

COLOR CHANGES OF WOOD FROM *Pinus taeda* AND *Schizolobium parahybum* TREATED BY *in situ* POLYMERIZATION OF METHYL METHACRYLATE USING CROSS-LINKERS

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ABSTRACT

The aim of this study was to evaluate the colorimetric properties of *Pinus taeda* and *Schizolobium parahybum* woods treated by *in situ* polymerization. The wood samples were impregnated in a vacuum/pressure system and polymerized in an oven at 90°C for 10h, using benzoyl peroxide at 1,5wt% as the catalyst. The treatments were characterized using attenuated total reflectance infrared (ATR-IR) spectroscopy and weight percentage gain (WPG). The color evaluation was performed using CIEL*a*b* concepts, specular gloss, and UV-Visible spectrophotometry. Treated woods showed increases in band intensity related to polymers (1730, 1460 and 1145 cm⁻¹), and WPG ranged from 39 to 164%, depending of the wood species and treatments. Lightness decreased, while the Chroma, gloss and the color coordinates increased. A darkening of the all treated samples was observed, and confirmed by the decrease in the reflectance intensity between 400 and 700 nm.

Keywords: CIEL*a*b*, free radical polymerization, heat catalyst, UV-Vis, wood-polymer composites.

INTRODUCTION

Wood color is related to non-structural chemicals present in the xylem such as polyphenols, flavonoids, stilbenes and quinones. The variations in these substances gives colors to wood from different species.

According to Sandoval-Torres *et al.* (2010), unsaturated chemical bonds present in these substances can be easily transferred to a chemically excited state with a minimum amount of energy – these groups are named chromophores. The chromophores are functional groups that provide color to the materials because they are able to absorb ultraviolet and/or visible radiation (Loureiro *et al.* 2010). Furthermore, a functional group containing one isolated pair of electrons, such as –OH, COOH or –OR is an auxochrome. These compounds can assist in the action of the chromophore groups by means of intensification or absorption of light at longer wavelengths, which correspond to the reddish color characteristic of wood (Hon and Shiraishi 1991).

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Wood color is an important factor for aesthetic purposes, and, in some cases, can influence the market value of this material (Rosu *et al.* 2010). Wood and wood-based products can be found in offices, houses and building construction. In such places, wood is used as furniture, decorative panels, flooring, doors, arches, stairs, sculptures or handicrafts, which create a pleasant environment, especially due to the nature of wood and its aesthetically soft look.

To stabilize or modify the color of wood, many treatments are commonly carried out using high temperatures and steam (Cademartori *et al.* 2014, Cademartori *et al.* 2013, Cermák and Dejmál 2013, Garcia *et al.* 2014, Hu *et al.* 2012, Kačíková *et al.* 2013). Thermo-mechanical or thermo-hydro-mechanical densification also can be used to modify the color of wood (Bekhta *et al.* 2014, Diouf *et al.* 2011). Nevertheless, these treatments always result in a similar pattern, i.e., a strong darkening of the samples, regardless of the wood species, and degradation of wood chemical constituents during heat or mechanical processes.

On the other hand, treatments of wood by *in situ* polymerization method have been carried out to enhance physical, biological and mechanical properties (Baysal *et al.* 2007, Hadi *et al.* 2013, Li *et al.* 2012), and promising results have been achieved. Nevertheless, not much is known about the colorimetric properties of these materials. Furthermore, studies on the topic are scarce (Mamiński *et al.* 2013), even considering the potential applications of these materials for commercial aesthetic products.

The quantitative measurement of color changes in wood is essentially performed with an efficient technique regulated by the *Commission International de L'Eclairage (CIE)*, whereby the parameters of lightness (L^*), chromaticity coordinates (a^* and b^*), chroma (C^*) and hue angle (h^*), can be measured. The *CIEL*a*b** method has been widely applied in other research to evaluate changes in wood color (Cademartori *et al.* 2014, Hu *et al.* 2012, Mamiński *et al.* 2013, Tuong and Li 2010), though UV-Visible spectrophotometry and specular gloss tests are also good tools to assist in color evaluation and, consequently, to provide more accurate information about the aesthetic properties of wood and its composites (Butylina *et al.* 2013, Obaid *et al.* 2013).

The aim of this study was to evaluate the color properties of composites prepared by *in situ* polymerization treatment of *Pinus taeda* and *Schizolobium parahybum* wood, using methyl methacrylate (MMA) as the base monomer, and glycidyl methacrylate (GMA) and methacrylic acid (MAA) as cross-linkers and coupling agents.

MATERIALS AND METHODS

Materials

Three flatsawn heartwood planks (25 x 25 x 270 cm³) including the pith of Loblolly pine (*Pinus taeda*) were provided by a local sawmill (Madarco S.A., Pelotas-RS, Brazil). Three heartwood planks of Guapuruvu (*Schizolobium parahyba*) including the pith and with straight grain (8 x 50 x 200 cm³) were obtained from an experimental forest plantation in Southern Brazil (21 years old). From these materials, samples were cut into small defect-free pieces with dimensions of 1 x 5 x 5 cm³ (thickness, width and length).

Methyl methacrylate (MMA) was used as the main monomer. Glycidyl methacrylate (GMA) and methacrylic acid (MAA) were used as additives (cross-linker and coupling). All monomers were purchased from Sigma Aldrich and used as received. Benzoyl peroxide (BPO) from Vetec Química Fina was selected as the heat catalyst.

In situ polymerization treatments

The samples were oven-dried at 90±2°C until reaching constant mass (~48 hours) and then cooled in a desiccator with silica gel in order to avoid water vapor absorption until the impregnation step. The monomeric solutions were prepared according to Table 1; 1,5 wt.% of benzoyl peroxide was added, and homogenized in the solution using a magnetic stirrer.

Table 1. Parameters of *in situ* polymerization treatments for each wood.

Treatment	ml			g
	MMA	GMA	MAA	BPO
W (Control)	-	-	-	-
W/M	1000	-	-	15
W/M:G (2:1)	665	335	-	15
W/M:G (3:1)	750	250	-	15
W/M:A (2:1)	665	-	335	15
W/M:A (3:1)	750	-	250	15

MMA = methyl methacrylate; GMA = glycidyl methacrylate; MAA = methacrylic acid ; BPO = Benzoyl peroxide.

Half of a stainless steel cylinder (2L) was filled with the samples and vacuumed at 800 mbar for 30 min. Subsequently, 1L of the solution (Table 1) was released into the cylinder and the cylinder was pressurized by air compression at 6,08 bar for 1 h. Samples were then taken out of the cylinder and excesses of the solution were wiped from the samples' surface. Lastly, all the samples were wrapped in aluminum foil and heat polymerized at $90\pm 2^\circ\text{C}$ for 10 h. This step was followed by drying at the same temperature for another 24 h.

ATR-IR Evaluation

Fourier Transform Infrared spectra was qualitatively used to evaluate the chemical structure modification of treated woods using monomer and untreated wood as references. The spectra were acquired in a Nicolet Nexus 570 spectrometer, equipped with an attenuated total reflectance device (ATR-IR), and configured at a resolution of 4 cm^{-1} for 32 scans in the range of 700 cm^{-1} to 4000 cm^{-1} . Alignment of the light equipment, and the background spectra was performed before all the tests.

Weight percentage gain

The weight percentage gain (WPG) after the treatments was calculated using equation 1, as previously mentioned in other studies (Devi and Maji 2013b, Ding *et al.* 2013, Hazarika and Maji 2013, Islam *et al.* 2013).

$$WPG = \left[(W_p - W_0) / W_0 \right] \times 100 \quad (1)$$

where: W_p = oven-dried weight of sample after the treatment; m_0 = weight of sample before the treatment.

Scanning electron microscopy characterization

Before the acquisition of the images, the cross-sections of the samples were prepared with a microtome Leica model SM2010R. After the surface preparation, the samples were oven-dried at $103\pm 2^\circ\text{C}$ until reaching constant weight. The images were captured with magnification of 1k through a Shimadzu scanning electron microscopy, model SSX 550 Superscan.

CIEL*a*b* color evaluation

The color was measured using a Konica Minolta CR-400 equipment, configured to use a D65 light source and 10° of observation angle, as described by the *Commission Internationale de L'éclairage*

($CIEL^*a^*b^*$ standard). Before measurement, the equipment was calibrated using the spectral reflectance of a white calibration plate as the standard. Ten replicates for each treatment were collected to measure the parameters of lightness (L^*), and green-red (a^*) and blue-yellow (b^*) chromatic coordinates. Chroma (C^*), hue angle (h^*) and color variation parameters of ΔE , ΔL^* , Δa^* and Δb^* were obtained through equations 2 to 7, respectively.

$$C^* = (a^{*2} + b^{*2})^{1/2} \quad (2)$$

$$h = \text{tang}^{-1}(b^*/a^*) \quad (3)$$

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad (4)$$

$$\Delta L^* = L^*_t - L^*_{ut} \quad (5)$$

$$\Delta a^* = a^*_t - a^*_{ut} \quad (6)$$

$$\Delta b^* = b^*_t - b^*_{ut} \quad (7)$$

ΔE , ΔL^* , Δa^* , Δb^* = color difference, variation of lightness, variation of green-red chromatic coordinate and variation of blue-yellow chromatic coordinate, respectively; t = treated; ut = untreated.

Specular gloss determination

The reflected specular gloss at an incidence angle of 85° was measured in the radial section along the grain of the samples, according to ASTM D 523-08 (2008). For this, a Konica-Minolta Multi Gloss 268 plus equipment was used. Ten measurements for each treatment were performed. The results were expressed in gloss units, which are related to a standard black glass surface highly polished with gloss, valued near 100.

UV-visible spectrophotometry

Tests of reflectance ranging from 200 to 700 nm were performed using a Shimadzu UV-Vis-NIR 3600 equipment to assist the color evaluation. The spectra were the average of three measurements for each sample. The measurements were performed in the radial section surface of the solid samples.

RESULTS AND DISCUSSION

Treatment evaluation

Expected crosslinking and coupling reactions between the copolymers formed from the insertion of GMA and MAA and the wood cell wall happened via epoxy ring and -COOH with free OH groups, respectively (Li *et al.* 2012, Zhang *et al.* 2013).

Figure 1 shows the ATR-IR spectra of untreated and treated woods by *in situ* polymerization, and Table 2 details the ratio of peaks corresponding to the polymeric chemical structures. Typical infrared peaks related to methacrylate and methacrylic polymer structures were observed at 1145, 1460 and

1730 cm^{-1} , which correspond to C-O stretching ether group, C-H deformation and carbonyl groups (C=O), respectively (Li *et al.* 2013, Zhang *et al.* 2013).

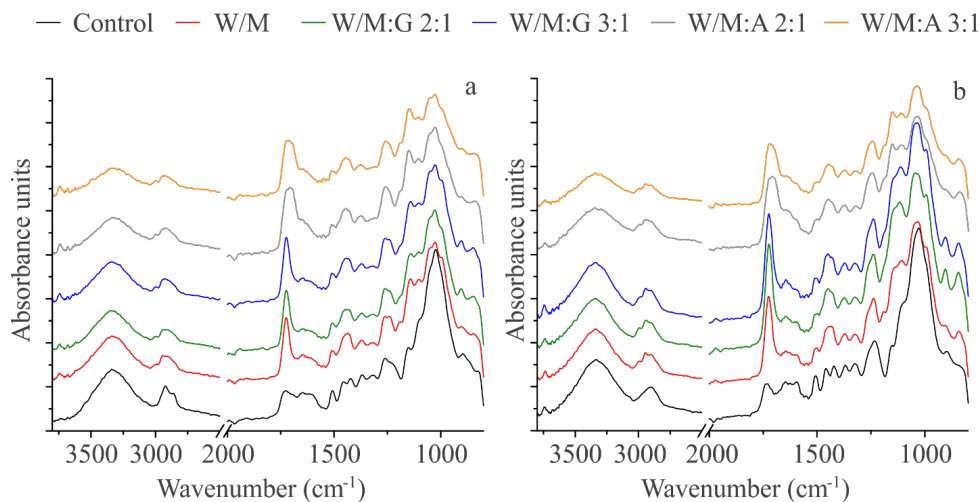


Figure 1. ATR-IR spectra of pine (a) and guapuruvu (b) treated woods.

The peak at 1050 cm^{-1} was used as the internal standard to obtain the ratios of peaks related to the chemical structures of the polymers. This peak corresponds to C-H in plane deformation and symmetrical C-O stretching of cellulose – two very unreactive structures of wood in chemical or thermal treatments (Chen *et al.* 2012, Schwanninger *et al.* 2004). No changes were observed in these regions after *in situ* polymerization treatments of wood (Devi and Maji 2013a, Hazarika *et al.* 2014, Islam *et al.* 2011).

An increase in $I_{1730/1050}$ and $I_{1460/1050}$ ratios was evident in the treated woods (Table 2), and proves that polymers and copolymers were present/synthesized inside of the two woods. Both decreases in $I_{3350/1050}$ and the increase in $I_{1145/1050}$ for treatments with GMA and MAA were due to the partial substitution of wood hydroxyl groups by new ether bonds after the *in situ* polymerization – W/M:A treatments presented the lowest ratio of 3350 cm^{-1} and the highest ratio of 1145 cm^{-1} (Table 2).

Table 2. Ratio of peaks corresponding to the polymeric chemical structures.

Wood	Sample	$I_{1730/1050}$	$I_{1145/1050}$	$I_{1460/1050}$	$I_{3350/1050}$
Guapuruvu (<i>Schizolobium parahybum</i>)	Control	0.215	0.416	0.293	0.338
	W/M	0.506	0.728	0.344	0.351
	W/M:G 2:1	0.529	0.801	0.339	0.306
	W/M:G 3:1	0.521	0.771	0.359	0.322
	W/M:A 2:1	0.477	0.761	0.377	0.305
	W/M:A 3:1	0.496	0.809	0.365	0.318
Pine (<i>Pinus taeda</i>)	Control	0.227	0.499	0.278	0.357
	W/M	0.449	0.772	0.340	0.359
	W/M:G 2:1	0.433	0.741	0.324	0.343
	W/M:G 3:1	0.462	0.777	0.340	0.345
	W/M:A 2:1	0.498	0.867	0.391	0.342
	W/M:A 3:1	0.536	0.895	0.406	0.336

The polymers and copolymers formed inside the woods reached high loading levels, mainly in the

treatments with guapuruvu wood. Differences in density and porosity of guapuruvu (270 kg m^{-3} and 80%, respectively) and pine (520 kg m^{-3} and 63%) woods resulted in WPG values substantially higher for the guapuruvu wood (Figure 2). Therefore, anatomical differences between hard and softwood – mainly due to vestured pits for guapuruvu and bordered pits for pine – lead to differences in WPG.

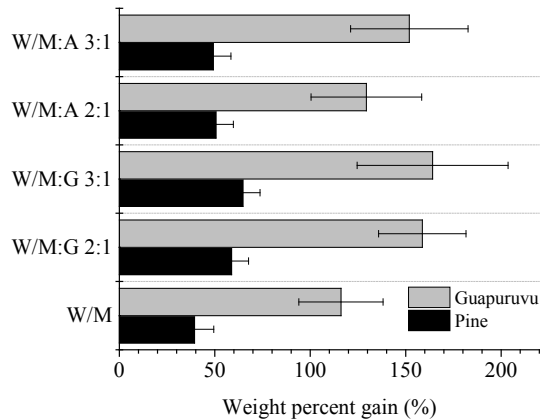


Figure 2. Weight percentage gain of two woods Guapuruvu (*Schizolobium parahybum*) and Pine (*Pinus taeda*) after *in situ* polymerization treatments.

The W/M treatment presented the lowest WPG, while the W/M:G (2:1) treatment showed the highest value of WPG. A lack of adhesion of the poly (MMA) with the wood cell wall's internal surface explains the lowest WPG for the W/M treatments. Nevertheless, after insertion of the polar additive – such as the GMA and MAA monomers – WPG increased, due to the higher compatibility between polymeric reinforcement and the wood (Figure 3c, 3d, 3g, and 3h). Other authors reported similar results using different polymers and wood (Devi and Maji, 2013b, Islam *et al.* 2011, Li *et al.* 2012).

W/M treatments for both wood (Figure 3b and 3f) showed a lack of adhesion of poly (MMA) to the wood cell wall's internal surface, even when the lumen were completely filled. Due to shrinkage of the poly (MMA) after polymerization, clearance space between the polymer and the cell wall became visible.

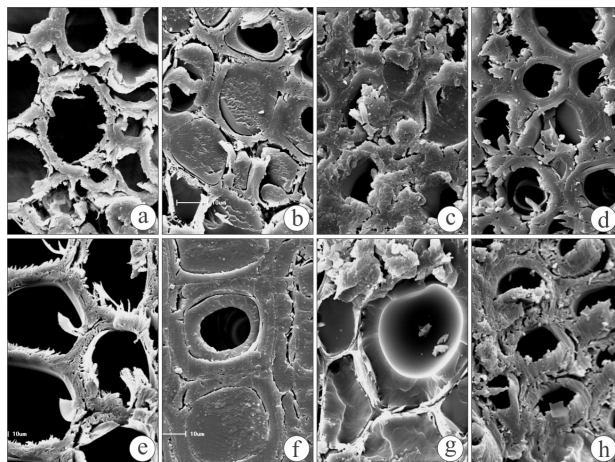


Figure 3. Morphology of the untreated woods and wood/polymer composites prepared by *in situ* polymerization (a = control, b = W/M, c = W/M:G 2:1 and d = W/M:A 2:1 for guapuruvu (*Schizolobium parahybum*) wood; e = control, f = W/M, g = W/M:G 2:1 and h = W/M:A 2:1 for pine wood).

In the crosslinked treated wood (Figure 3 c, 3d, 3g and 3h), filling the cellular elements of both wood was not completed, which occurred because a fraction of the polymer is now inside of the wood cell wall. Penetration and polymer adhesion – coating – to the cell wall was due to the reaction between the carboxyl groups of the MAA or epoxy ring of the GMA with reactive OH from the wood (Mattos *et al.* 2014).

Color evaluation

The natural color of guapuruvu and pine wood was yellow and blanch pink (salmon) (Figure 4). Color changes were observed after *in situ* polymerization treatments. Nevertheless, these changes were less intense than previously found in other types of treatments such as thermal modification (Cademartori *et al.* 2014, Hu *et al.* 2012).

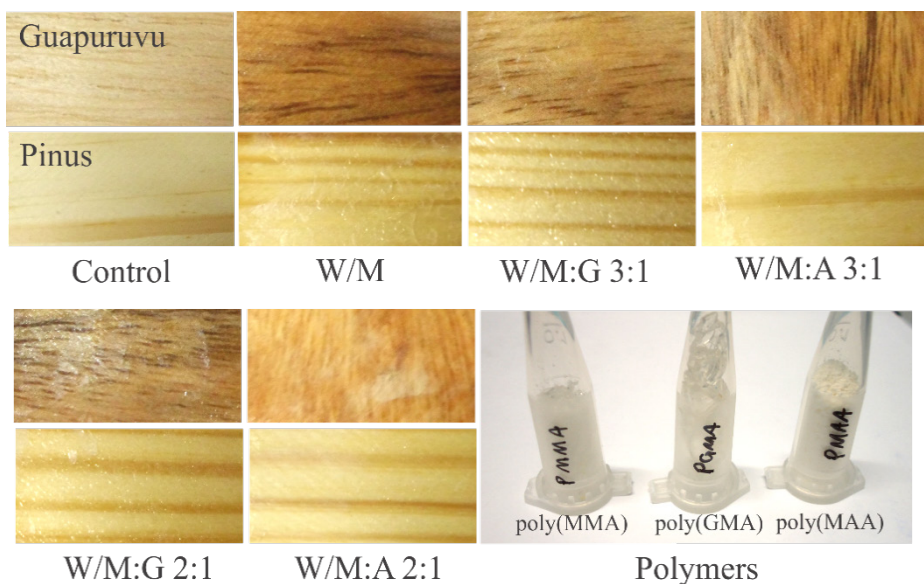


Figure 4. Visual aspects of raw materials and guapuruvu (*Schizolobium parahybum*) and pine (*Pinus taeda*) treated wood.

$CIEL^*a^*b^*$ parameters significantly varied after the treatments (Table 3). A decrement in the lightness of the samples (L^*) was observed, which resulted in a darkening of the wood. Guapuruvu wood presented the highest decrement of lightness. A decrement of L^* after *in situ* polymerization treatments was also observed by Mamiński *et al.* (2013), who treated beech wood with butyl acrylate and butyl methacrylate.

Both chromatic coordinates a^* , and b^* of guapuruvu and pine wood increased after the *in situ* polymerization treatments. The increase of a^* in guapuruvu wood was twice higher as that of the pine wood (Table 3). An increment of a^* denotes a reinforcement of the reddish tones in the guapuruvu treated wood.

The variation of a^* in the pine wood treatments did not represent any specific modification due to the absence of red tones in the samples. Nevertheless, increase of both chromatic coordinates (a^* and b^*) infers a color change from opaque yellow to vivid yellow, nearly orange (Konica Minolta, 2007). The highest increase of a^* and b^* was observed in W/M and W/M:G (2:1) treatments, as can be seen through the results of Δa^* and Δb^* (Table 3). Chroma increases with increased a^* and b^* . Also, decrease of the hue angle were associated to the intensification of the red tones of wood (Figure 5.)

Table 3. Color differences of the treated wood in relation to the untreated wood.

Wood	Treatments	ΔL^*	Δa^*	Δb^*	ΔE	$\Delta Chroma$	Δhue
Guapuruvu (<i>Schizolobium parahybum</i>)	W/M	-15.2	7.2	12.2	20.7	13.8	-6.3
	W/M:G 2:1	-22.4	8.0	8.5	25.3	10.8	-10.5
	W/M:G 3:1	-11.7	4.8	10.9	16.7	11.9	-3.4
	W/M:A 2:1	-10.8	5.7	9.4	15.4	10.9	-5.5
	W/M:A 3:1	-12.6	5.5	9.0	16.5	10.3	-5.6
Pine (<i>Pinus taeda</i>)	W/M	-7.2	2.5	5.8	9.5	6.1	-3.2
	W/M:G 2:1	-7.9	2.8	5.2	9.8	5.6	-3.5
	W/M:G 3:1	-6.3	1.5	4.1	7.6	4.2	-2.0
	W/M:A 2:1	-1.9	1.1	3.7	4.4	3.8	-1.3
	W/M:A 3:1	-3.9	1.4	5.5	6.9	5.6	-1.5

The behavior presented in Table 3 (increase of L^* and decrease of both a^* and b^*) typically does not occur in other treatments performed to stabilize wood color – normally, a decrease of L^* , a^* and b^* is observed (Cademartori *et al.* 2014, Tuong and Li 2010). Decrease of $CIE L^*a^*b^*$ parameters are associated mainly with chemical modifications caused by the high temperatures in the thermal treatments, or thermochemical reactions involved in chemical treatments (Mattos *et al.* 2015). However, high temperatures were not necessary to polymerize methacrylate and methacrylic monomers inside the wood. The Lightness vs. chromaticity diagram shows that the lowest initial C^* of the untreated samples resulted in the highest color changes after the treatments (Figure 5).

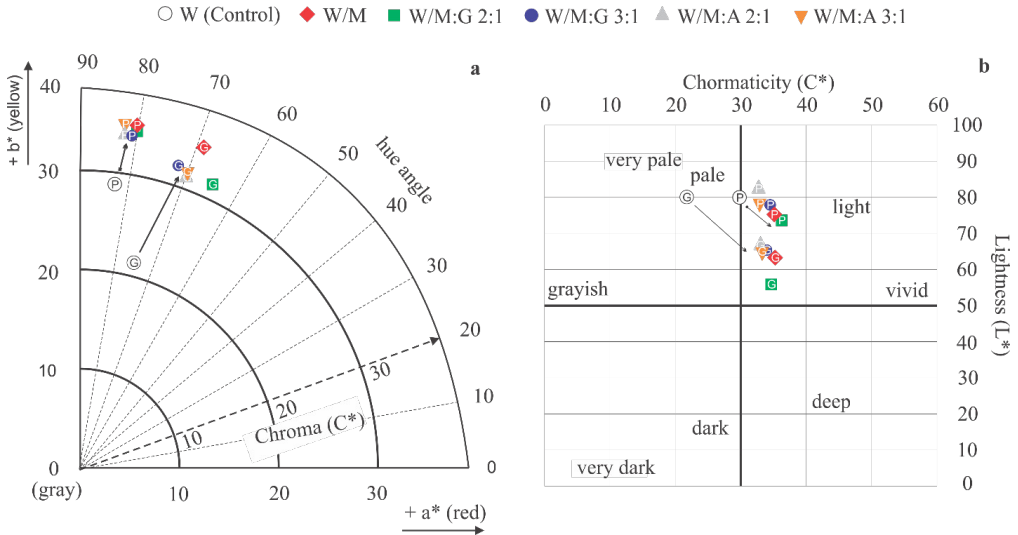


Figure 5. Hue angle displacement diagram (a) and lightness vs. chromaticity diagram (b).

The hue angle displacement and lightness vs. chromaticity diagrams clearly showed a color dislocation from pale tones to light and vivid tones (loss of grayish tones) in two woods after the treatments – which was more pronounced in guapuruvu wood. Higher darkening of guapuruvu treated wood was observed, which resulted in more mild colors, and even increased gloss (Table 4).

The W/M:G 3:1 treatment in guapuruvu wood was the nearest to the dull zone in the chromaticity diagram, even when it presented the highest specular gloss (7,92; Table 4). On the other hand, the highest reduction of L^* (ΔL^* of -22,4) was observed in this same treatment, i.e., L^* was more significant than the gloss to determine the vivacity of colors of the wood treated samples.

Overall, significant increases in the specular gloss of the samples were observed after *in situ* polymerization treatments, with exception of the W/M:A 2:1 treatment (Table 4).

Table 4. Specular gloss of untreated and treated woods

Wood	Control	W/M	W/M:G 2:1	W/M:G 3:1	W/M:A 2:1	W/M:A 3:1	F-ratio
Pine (<i>Pinus taeda</i>)	0.18 a (0.06)	2.45 d (0.31)	3.55 e (0.34)	1.97 c (0.57)	0.3 ab (0.07)	0.49 b (0.18)	207.44*
Guapuruvu (<i>Schizolobium parahybum</i>)	2.03 b (0.49)	3.45 c (0.79)	7.92 e (1.84)	6.40 d (0.73)	1.22 a (0.06)	2.2 b (0.31)	90.47*

* Significant at 1% of error

The treatments with methacrylic acid (MAA) presented the lowest improvement in the specular gloss, mainly because the copolymer poly(MMA-co-MAA) formed is whitish and very pale, while poly(MMA-co-GMA) has a naturally high gloss, similar to poly(MAA) and poly(GMA) (Figure 4).

The reflectance curves in the visible region confirm the color changes in both treated wood. In summary, both untreated and treated wood show low reflectance until 400-500nm, followed by high reflectance at longer wavenumbers (Figure 6). This reflectance pattern was also observed by Obaid *et al.* (2013) in polystyrene-wood composites and by Butylina *et al.* (2013) in composites prepared with polypropylene and wood particles.

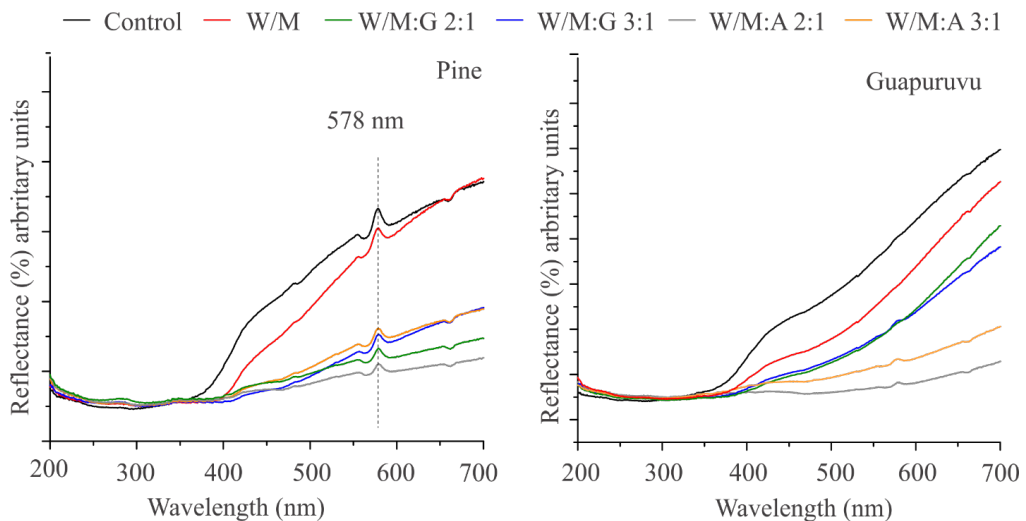


Figure 6. UV-Vis reflectance curves for untreated and treated wood: Guapuruvu (*Schizolobium parahybum*) and Pine (*Pinus taeda*).

According to Pandey and Vuorinen (2008), the intense absorption below 400 nm occurs due to the

large amount of chemical chromophore structures, mainly carbonyl groups in lignin, which absorb light in this spectral band. A peak at 578 nm related to the yellow color was observed in both untreated and treated pine wood. On the other hand, no characteristic peak related to the color of guapuruvu wood was verified, mainly because its blached pink color is not well-defined in the electromagnetic spectra.

After all the treatments, a decrement of the reflectance in the visible range was observed, which was more pronounced in the W/M:G and W/M:A treatments. This decrease is due to the new chemical groups from polymers, which are able to absorb light in the visible range. Another reason is the darkening of the samples after the treatments, as found by Chen *et al.* (2012) and Huang *et al.* (2012). These authors observed an increase in absorption for different wavenumbers in the visible region due to the darkening of wood after heat treatments.

A peak at 578 nm in the pine treated wood indicated the maintenance of the original color. Nevertheless, as previously verified in the *CIEL* *a*b* evaluation, a darkening of the samples was observed, resulting in treated wood with lower reflectance at regions above 500 nm. This behavior was also observed for guapuruvu wood.

CONCLUSIONS

Regardless of the treatment used, guapuruvu (*Schizolobium parahybum*) treated wood was more susceptible to colorimetric changes than pine wood (*Pinus taeda*). The lightness decreased significantly and the dullness increased. However, most of the treated woods presented an aspect of glossy surface.

The treatments with methacrylic acid (MAA) resulted in the lowest improvements in the specular gloss, and in the lowest changes in both chroma and lightness. L^* was more influent than the specular gloss to change the vivacity of wood colors after *in situ* polymerization treatments.

Decrease in the reflectance at 400-700 nm confirmed the darkening of treated woods.

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