

Chemical modification of fast-growing eucalyptus wood

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Abstract In this study, a new simple method for chemical modification of wood from fast-growing *Eucalyptus saligna* (blue gum) was tested by a two-step treatment with methacryloyl chloride. The wood samples were submerged in a solution of 10 % methacryloyl chloride in dichloromethane for 15 h and then exposed to three temperatures: air dried, 50 and 100 °C for 2 h. The chemical modifications of the wood were examined by ATR-IR and ¹³C CP/MAS solid-state NMR; quantitative chemical composition of wood samples by means of wet chemical quantification, HPLC, TGA; colorimetric evaluation by *CIELAB* method and UV–Vis spectroscopy. Water uptake tests were also performed. A partial substitution of the hydroxyl by methacrylate groups on the cell wall of blue gum wood was observed, and also loss of a hemicelluloses fraction after the treatments. The colour change increased with increasing temperature in the second step of the treatment. Dimensional stability and water repellence were improved by 40–50 and 60–75 %, respectively.

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Introduction

The fibrous nature of wood has made it one of the most appropriate and versatile raw materials for a variety of proposed technical applications (Papadopoulos 2005). However, wood is highly hygroscopic and dimensionally unstable. These two negative properties restrict the use of wood due to the hydrophilic character of the polymeric compounds present in the wood cell wall: cellulose, hemicelluloses and lignin. All these polymers contain OH and other oxygen groups that attract moisture through hydrogen bonding in abundance (Rowell 2006).

Furthermore, wood suffers from the photodegradation process by weathering action (rainfall, sun light and wind), mainly in outdoor applications. Natural weathering is responsible for significant colour changes in eucalyptus wood exposed outdoors, showing a greyish colour dependent on exposure, with highest intensity after ~4 months (Mattos et al. 2014). In indoor applications, the wood also suffers from discolouration, which occurs due to oxidation of lignin, albeit with lower intensity (Feist and Hon 1984).

To eliminate or decrease these disadvantages of wood, various techniques have been used for bulk or surface treatments, such as heat treatment (Cademartori et al. 2013), hydrothermal treatment (Dagbro et al. 2010; Grinins et al. 2013), oil heat treatment (Palanti and Susco 2004; Palanti et al. 2011), hot pressing treatment (Candan et al. 2013) and also in situ polymerisation (Li et al. 2013; Islam et al. 2014), which has been used to improve the hydrophobicity and dimensional stability of wood. Moreover, extensive chemical modification techniques have been used to enhance the photostabilisation of wood, as well as dimensional stability and hydrophobicity (Prakash and Mahadevan 2008; Farahani and Taghizadeh 2010; Jebrane et al. 2011; Xiao et al. 2012; Thybring 2013).

According to Rowell (2005), the chemical modification of wood can be performed via: acetylation, acid chlorides, several anhydrides, carboxylic acids, isocyanates, formaldehyde and other aldehydes, methylation, alkyl chlorides, β -propiolactone, acrylonitrile and epoxides. Furthermore, ionic liquids have been used for the treatment of wood (Yuan et al. 2010). Many variables are involved in chemical modifications of wood, such as the catalysis systems (Jebrane et al. 2011), the method applied to impregnate the samples (Xiao et al. 2012), as well as preparation of the substrate (Jebrane and Sèbe 2008; Farahani and Taghizadeh 2010; Pries et al. 2013). Simple experimental conditions are preferable for industrial applications and to increase the economic viability.

Chemical treatments gain greater attractiveness in tropical countries, where the raw material used to meet market demand comes from fast-growing forests, which typically have low quality material. To improve the hydrophobic, dimensional stability and colour properties of this natural resource of great commercial expansion, this study aimed at testing a new simple method of chemical modification of wood from fast-growing *Eucalyptus saligna* (blue gum) by treatment with methacryloyl chloride. The technique presented here is an easy method to chemically modify wood. Complex systems or catalysts are not necessary. It is a simple way to modify the colour, water absorption properties and dimensional stability of wood for increasing the end use.

Materials and methods

Materials

Blue gum wood (*Eucalyptus saligna* Smith) from a Brazilian fast-growing forest (Southern Region) was cut into sapwood blocks of $10 \times 10 \times 25 \text{ mm}^3$ (radial, tangential and longitudinal) to use as starting material. The wood samples were oven dried at $103 \pm 2 \text{ }^\circ\text{C}$ until constant weight and subsequently cooled to room temperature in a silica gel desiccator.

The chemicals used were methacryloyl chloride ($\text{C}_4\text{H}_5\text{ClO}$, $M_w = 104.53 \text{ g/mol}$) and dichloromethane (CH_2Cl_2 , $M_w = 84.93 \text{ g/mol}$), both purchased from Acros Organics.

Chemical modification of wood cell wall

Methacryloyl chloride was dissolved in dichloromethane to 10 % concentration. Thereafter, 30 dried samples were submerged in 100 ml of solution for 15 h.

Then, one-third of the samples were kept in an oven at $100 \text{ }^\circ\text{C}$ and another third at $50 \text{ }^\circ\text{C}$ for 2 h. The remainder of the samples was air dried to compare the effect of temperature on the modification. After the treatments, the samples were washed with dichloromethane to remove unreacted materials—expected reaction is shown in Fig. 1.

The weight percent gain (WPG) of modified samples was calculated using Eq. (1), where W_0 and W_m are oven-dried weight of unmodified and modified samples, respectively.

$$\text{WPG} = [(W_m - W_0)/W_0] \times 100 \quad (1)$$

Infrared spectroscopy

The infrared spectra of modified wood milled samples were measured using a Nicolet Nexus 570 equipment, by attenuated total reflectance (ATR top plate fixed to an optical beam condensing unit with a ZnSe lens) with a MKII Golden Gate SPECAC instrument. The tests were conducted with a resolution of 4 cm^{-1} for 32 scans in the range from 700 to $4,000 \text{ cm}^{-1}$.

The alignment of the light equipment and background spectra were collected prior to any of the tests, and the infrared spectra were mean centred. Presentation of

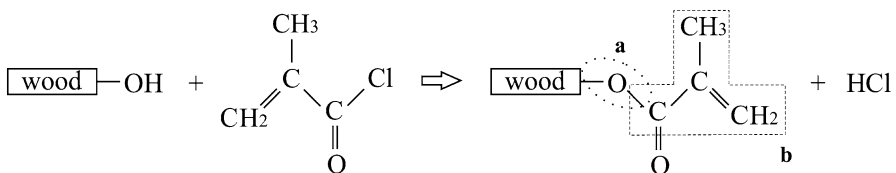


Fig. 1 Esterification of wood cell wall (a) and methacrylate group formed (b) by reaction between wood and methacryloyl chloride

the spectra was made by the average of three measurements for each treatment. Data elaboration was made using the Omnic 6.2 and Origin Pro 9 software.

^{13}C CP/MAS solid-state NMR

A Bruker 400 WB Plus spectrometer was used to conduct the ^{13}C solid-state NMR spectroscopy. Spectra were collected using a 4-mm CP/MAS probe at a spinning of 10,000 Hz. ^{13}C CP/MAS spectra of solid samples were recorded for 12 h using the standard pulse sequence at 100.6 MHz, time domain of 2 K, spectral width of 29 kHz, contact time of 1.5 ms and an inter pulse delay of 5 s. For each analysis, 100 mg of sample was used.

Thermogravimetric analysis (TGA)

The tests were carried out in Mettler Toledo equipment in nitrogen atmosphere (gas flow of 50 mL/min). Each milled wood sample (<60 mesh) was heated from room temperature to 600 °C at a heating rate of 10 °C/min. Between 5 and 10 mg were used in TGA tests.

Quantitative chemical analysis

Triplicates were used to perform quantitative chemical analysis of control and modified wood samples. The samples were milled in a knife mill (Wiley type) to 60–40 mesh according to TAPPI standard (T257 cm-12). The ethanol–toluene extractives (adapted from TAPPI T204 om-97), acid insoluble lignin (TAPPI T222 om-98), holocellulose (Wise et al. 1946) and α -cellulose (Rowell 1983) were determined. The hemicelluloses content was estimated by the difference between holocellulose and α -cellulose.

The monomeric sugars in the first filtering of Klason lignin tests were characterised by high-performance liquid chromatography (HPLC). Jasco LC-Net II/AD equipment was used with a photodiode array detector MD-2018Plus, refractive index detector RI-2031Plus equipped with RezexROA-organic acid H+ (8 %) column. Dissolution of 0.005 N of H_2SO_4 with 100 % of degassed and deionised water was used as mobile phase. The injection conditions of the samples were 30 °C, flow of 0.35 mL/min and volume of 40 μL . For the calibration curves, different high-purity standards were used (such as glucose, xylose, arabinose or furfural).

Colour evaluation by CIELAB

The Konica Minolta colorimeter CR-400 configured with D65 illuminant source and observation angle of 10° was used for colour evaluation. Ten measurements of lightness (L^*), green–red (a^*) and blue–yellow (b^*) chromatic coordinate were taken from each treatment. The ΔE (colour difference between modified and control wood), C^* (Chroma) and h^* (hue angle) were measured by Eqs. (2), (3) and (4), respectively.

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

$$C^* = (a^{*2} + b^{*2})^{1/2} \quad (3)$$

$$h = \text{tang}^{-1}(b^*/a^*) \quad (4)$$

where ΔL^* , Δa^* and Δb^* are variation of lightness, chromatic coordinate green–red and chromatic coordinate blue–yellow for untreated and modified samples.

UV–Vis spectroscopy

UV–Vis spectroscopy was carried out in reflectance in a range between 200 and 700 nm with a spectrophotometer UV–Vis–NIR Shimadzu 3600. The spectra of each treatment are an average of three readings and were performed on the sample surface.

Water uptake and dimensional stability tests

Hydrophobicity of control and modified samples was evaluated by the percentage of weight of water absorbed (%WA). The %WA curves were established by measuring the weight of the samples after 2, 4, 8, 12, 24, 48, 72 and 96 h of immersion in distilled water. The %WA was calculated by Eq. 5.

$$\%WA = [(W_f - W_i)/W_i] \times 100 \quad (5)$$

where W_f is the weight of sample at time of immersion; m_i is the initial weight (after treatment).

The levels of anti-swelling (ASE) and water repellence (WRE) efficiency of modified samples were assessed during 2, 24, 48 and 96 h. WRE and ASE were calculated according to Eqs. 6 and 7, respectively.

$$WRE = [(\Delta W_{un} - \Delta W_m)/\Delta W_{un}] \times 100 \quad \text{where } \Delta W = (W_{sat} - W_{dry})/W_{dry} \quad (6)$$

$$ASE = [(S_{un} - S_m)/S_{un}] \times 100 \quad \text{where } S = (V_{sat} - V_{dry})/V_{dry} \quad (7)$$

where S is the percentage of swelling; V_{sat} , volume of saturated wood; V_{dry} , volume of dried wood; m, modified; un, unmodified; $\% \Delta W$, percentage of weight variation; W_{sat} , weight of saturated wood; and W_{dry} , weight of dried wood.

Results and discussion

Qualitative chemical analysis

Figure 2 shows the ATR-IR spectra for control and two-step modified blue gum wood (air dried, 50 and 100 °C), while Table 1 presents the assignments of the more usual peaks of eucalyptus wood and peaks related to methacrylate group proposed.

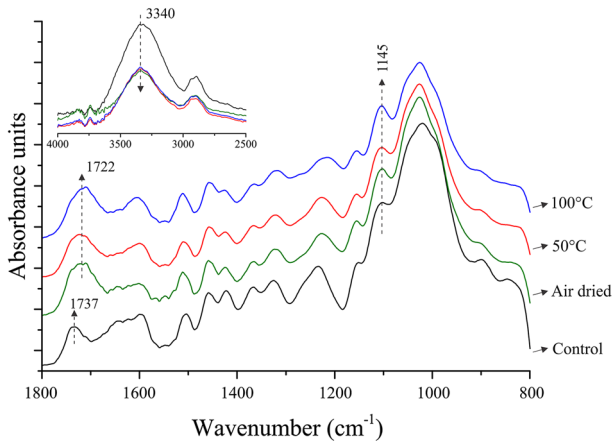


Fig. 2 ATR-IR spectra of control and modified blue gum wood

Table 1 Assignments of the peaks characterised in the ATR-IR spectra of the control and modified samples (Silverstein et al. 2005; Xiao and Dong 2011; Huang et al. 2012; Li et al. 2013)

Peaks	Assignments
3,340	OH stretching
2,912 and 2,849	C–H and CH ₃ stretching in methacrylate
1,722	C=O stretching of carbonyl group from methacrylate
1,737	C=O symmetric stretching in xylan and C=O stretching of acetyl or carboxylic acid
1,592	Benzene ring stretching in lignin
1,504	Benzene ring stretching in lignin; C=C stretching of the aromatic ring in lignin
1,460	C–H deformation in polymers
1,367	CH ₂ bending in cellulose and hemicellulose
1,321	CH ₂ wagging vibration in cellulose
1,230	C–O stretching vibration in xylan
1,157	C–O–C asymmetric band in cellulose and hemicellulose
1,145	C–O ether bond stretching vibrations in methacrylate reaction
896	C1 group frequency in cellulose and hemicellulose

The band at 3,340 cm^{-1} corresponding to OH stretching vibration showed a slight decrease after the treatments, which indicates that a portion of OH groups has been replaced.

The treatment is most evident when analysing the shift of the peak at 1,737–1,722 cm^{-1} due to the new carbonyl groups linked to the wood. In addition, double bond between carbon and oxygen (C=O) also increases, maybe due to lignin autocondensation and condensation reactions as it happens in thermal treatments (Fengel and Wegener 2003; Kim et al. 2014). The conjugated carbonyl bonds, proposed in Fig. 1, appear around 1,680 cm^{-1} and may be overlapped by a peak related to unconjugated carbonyl (Kim et al. 2014).

Further, a significant increase of the peak was observed at $1,145\text{ cm}^{-1}$ corresponding to C–O ether bond stretching vibrations in methacrylate group formed after the treatment (Fig. 2). In addition, the infrared peaks, which appear at $1,463\text{ cm}^{-1}$ (CH_2 scissoring assigned to methylene groups), $1,411\text{ cm}^{-1}$ (C–H bending vibration), $1,230\text{ cm}^{-1}$ (CH_3 bending) and also at $1,233\text{ cm}^{-1}$ (carbonyl groups), are commonly associated with chemical modifications through esterification or acetylation (Jebrane and Sèbe 2008; Pandey et al. 2010; Jebrane et al. 2011; Thybring 2013). However, these peaks did not show any significant changes.

According to Rowell (2005), the HCl released as a by-product of chloride treatments causes extensive degradation of the wood; however, by infrared spectroscopy (Fig. 2), it was not possible to observe significant changes in the major peaks related to the wood polysaccharides ($1,367$, $1,157$, $1,105$, 896 cm^{-1} corresponding to CH_2 bending, C–O–C asymmetric band, OH association, and C1 group frequency of cellulose and hemicelluloses, respectively), whereas these constituents are more sensitive to thermal decomposition (Cademartori et al. 2013).

For information about the chemical modification of blue gum wood, ^{13}C CP/MAS solid-state NMR (Fig. 3) was used. The cellulose carbons and methacrylate group formed on the wood cell wall are assigned directly to the spectra, whereas the

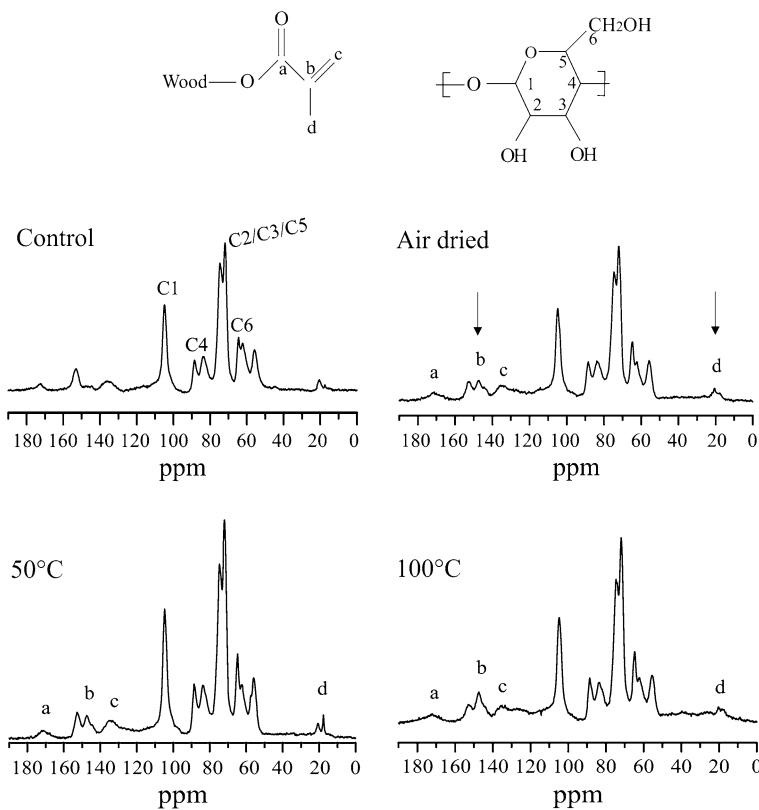


Fig. 3 ^{13}C CP/MAS solid-state NMR spectra of control and modified blue gum wood

signals of the region at 110–160 ppm, related to lignin (Yuan et al. 2013), were not characterised in this study—the carbons of hemicelluloses are hidden by the strong cellulose signals and were also not characterised.

The control wood spectra showed signals at 105.1, 88.9 and 65.1 ppm due to the ordered cellulose C1, C4 and C6 carbons, respectively, and the signals between 72.5 and 74.7 ppm assigned to the C2, C3 and C5 carbons of cellulose. The signals at 83.5 and 62 ppm are due to the amorphous cellulose C4 and C6 carbons, as well as to the less-ordered cellulose chains of the crystallite surfaces (Jebrane et al. 2011; Yuan et al. 2013).

After the chemical modification, additional signals were observed at 147.7 and 18.3 ppm corresponding to carbons structures from the methacrylate group formed on the wood cell wall. These peaks are attributed to the new saturated methylene group formed and to carbon linked to a CH_2 and CH_3 , marked as b in Fig. 3 (Jebrane and Sèbe 2008).

Moreover, a significant reduction of C6 amorphous carbon and a change of the signal of the carbons C2, C3 and C5 were observed. The modification in the signal between 70 and 80 ppm could indicate that cellulose reacted at the C2 and/or C3 position (Salla et al. 2012).

The reduction of amorphous C6 carbon indicates a substitution of this carbon in the chemical modification; however, the decreased intensity of this signal can also be associated with the degradation of the fragile regions of the cellulosic chain due to the heat catalyst step of the treatment combined with the hydrochloric acid release. This reduction of the C6 and changed sign of the carbons C2, 3 and 5 were also observed by Jebrane and Sèbe (2008) in a study on the chemical modification of wood with vinyl methacrylate.

Quantitative chemical analysis

The first weight loss of the TG curves occurs between 35 and 100 °C for all samples, where the moisture loss of the samples was observed and further thermal degradation takes place as a two-step process (Fig. 4). Peak 1 of the DrTG thermogram (Fig. 4b) shows a lower desorption of water on the modified samples than on control wood—the water adsorption decreases with increased temperature of the catalysis treatment (desorption < 100 °C < 50 °C < air dried).

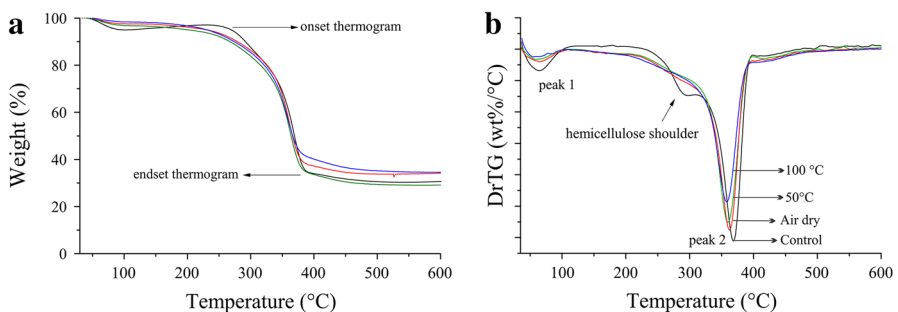


Fig. 4 Thermograms (a) and derivatives (b) of control and modified blue gum wood

Table 2 Thermal degradation temperatures, T_{shoulder} , DrTG peak and residue at 400 °C

Samples	T_i (°C) 3 wt% loss	T_{shoulder} (°C)	Peak 2 (°C)	Residue at 400 °C (%)
Control	270	290	367	34
Air dried	168	–	362	33
50 °C	169	–	360	38
100 °C	191	–	357	40

The initially significant weight loss temperature (T_i) of all samples was considered as the temperature at which the sample loses 3 % of its weight. The lowest T_i value was attributed to the air-dried treatment followed by 50 and 100 °C heat treatments, while the T_i of control wood is 270 °C (Table 2). The modified woods showed low thermal stability, contrary to what was observed by Khalil et al. (2011) and Yuan et al. (2013) who found increments in the thermal stability of the wood after propionylation and benzylation treatments, respectively. Wood species, WPG and chemical groups formed may have contributed to this disparity between studies.

Between treatments, the increase of temperature in the thermal step increased the thermal stability of wood, mainly due to partial elimination of hemicelluloses. Hemicelluloses decomposition (signalled as a shoulder in DrTG curve) was observed only in the control wood at a range of 225–320 °C and maximum value at 290 °C (Table 2). Poletto et al. (2012) stated that the degradation temperatures of hemicelluloses and cellulose can partially overlap with each other, where hemicelluloses decomposition usually appears as a less-pronounced shoulder instead of a well-defined peak.

The absence of the shoulder in the DrTG curves related to modified woods shows a partial degradation of hemicelluloses and amorphous cellulose during the treatment, in accordance to what has been previously stated in the ^{13}C CP/MAS solid-state NMR analysis.

The temperature of cellulose fibres degradation was between 310 and 400 °C (DrTG peak 2 in Table 2), with the maximum peak near 357–367 °C. The cellulose degradation peak is higher for the control wood and decreased gradually until the thermal treatment at 100 °C. A displacement of the cellulose fibres degradation peak also occurs at lower temperatures—the chemical modification formed a new wood material with lower thermal stability.

The degradation of the lignin had occurred along the increase in temperature, and the weight loss was not characterised due to the absence of a significant peak. Lignin exhibits high structural diversity, and according to Yang et al. (2007), lignin degradation is slow and occurs from 100 to 900 °C with low weight loss (<0.14 wt%/°C).

The temperature of the second step of the treatment also increases the residual carbon, stated by the residual mass at 400 °C. This increase can be associated with higher proportion of lignin content in modified wood, as shown in Table 3.

The results of chemical quantification confirmed some information observed in solid-state NMR (Fig. 3) and thermogravimetric analysis (Fig. 4). The proportion of lignin was higher for modified woods with thermal catalyst in the treatment (50 and 100 °C), since the holocellulose content decreased in a similar way.

Table 3 Quantitative chemical analysis (SD in parentheses)

Compound (%)	Control	Air dried	50 °C	100 °C
Extractives	1.66 (0.18)	2.72 (0.08)	4.23 (0.04)	8.15 (1.13)
Lignin	32.73 (1.12)	34.41 (0.61)	38.30 (1.45)	37.84 (0.31)
Holocellulose	61.7 (0.44)	55.30 (1.32)	52.96 (0.84)	51.77 (0.78)
α -Cellulose	43.77 (0.36)	49.23 (1.21)	49.18 (1.16)	49.09 (1.22)
Hemicelluloses	17.93 (4.83)	6.06 (0.10)	3.77 (0.32)	2.68 (0.44)
Glucose	33.69 (3.98)	39.97 (2.59)	40.23 (2.35)	44.64 (0.22)
Xylose	11.15 (1.24)	7.47 (0.35)	7.11 (0.17)	4.43 (0.11)

The hemicelluloses content of control wood was 17.93 %. Nevertheless, after the chemical modification without the thermal step, it decreased to 6.06 % (11.87 % lower), while in the chemical modification with the thermal step at 50 and 100 °C, the hemicelluloses content was 3.77 and 2.68 %, respectively, i.e. 14.16 and 15.25 % lower compared with the original content. The hemicelluloses degradation is also confirmed by an increase of glucose (principal cellulose sugar) in proportion to the decrease in xylose, a typical sugar present in hemicelluloses of eucalyptus wood. The hemicelluloses degradation occurs due to the strong release of HCl as a by-product reaction combined with the temperature used in the catalyst.

The WPG obtained for modified woods were 3.94, 4.75 and 3.32 for the air dried, 50 and 100 °C treatments, respectively. On the other hand, after treatment, it was found that a fraction of hemicelluloses was lost. Considering the loss of hemicelluloses together with WPG, one can estimate the real weight gain due to a replacement of hydroxyl groups by methacrylate groups.

That is, on the one hand, the mass of samples increases due to substitution of the functional groups, while on the other, it decreases due to loss of hemicelluloses. Thus, the estimate WPG corrected by loss of hemicelluloses were 15.8, 18.9 and 18.6 % for air dried, 50 and 100 °C treatments, respectively.

Colour evaluation

By visual analysis, a gradual browning of the samples directly related to the temperature of the heat catalyst was observed. The highest darkening was verified at the highest catalyst temperature (100 °C) used in the second step of the modification (Fig. 5).

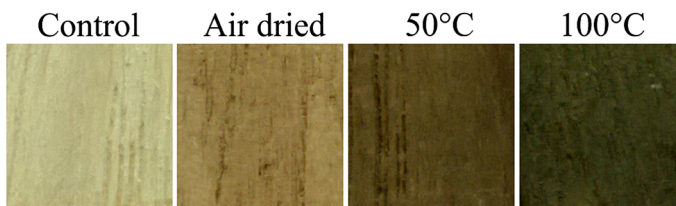
**Fig. 5** Visual appearance of modified wood as a function of thermal treatment step

Table 4 CIELAB colour evaluation

Parameters	Treatment			
	Control	Air dried	50 °C	100 °C
L^*	72.03 ± 2.18	58.35 ± 3.84	55.28 ± 2.89	36.38 ± 3.80
a^*	9.35 ± 1.76	16.76 ± 1.39	11.39 ± 2.80	5.97 ± 1.78
b^*	18.70 ± 1.69	18.29 ± 2.33	15.12 ± 1.09	9.41 ± 2.41
Chroma	20.93 ± 2.23	24.84 ± 2.34	19.13 ± 0.92	11.18 ± 2.86
h^*	63.65 ± 2.82	47.37 ± 3.15	53.34 ± 5.68	57.64 ± 4.56
ΔE	–	15.74 ± 4.01	17.42 ± 3.25	37.05 ± 4.31

Table 4 shows that the two-step treatment was responsible for significant changes in all parameters of the CIELAB evaluation in relation to the control wood. Lightness (L^*), corresponding to clarity of the samples, significantly decreased with increased temperature—treatment at 100 °C showed a reduction of ~50 % for L^* .

Overall, the polysaccharides of wood are very sensitive to higher temperatures, as reported by Ayadi et al. (2003), Yildiz et al. (2013) and Tomak et al. (2014). Here, the highest temperature used was 100 °C—about 50 % lower than the temperatures at which significant darkening of wood occurs—however, the combined action of acid release and temperature may have catalysed a thermochemical degradation as influential in the wood colour as the high temperatures used in the heat treatments (>200 °C), since in the air-dried treatment, no significant colour change was observed.

The parameter a^* , concerning the green–red axis, presented an initial increment in the air-dried treatment compared with control wood, showing a colour change to red. In contrast, the a^* decreased with insertion of temperature in the thermal step, indicating that the colour of wood was changed to reddish brown and very dark at 50 and 100 °C, respectively.

The chromatic coordinate b^* , corresponding to the blue–yellow axis, did not present any difference between the air-dried treatment and the unmodified samples; however, a slight decrease was observed in 50 and 100 °C treatments. The decrease of b^* shows a loss of initial yellowish colour of wood. In agreement with a^* and b^* , the reduction of h (Table 4) represents a substitution of yellow tones by red tones. Tolvaj and Németh (2008) affirmed that hue angle varies between 0° and 90°, where 0° is related to red colour and 90° is related to yellow colour.

The Chroma showed the same behaviour of the a^* , i.e. a slight increase for the air-dried treatment followed by significant decrease for the 50 and 100 °C thermal treatments (Table 4). The Chroma is related to opacity of the colour, which means that the reduction of the parameter causes changing of the colour to dull and dark tones. As expected, colour difference (ΔE) increased as a function of the temperature. The colour difference of the 100 °C thermal treatment was two times higher than the air-dried treatment and 50 °C treatment.

The treatments proposed here showed colour of wood very similar to heat-treated woods, which made us to consider an expected increase in colour stability.

Previously, many studies stated that the darkened heat-treated wood tends to be more resistant to the weathering effects for longer times. This protection is due to the formation of many monomers of phenol from lignin and extractives that could act as antioxidant compounds, preventing the degradation caused by oxidation (Ayadi et al. 2003; Yildiz et al. 2013; Tomak et al. 2014).

The spectrophotometric measurements of wood samples in the UV–visible range show a very strong absorption up to 400 nm followed by high reflectance at longer wavelengths, except for the modified wood at 100 °C that showed low reflectance in the whole visible range (Fig. 6).

At 577 nm the control samples showed a peak related to natural colour of blue gum wood, i.e. opaque yellow. The same peak was observed with lower intensity for the air dried and 50 °C modified woods, and disappeared for the 100 °C, showing the strong colour change of wood modified by the two-step treatment, mainly using temperature as catalyst.

According to colorimetric evaluation, a strong influence of temperature on the final colour of wood modified by methacryloyl chloride was observed. Without the thermal catalyst, little change in the colour of wood was verified, which corroborates previous reports by Pandey and Chandrashekar (2006) on chemical modification of wood via esterification with benzoyl chloride.

Hydrophobicity, hygroscopicity and dimensional stability

After 2 h, all samples showed similar WA \sim 5 %; however, at 4 h, the control wood presents WA two times higher than the modified woods (Fig. 7). This initial similarity is due to the physical porosity of samples and not due to chemical affinity with water. At the end of the test (96 h), modified samples absorbed between 5 and 10 %, approximately 4–7 times less than the control wood (\sim 35 %). These results corroborate other authors reporting on similar treatments using distinct mechanisms and woods (Islam et al. 2012; Salla et al. 2012; Pries et al. 2013).

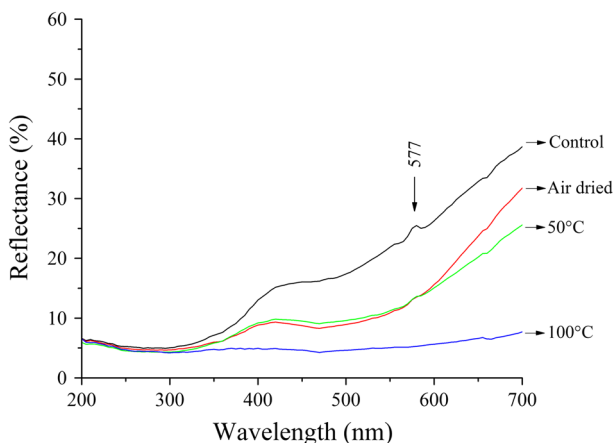


Fig. 6 UV–Vis spectra from unmodified and modified samples

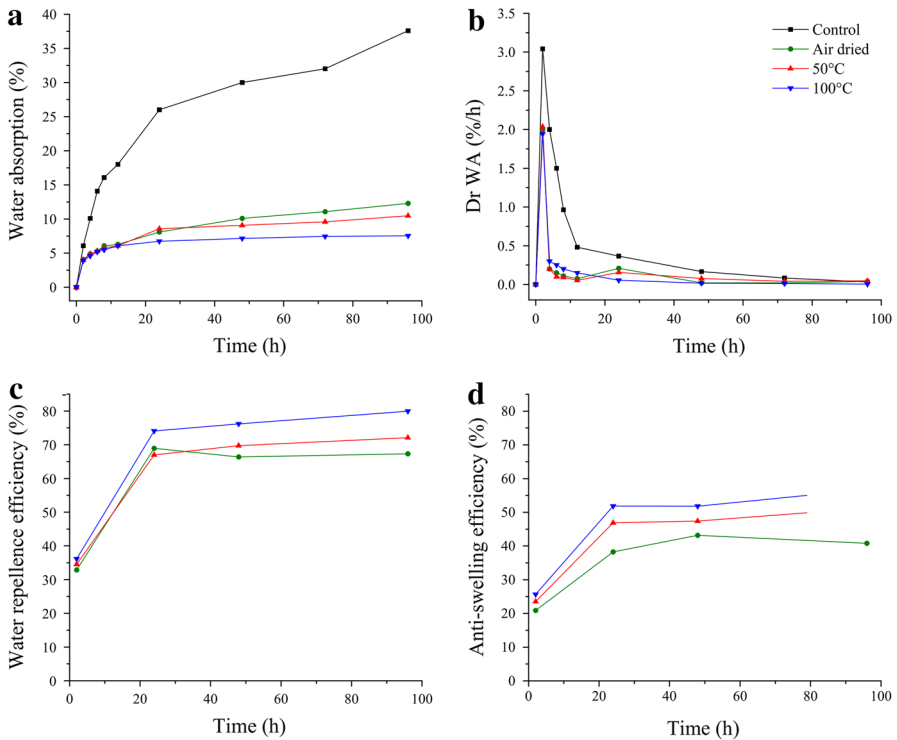


Fig. 7 Water uptake and dimensional stability results

Therefore, the proposed modification is able to decrease the wood hygroscopicity, suggesting the methacrylate groups formed in the wood are a barrier against moisture. However, this treatment did not eliminate hygroscopicity.

The high rate of water absorption (DrWA) occurred in the first 2 h of immersion (Fig. 7b). WRE and ASE (Fig. 7c, d) are at a minimum at 2 h, followed by increases between 2 and 4 h and remaining stable until 96 h—showing an increase in the efficiency over time, which occurs mainly due to the initial similarity in the water absorption of all treatments. Similar results were observed by Prakash and Mahadevan (2008) and Jebrane et al. (2011) with wood modifications through palmitoyl chloride, vinyl acetate and acetic anhydride.

The values of ASE and WRE are higher in the 100 °C treatment, followed by 50 °C and air dried, respectively. Highest efficiency for treatments with thermal catalysis occurs due to higher WPG—non-polar structures linked onto the wood cell wall by substitution of OH by methacrylate groups—and further degradation of hemicelluloses, since these compounds have a high affinity for water.

Conclusion

The treatment by methacrylation of wood OH groups proved to be a simple way to modify the colour and technological properties of water absorption and dimensional stability of blue gum wood—and thus increase the applications of end-use products from wood of the fast-growing species.

By ATR-IR and ^{13}C CP/MAS solid-state NMR some considerations about this treatment were verified, such as autocondensation of lignin structures and chemical reaction of methacryloyl chloride and wood. By wet chemical and thermogravimetric analysis, loss of a fraction of hemicelluloses of the blue gum wood during the treatment was observed.

It is expected, based on the reported literature, that the darkening of wood samples after modifications improved weathering resistance. On the other hand, it is also expected that the mechanical properties present a little decrease due the degradation of the hemicelluloses from blue gum wood. Further studies will be conducted on these topics.

The partial substitution of OH combined with hemicelluloses degradation resulted in an increase in the hydrophobicity and dimensional stability of modified woods.

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