symmetric angular deformation and CH$_3$ angular asymmetric angular deformation	Lignin[1]; Oils and waxes[3]
≈ 1342	C-H$_2$ deformation vibration; CH$_3$ symmetric deformation	Cellulose and hemicelluloses[1]; oils[3]
≈ 1245	C-C, C-O and C=O stretching; G condensed > G etherified; C-O stretching	Lignin[1]; oils[3]
≈ 1175	C-O-C stretching; C-O stretching	Cellulose and hemicelluloses[6]; oils[3]
≈ 1074	C-O stretching of secondary alcohol; C-O stretching of the ester methoxyl group and B-O-4 links in lignin	Cellulose and hemicelluloses[1]; lignin[7]
≈ 1000	C-O stretching of primary alcohol	Cellulose and hemicelluloses[1]
≈ 720, ≈ 760	(CH$_2$)n out-of-plane angular deformation, n>4	Oils and waxes[3]

[1] Faix (1992). [2] Faix (1991). [3] Barbosa (2007). [4] Fengel and Ludwig (1991). [5] Lionetto *et al*. (2012). [6] Pandey (1999). [7] González-Pena and Hale (2011).

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The peak intensities (height) at 3470 cm^{-1} assigned to the OH groups decreased significantly to thermally-modified heartwood and sapwood (Figures 1 and 2). The heartwood and sapwood treated at 180ºC had a decrease in the order of 31% and 11%, respectively, whereas for the treatment at 200ºC was around 33% and 19%. Thus, the OH group decrease was more pronounced to heartwood in both temperatures. These decrease of the OH groups could be explained by its thermal degradation but also by different amount of water contained unmodified and thermally-modified heartwood and sapwood. The thermally-modified woods have lower equilibrium moisture content (EMC) compared to unmodified woods therefore a smaller amount of water while heartwood has a lower EMC than sapwood (Lopes 2018).

The hemicelluloses are largely responsible for moisture absorption, but the accessible cellulose, nanocrystalline cellulose, lignin and crystalline cellulose also play an important role (Mohanty *et al*. 2000). Therefore, the relative contents of the cellulose crystallinity, amorphous region of cellulose and lignin were calculated (Table 2). The relative cellulose crystallinity was estimated by the ratio between 1474 cm^{-1} and 897 cm^{-1} peak intensities assigned to the C-H in lignin and C-H$_1$ deformation of cellulose glucose ring, respectively; and 1342 cm^{-1} and 2900 cm^{-1} peaks intensities assigned to C=O stretching in carbonyls and CH-sp^3 stretching (Ates *et al*. 2009, Tuong and Li 2010). For the amorphous region of cellulose was used the 2900 cm^{-1} and 1074 cm^{-1} peak intensities assigned to the CH-sp^3 and C-O stretching of secondary alcohol, respectively; and 2900 cm^{-1} and 3474 cm^{-1} peak intensities assigned to the CH-sp^3 and O-H stretching (Fackler *et al*. 2011, Temiz *et al*. 2006).

Table 2. Relative values of cellulose crystallinity and amorphous regions, and lignin of unmodified and thermally-modified teak heartwood and sapwood.

Wood	Temperature (ºC)	Cellulose crystallinity		Amorphous region of cellulose		Lignin
		C-H/CH$_2$	CH$_2$/C-H	C-H/C-O-C	C-H/O-H	
		1474/897	1342/2900	2900/1074	2900/3474	1514/897
Heartwood	control	0,074	2,33	1,40	2,31	0,46
	180	0,099	2,51	1,23	2,24	0,67
	200	0,1	3,00	0,84	2,18	0,75
Sapwood	control	0,13	2,78	1,98	4,58	0,58
	180	0,15	2,79	0,98	4,46	0,59
	200	0,17	3,32	0,92	4,31	0,61

The relative content of cellulose crystallinity of thermally-modified wood increased in comparison to unmodified wood (Table 2) which agrees with the results of other authors (Tuong and Li 2010). The cellulose crystallinity of thermally-modified heartwood increased 20.4% and 31.5% whereas in thermally-modified sapwood increased 7.65% and 9.65% for 180ºC and 200ºC, respectively (Table 2). Therefore, the increase in crystallinity cellulose was more important to the highest temperature (200ºC) and to heartwood. This increasing in cellulose crystallinity following thermal modification has been reported by various authors for different wood species. Bhuyian *et al*. (2000) studied the effect of the thermal modification on the cellulose crystallites of different wood species and pure cellulose under oven-dried and high moisture conditions by X-ray diffractometer and observed a rearrangement of the cellulose molecules in the amorphous regions leading to crystallization. The cellulose crystallinity was almost twice higher in moisture condition than oven-dried condition to wood; but pure cellulose had almost the same crystallization under both conditions. Thus, according to these authors, other components of cell wall such as xylose and mannose not degraded during thermal modification are involved in the crystallinity increase. Li *et al*. (2015) studied the steam-heat treated teak wood by FTIR and second derivative IR (SD-IR) spectroscopy and observed an increase in the stretching vibration of glucose ring, probably due to cleavage and dehydration of amorphous carbohydrates and/or crystallization of the paracrystalline region of cellulose, which may cause the increase of the proportion of crystalline cellulose.

The degradation of hemicelluloses and amorphous region following thermal modification contributes to an increase in the proportion of crystalline cellulose of wood (Hill 2006). Besides the degradation of OH groups, the increased cellulose crystallinity also could contribute to higher hydrophobicity of the thermally-modified wood. Tjeerdsma *et al*. (1998) found a reduction on water adsorption of thermally-modified wood and they attributed it to the increase in the relative proportion of cellulose crystallinity. Tsuchikawa and Siesler (2003) showed that solvent penetration in the amorphous region is faster than in crystalline regions.

The relative lignin content was calculated by the ratio between 1514 cm^{-1} and 897 cm^{-1} peak intensities assigned to aromatic ring vibration in lignin and C-H$_1$ deformation of cellulose glucose ring. A relative increase in lignin content was observed after thermal modification to both heartwood and sapwood (Table 2). These results agree with those of other authors (Poubel *et al*. 2013, de Moura *et al*. 2012, Batista *et al.* 2016, Yalcin and Sahin 2015). Thermally-modified heartwood had an increase of 45% and 63% in relative lignin content for 180ºC and 200ºC, respectively, whereas in thermally-modified sapwood, they increased approximately 1.7% and 5.1%. These results show that heartwood is more susceptible to degradation by heat than sapwood. According to Li *et al*. (2015), during thermal modification, some reactions such as condensation and degradation reactions in lignin as well as depolymerization reactions of carbohydrates can occur under catalysis of released acetic acid. These authors observed an increase at 1328 cm^{-1} peak intensity assigned to C$_1$-H vibration in cellulose and C$_1$-O vibration in syringyl derivatives-condensed structures in lignin, suggesting the condensation reactions in lignin structure of teak wood.

Teak heartwood has high natural durability due to tectoquinone, a bioactive compound against brown-rot fungi (Haupt *et al.* 2003); and high dimensional stability due to the waxes and oils formed and deposited in cell which are responsible by weak water absorption. Therefore, to evaluate the compounds modification following thermal modification, the extractive, quinone and oil contents of unmodified and thermally-modified heartwood/sapwood were determined (Table 3). The relative amount of extractives, quinones and oils were estimated by the ratio between their respectively peak intensity and the 1514 cm^{-1} wavenumber assigned to the aromatic skeletal vibration (C=C) in lignin (Sarkanen *et al*. 1967a, Sarkanen *et al*. 1967b, Sun *et al*. 2011, Gonçalves and Schuchardt 1999) which was chosen as reference due to relative constant intensity (Faix 1992).

Table 3. Relative contents of extractives, quinones and oils of the unmodified and thermally-modified teak heartwood and sapwood.

Wood	Temperature (ºC)	Extractives	Quinones	Oils	Oils and waxes
		1600/1514	1640/1514	1725/1514	722/1514
Heartwood	control	0,32	0,21	1,52	0,13
	180	0,16	0,015	1,37	0,089
	200	0,10	0,004	0,89	0,046
Sapwood	control	0,13	0,020	0,95	0,07
	180	0,08	0,010	0,51	0,03
	200	0,07	0,005	0,46	0,02

The relative amount of extractives in unmodified heartwood was 60% higher than those of unmodified sapwood. After heating at 180ºC and 200ºC, the relative amount of extractive shut down 50% and 31% in heartwood and 61.5% and 53.8% in sapwood, respectively. The quinone was more abundant in unmodified heartwood with a relative amount of 21%, whereas unmodified sapwood had 2%. The peak intensity at 1640 cm^{-1} assigned to conjugation of C=O in quinones decreased with the temperature increase. A decrease was also observed on the peak intensity at 1600 cm^{-1} assigned to C=C stretching of aromatic rings, signal used to evaluate the peak intensity of wood extractives. The

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peak intensities at 1730 cm^{-1} are assigned to C=O stretching in oils and at 720 cm^{-1} and 760 cm^{-1} to CH$_2$ deformation in oils and waxes. These peak intensities were higher in heartwood and decreased following thermal modification.

CONCLUSIONS

This study permitted to observe the chemical modifications of the surfaces of thermally-modified teak heartwood and sapwood by FTIR spectroscopy. The thermal modification causes a relative increase in the degree of cellulose crystallinity and consequent reduction of the amorphous region of cellulose; and also a relative increase in the lignin content.

The extractive content of the heartwood is higher than that of sapwood. The treatment reduced the quinone content, oils and waxes in the wood and this was enhanced with increasing temperature.

Heartwood surface is more susceptible to degradation by heat than that of sapwood.

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