

Article

Thermochemical and Mechanical Properties of Pine Wood Treated by In Situ Polymerization of Methyl Methacrylate (MMA)

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Abstract: The impregnation of low-molecular-weight monomers prior to polymerize them inside the wood may be an efficient way to improve some important wood properties. This work aimed to determine some technological properties of wood-based composites (WPC) produced by in situ polymerization, using a pine wood (*Pinus elliottii* Engelm.) impregnated with methyl methacrylate (MMA). For that, samples taken from both juvenile (JV) and mature (MT) pine woods were treated with MMA. Physical, mechanical, chemical, thermal and morphological features were evaluated. MMA-treated woods from both juvenile and mature woods presented superior physical, mechanical (expect brittleness) and thermal properties when compared to pristine ones. The infrared spectra and morphological analysis by scanning electron microscopy (SEM) confirmed the presence of the monomer inside the pine wood. The juvenile wood presented higher treatability than the mature wood, due to its higher content of intra- and inter-cellular spaces.

Keywords: thermal stability; juvenile wood; infrared spectroscopy; in situ polymerization; wood quality

1. Introduction

Pine trees are important raw materials and may meet some current market demand, due to their rapid growth and high adaptability to different environmental conditions. Their woods present a large range of applications, such as for civil construction, panels, furniture and packaging. However, the juvenile pine wood has a lower performance than the mature wood due to its high proportion of early wood, which negatively affects wood quality and limits its use, especially in certain structural applications [1]. Because of that, treatments have been applied to produce modified wood capable of meeting the requirements of each intended purpose.

According to Mantanis [2], some recently developed wood treatments have given rise to new modified products, which gradually changed mistaken perspectives of some customers about wood being a fragile, unstable, and easily degraded construction material. For Sandberg et al. [3], the increased interest during the last decades in wood modification can be satisfactorily explained for four reasons: (i) development of silviculture practices able to produce wood with improved properties, (ii) to avoid

the use of rare species with outstanding properties, (iii) to add value to sawn timber and some of its by-products, and (iv) to follow public policies focused on sustainability.

These wood treatments can be divided into four categories: thermal, chemical, surface and impregnation treatments [4]. Currently, impregnation is the most performed method, because of its effects on wood properties. In this context, different synthetic monomers and resins were already in use, including methyl methacrylate (MMA) and furfuryl alcohol [2,5,6]. It is important to mention that some key catalysts also play an important role for the final treated woods. For instance, some cyclic carboxylic anhydrides such as maleic anhydride for furfuryl alcohol may be incorporated in the treatment solution [2].

The use of MMA to produce impregnated wood parts is due to its easy synthesis, low cost, translucency, good chemical stability and ease of catalysis [7]. The in situ polymerization of MMA into wood parts may provide improvements in several technological parameters, such as dimensional stability, density and mechanical properties [8]. These changes are associated with the confinement of polymer segments into wood cells and/or wood cell walls.

High polymer retentions can be reached with in situ polymerization of MMA into the wood, but it may depend on wood anatomical features [9]. Hadi et al. polymerized MMA into four wood species, namely sengon (*Falcataria moluccana* Barneby and JW Grimes), jabon (*Anthocephalus cadamba* (Roxb.) Bosser), mangium (*Acacia mangium* Wild), and pine (*Pinus merkusii* Junghuhn and De Vriese). They observed that the treated woods presented increased resistance to subterranean termite attack compared to their respective pristine ones. More recently, wood-based composite (WPC) was produced by in situ polymerization of MMA into three fast-growing wood species, namely jabon (*Anthocephalus cadamba*), mangium (*Acacia mangium* Wild) and pine (*Pinus merkusii* Junghuhn and De Vriese) [10]. The authors reported that the treatment led to an increase in both density and strength at bending. Also, their lightweight woods presented better treatability than the heavy ones, which suggests that a JV may behave differently to an MT from the same specie if treated by in situ polymerization with MMA.

Therefore, MMA impregnation is a promising treatment and may lead to improvements in physical and mechanical properties of pine woods, especially JV. The objective of this study was to produce and characterize WPC by in situ polymerization of MMA into JV and MT from pine.

2. Materials and Methods

2.1. Raw Material

Pine trees that were 20 years old (*Pinus elliottii* Engelm.) were selected in a homogeneous forest located at Piratini/Brazil. This forest was planted in an initial spacing of 2 m × 2 m and then no silvicultural practice was carried out. Afterwards, 20 prismatic wood samples were cut from near to the pith (juvenile wood; JV) and 20 near the bark (mature wood; MT) with two different dimensions: 25 mm × 25 mm × 100 mm and 15 mm × 15 mm × 250 mm (radial × tangential × longitudinal); of these samples 20 of each were treated. For the JV, only the first 5 growth rings near the pith were selected, while only the last 3 growth rings were selected to represent the MT. Then the samples were placed in a climatic chamber (adjusted to a temperature of 20 ± 2 °C and 65 ± 3% relative humidity) until reaching constant mass.

2.2. Treatment by Methyl Methacrylate (MMA) Impregnation

The wood samples were oven dried at a controlled temperature of 70 °C until reaching constant mass, in order to remove the wood moisture, since the MMA is immiscible in water and this could spoil its polymerization process. Then, benzoyl peroxide (1.5 wt %) was added to an aqueous solution of 99% MMA and this mixture was manually homogenised for 60 s. The dried wood samples were placed inside a small horizontal autoclave (capacity of 2.3 L) and the empty space was filled with a ceramic material. Afterwards, the chamber was subjected to an initial vacuum of 40 min, using a vacuum pump (600 mmHg), in order to remove internal air.

The MMA solution was poured into the autoclave using the difference of pressure between the internal and external environment. After filling the autoclave cavity with about 1.5 L of solution, a pressure of $8 \text{ kgf}\cdot\text{cm}^{-2}$ was applied for 180 min, using compressed air. Then, the impregnated samples were coated with aluminium foils and heated at a constant temperature of $50 \text{ }^\circ\text{C}$ for 24 h, followed by extra $70 \text{ }^\circ\text{C}$ for 72 h. The final samples were conditioned at room temperature ($20 \text{ }^\circ\text{C}$) until reaching the equilibrium moisture content.

2.3. Characterization of Physical and Mechanical Properties

Weight percentage gain (WPG) was calculated by a simple perceptual difference between the masse before and after the MMA impregnation, as indicated by Equation (1). The density at 12% of moisture content (ρ) was calculated based on the mass and the volume, as indicated in Equation (2), following an adapted procedure based on the ASTM D2395 [11]. To determine the equilibrium moisture content (M_C), the samples were waterlogged and then oven dried at $103 \pm 2 \text{ }^\circ\text{C}$ until constant mass. Equation (3) was used to calculate M_C .

$$\text{WPG} = \left(\frac{M_A - M_B}{M_B} \right) * 100 \quad (1)$$

$$\rho = \frac{M_{12}}{V_{12}} \quad (2)$$

$$\text{MC} = \left(\frac{M_1 - M_2}{M_2} \right) * 100 \quad (3)$$

where: WPG is weight percentage gain (%), M_B and M_A are masses (g) before and after the treatment, respectively; ρ is density (g cm^{-3}); M_{12} and V_{12} are mass (g) and volume (cm^3), respectively; M_C is the equilibrium moisture content (%); M_1 and M_2 are masses (g) at waterlogged and dry conditions, respectively.

All the mechanical tests were performed with the help of a DL 3000 universal test machine (Emic brand), and according to ASTM D 143 [12]. Modulus of elasticity (MOE), modulus of rupture (MOR) and brittleness (B_T) were determined based on the results obtained by static bending tests, which were carried out in prismatic samples with the dimensions of $25 \text{ mm} \times 25 \text{ mm} \times 100 \text{ mm}$ (radial \times tangential \times longitudinal).

To calculate the B_T , load vs. deflection curves were analysed following the methodology proposed by Phuong et al. [13], as described in Equation (4). Hardness tests were performed on the tangential face of prismatic samples with the dimensions of $15 \text{ mm} \times 15 \text{ mm} \times 250 \text{ mm}$ (radial \times tangential \times longitudinal), using a 0.55 cm diameter steel hemisphere and following the Janka method.

$$B_T = \left(\frac{E_A}{E_A + P_A} \right) * 100 \quad (4)$$

where: B_T is brittleness (%) and E_A and P_A are the elastic and plastic areas from load vs. deflection curves from static bending tests.

2.4. Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared (FT-IR) spectroscopy analysis was performed on a 4100 equipment (Jasco brand), wherein each spectrum resulted from 32 scans performed in the 2000 cm^{-1} to 600 cm^{-1} wavelength range, with a resolution of 4 cm^{-1} , scanner speed of 2 mm/sec and filter of $30,000 \text{ Hz}$.

2.5. Scanning Electron Microscopy (SEM)

A MMA-treated JV sample was placed on an aluminium stub and pre-coated with gold particles. Then, its transverse plane was analysed in a Pro-X (Phenon World brand) scanning electron microscope (SEM) at an accelerating voltage of 10 kV.

2.6. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed in cubic samples (side equal to 10 mm), using a TGA-1000 equipment (Navas brand). The thermogravimetric curves were obtained using two heating ramps, both of them at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, under an inert atmosphere and nitrogen gas flow of $2\text{ L}\cdot\text{min}^{-1}$. The first ramp from $30\text{ }^{\circ}\text{C}$ to $105\text{ }^{\circ}\text{C}$ and the second from $105\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$.

2.7. Statistical Analyses

The statistical design used was completely randomized. The assumptions of homogeneity of variances and data normality were tested by Levene and Shapiro—Wilk methods, respectively. When any assumption was not attended, the data were transformed, using square root or logarithm. Whenever the null hypothesis was rejected based on analysis of variance (ANOVA) tests, Fisher tests were performed in order to compare the averages. All statistical analyses were developed at a significance level of 1%.

3. Results

The treatments with MMA resulted in changes in physical, mechanical, thermal and chemical properties for both JV and MT from pine. This was indicated by significant increases in WPG and ρ (Table 1). The smaller WPG for MT can be attributed to its anatomical features, since the MT is known by a high proportion of latewood, thick wood tracheids and narrow wood lumens [14].

Table 1. Average values for the evaluated physical properties.

Groups	WPG (%)	ρ ($\text{g}\cdot\text{cm}^{-3}$)	M_C (%)
MT	-	0.577 (0.048) b	14.40 (0.09) a
JV	-	0.536 (0.030) b	14.20 (0.17) a
MT + MMA	73.59 (1.15) b	0.984 (0.040) a	5.76 (0.40) b
JV + MMA	113.97 (1.01) a	0.978 (0.045) a	5.31 (0.62) b

JV: juvenile wood; MT: mature wood; MMA: methyl methacrylate; WPG: weight percentage gain; ρ : density; M_C : equilibrium moisture content; the values in parentheses show the standard deviations and averages in the columns do not differ from each other if followed by the same letter, according to Fisher tests.

Regarding the mechanical properties, the MMA treatment led to a significant increase in hardness, as well as in MOE and MOR for both JV and MT (Table 2). The impregnation and subsequent polymerization of this monomer inside the wood increased the hardness in 108% and 63% for the JV and MT, respectively.

Table 2. Average values for the evaluated mechanical properties.

Groups	Hardness(MPa)	Static Bending (MPa)		
		MOE	MOR	B_T (%)
MT	34.72 (0.08) b	11,409.0 (1.404.2) b	76.91 (1.10) bc	3.15 (1.13) a
JV	31.96 (0.06) b	8,024.9 (1.016.9) c	66.94 (1.03) c	7.81 (1.25) b
MT + MMA	56.67 (1.63) a	13,326.0 (1.200.2) a	127.94 (1.12) a	11.81 (1.25) c
JV + MMA	66.67 (0.42) a	9040.1 (1.753.0) c	83.66 (1.03) b	20.93 (1.35) d

JV: juvenile wood; MT: mature wood; MMA: methyl methacrylate; MOE: modulus of elasticity; MOR: modulus of rupture; B_T : brittleness; values in parentheses show the standard deviations and averages in the columns do not differ from each other if followed by the same letter, according to Fisher tests.

Qualitative chemical analyses before and after the treatment with MMA were performed, by FT-IR (Figure 1). As described in Table 3, it is known that the main chemical components of the wood (namely cellulose, hemicellulose and lignin) have certain functional groups that vibrate in particular wavelengths belong to the infrared spectrum (from 1800 to 600 cm^{-1}). FT-IR spectroscopy is an important tool for evaluating organic components in wood, as each molecule vibrates at a specific wavelength, making this technique a rapid method to ascertain some chemical changes in wood [15].

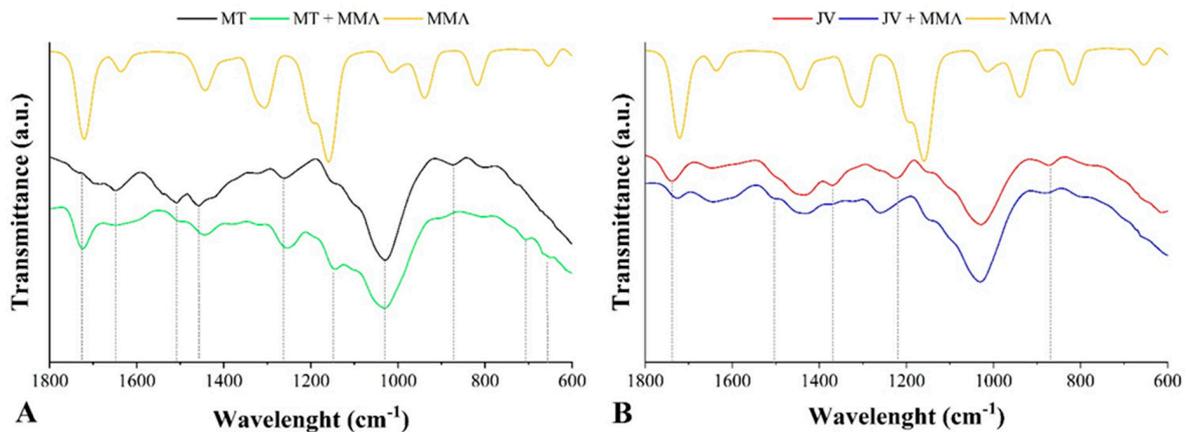


Figure 1. Fourier transform infrared (FT-IR) spectra for MMA-treated and untreated mature (MT; A) and juvenile (JV; B) woods from pine.

Table 3. Correspondence between infrared spectra wavenumbers with chemical compounds of the wood-based composite (WPC) obtained.

Wood			
Wavenumber (cm^{-1})	Molecular Vibrations	Wood Compounds	Reference
1740	Stretching of C=O bonds of the carboxylic groups	hemicellulose/lignin	[5,16,17]
1645	Stretching at the C=O conjugated bonds of the alkyl ketones of the carbonyl groups	lignin	[16]
1510	Stretching of C=C bonds on aromatic ring	lignin	[17]
1460	Deformation on C-H bonds of aromatic ring	lignin	[18]
1370	Deformation on C-H bonds	cellulose/hemicellulose	[17]
1260	Stretching on C-O bonds in xylans	hemicellulose	[18]
1030	Stretching on C-O bonds and deformation on C-H bonds of guayacil units	cellulose/hemicellulose/lignin	[18]
870	Stretching on C-OH bonds	cellulose	[16]
Methyl Methacrylate (MMA)			
Wavenumber (cm^{-1})	Vibration/Functional Groups	Reference	
1725	Stretching on C=O bonds of carbonyl groups	[19,20]	
1440	Asymmetric stretching on C-H bonds	[21]	
1305	Symmetric stretching on C-H bonds	[20,21]	
1160	Stretching on C-O-R bonds of ester	[21]	
1010/940/820	Stretching on C-C bonds	[21]	

The thermal gravimetric results were used to evaluate the thermal stabilities of studied woods. Based on both the TGA (Figure 2A) and DTG (derived from thermogravimetry) (Figure 2B) curves, it was observed that the impregnation with MMA increased the thermal stabilities of both JV and MT, compared to their respective pristine groups.

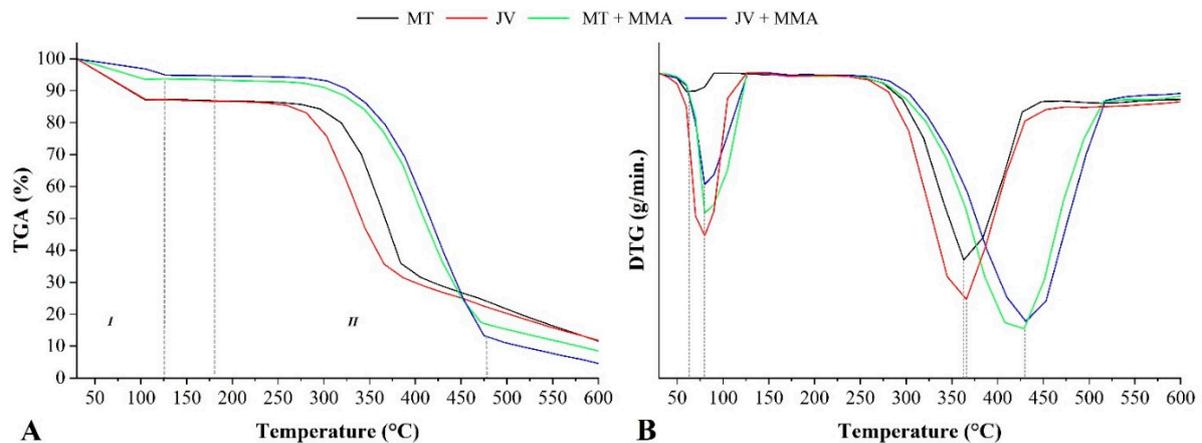


Figure 2. Thermogravimetric analysis (TGA) (A) and DTG (derived from thermogravimetry) (B) curves for MMA-treated and untreated mature (MT) and juvenile (JV) woods from pine.

The MMA-treated woods presented smaller mass loss (JV \approx 10% and MT \approx 5%) in the first region (from 30 °C to 125 °C), which is attributed to simple loss of moisture, confirming that the treatments also induces decreased equilibrium moisture contents. In the second region (from 160 °C to 460 °C), that corresponds to the degradation of hemicellulose and cellulose, the MMA-treated woods prolonged (in approximately 70 °C) the higher peak (i.e., higher thermal degradation in the DTG curve), when compared with their respective control groups. This is proven by the analysis of extrapolated temperatures associated to the beginning (T_{ONset}) and ending (T_{ENDset}) of the studied woods (Table 4).

Morphological details can be seen in Figure 3, which shows two SEM images taken at different magnifications for the JV treated by MMA impregnation. Most of the wood tracheids were fully or partly (as highlighted in white colour) filled by the MMA.

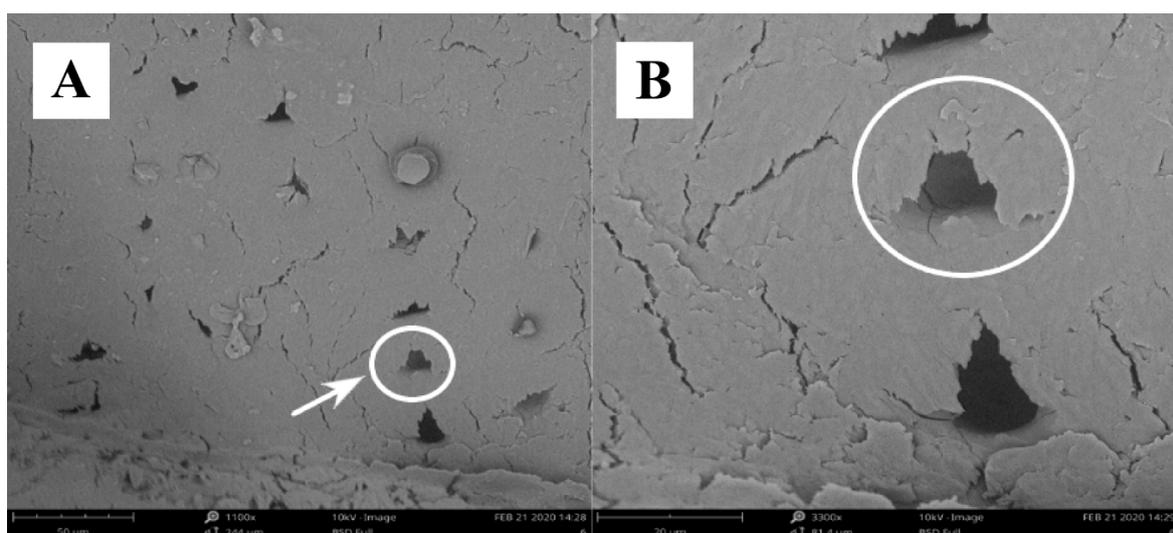


Figure 3. Morphology of treated wood samples; Approximation of 1100× (A) and approximation of 3300× (B).

Table 4. Main thermal events related to the thermal gravimetric analyses.

Groups	Region I		Region II	
	T _{ONset} (°C)	T _{ENDset} (°C)	T _{ONset} (°C)	T _{ENDset} (°C)
MT	30	105	320	386
JV	30	105	288	365
MT + MMA	30	105	349	465
JV + MMA	30	126	352	470

JV: juvenile wood; MT: mature wood; MMA: methyl methacrylate.

4. Discussion

The ρ was larger for MT when compared to the JV. The treatment with MMA significantly increased this property for both of them (increases of about 80% and 70% for JV and MT, respectively), when compared with the respective control groups. Moreover, the treatment with this monomer significantly reduced the M_C of both the JV and MT (reduction of about 60%).

Normally, JV develops within the first 10–20 growth rings from the pith and presents low density, low stiffness, and poor dimensional stability [22]. This is due to the smaller and shorter fibres in the JV, which also present thinner walls and larger microfibril angles when compared to those of the MT [23]. These characteristics facilitate the impregnation, flow and polymerization of the MMA within the wood, making the JV more susceptible to present a high WPG. Depending on anatomical features, it is well known that monomer loading directly influences WPG [24,25].

This WPG also directly reflects on the increase in ρ . In fact, there was an insignificant change in volume, since most of the synthetic monomers fill the lumens and do not penetrate inside the cell wall. This increase in ρ was also observed in previous studies of impregnation with MMA in jaborite [26], and poplar hybrid woods [27], woods with similar ρ compared to the present study reaching increases in ρ of 34% and 200%, respectively. The impregnation with MMA leads to changes in physical properties of wood, mainly due to its hydrophobic nature [21,26,28]. Once the wood is rich in hydroxyl groups with high affinity with water, the polymerized monomer forms a physical barrier inside the wood lumens, which reduces the availability of OH groups on the wood cell wall and directly reflects in the decrease in M_C , since leads impaired desorption and absorption of moisture on overall the wood [7].

This behaviour is also observed for the MOR under bending, wherein JV and MT showed significant increases of 25% and 66%, respectively, compared to their respective untreated ones. While the MOE presented a significant increase for MT (17%), the increase of this parameter in JV (13%) did not differ from the control group. In contrast, significant increases in the B_T for both JV and MT were observed.

The increases in mechanical properties due to the MMA impregnation were also observed in others studies [7,29,30]. This can be attributed to the filling of cellular lumens with the polymer segments of high mechanical properties, which act as mechanical supports from inside the wood pores. The impregnated polymer serves as a conductor and stabilizer of tensions from inside the wood cell wall, leading to increases in strength, while the small increase in MOE may be associated with the plastic nature of the polymer used [27,31]. Also, there is a hardening mechanism, marked by increases in brittleness and hardness, due to the plastic nature of the polymerized MMA, as evidenced in the present study and confirmed by Koubaa et al. [6].

Comparing only the FT-IR spectra of both the pristine JV and MT, the former showed some peaks associated with lignin with smaller intensities (1645 cm^{-1} , 1510 cm^{-1} and 1460 cm^{-1}) when compared to those belonging to the MT. Also, compared to the JV, the MT presented smaller intensities in certain peaks corresponding to cellulose and hemicellulose (i.e., 1740 cm^{-1} and 1370 cm^{-1}). This proves that the JV and MT present different amounts of primary compounds (c.a. cellulose, hemicellulose and lignin) [14,32].

Regarding the impregnation of MMA in the MT (Figure 1A), increases in the intensities of peaks at 1740, 1260, 1150, 710 and 660 cm^{-1} were noted, while the peaks in the wavenumbers of 1645, 1510, 1030 and 870 cm^{-1} presented slight decreases. The spectra of JV presented decreases in the peaks at 1740, 1370, 1220 (shifted to $\approx 1260 \text{ cm}^{-1}$) and 870 cm^{-1} , while the intensities at wavenumbers of 1030 and 1510 cm^{-1} increased (Figure 2B). When compared to their respective control groups, these changes in the spectra of treated woods may be explained by the filling of the cell wall lumens, possible bonds between the functional groups of the wood and monomer, or overlap of some bands that belong to the MMA with that spectrum related to the wood itself, as in the case of C=O bonds of lignin and MMA in 1730 cm^{-1} [5,30,31].

The peak 1720 cm^{-1} is associated with C=O in carboxylic groups and corresponds to two main components of wood: lignin and hemicellulose. This finding also indicates what possibly happened to the monomer inside the lumen, in other words, there were strong bonds between the monomer and both lignin and hemicelluloses from wood.

For instance, the peak at 1030 cm^{-1} corresponds to the elongation in C–O bonds and deformation in C–H bonds in guaiacyl units, which indicates the presence of the three main wood components: cellulose, hemicellulose and lignin. Gallio et al. [15] reported that reductions in this peak for their treated MT and increases in this peak for their treated JV. It is probably due to the high absorption of MMA on the wood cell wall in the JV, promoting a strong chemical change, which was captured by this peak.

However, the mass loss at the end of the second thermal region event ($\approx 430 \text{ }^\circ\text{C}$) was higher for those woods treated with MMA, possibly due to the degradation of the monomer. Among the main chemical compounds, the hemicellulose is the most thermally unstable, while lignin undergoes a slow thermal degradation (by means of complex transformations) from 220 $^\circ\text{C}$ until almost 400 $^\circ\text{C}$ [33].

The polymerization using MMA probably increased the thermal stability of the wood due to the physical barrier formed during the polymerization process and filling of the wood lumen [33], avoiding the degradation of wood compounds. In general, the MT tends to present a high thermal stability due its high amounts of cellulose and hemicellulose. The MMA exhibits a high resistance when subjected to high temperatures with a maximum degradation peak at approximately 400 $^\circ\text{C}$, and becoming totally degraded at approximately 425 $^\circ\text{C}$ [21,34].

The wood cell wall seems to have been penetrated by the MMA, which was also reported in some previous studies [28]. According to Georgianna et al. [35], impregnated vinyl monomers fill the capillaries, vessels, and other void spaces in the wood structure, where the MMA attaches itself to the wood cell wall, becoming a protective barrier [36]. This morphological feature explains the gains found in mechanical and thermal properties.

5. Conclusions

The impregnation of MMA into both the JV and MT provided improvements in all their evaluated physical properties, especially for the JV, due to its large tracheids, leading to a high WPG. Regarding the mechanical properties, although there were increases in hardness, MOE and MOR, the treatment also increased the wood brittleness. TG results indicated that both the MMA-treated JV and MT woods presented higher thermal stabilities than their respective untreated ones. FT-IR spectra and SEM images confirmed the presence of the MMA inside the wood, but it is not clear if the MMA is chemically linked to the wood. Further studies may include hygroscopic and bonding properties in order to ascertain the potential of this treated wood for outdoor use.

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