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Thermochemical and hygroscopicity properties of pinewood treated by *in situ* copolymerisation with methacrylate monomers

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ABSTRACT

This study aims to evaluate the hygroscopicity and thermochemical properties of pine wood/polymer composites prepared by *in situ* polymerisation of methyl methacrylate (MMA) using glycidyl methacrylate (GMA) and methacrylic acid (MAA) as cross-linkers. The pine wood samples were impregnated in a vacuum/pressure system and polymerised in an oven at 90 °C for 10 h, using benzoyl peroxide at 1.5 wt.% as catalyst. The composite was characterised through dynamic wettability, water uptake and dimensional stability tests, ATR-IR spectroscopy, TGA, and DSC. ATR-IR spectra show an increase of the peaks at 1746, 1460, and 1145 cm^{-1} corresponding to the chemical structures of the polymers into the pores and capillaries of treated wood. The TGA and DSC analysis pointed out a chemical interaction between the copolymer and the wood cell wall in composites with GMA and MAA. The composites prepared with MMA presented improvements for the hygroscopicity and dimensional stability properties by 50%. However, the addition of GMA and MAA resulted in the best increases for hydrophobicity and dimensional stability of the samples, ~65–78%.

1. Introduction

Among the main inherent characteristics of wood, hygroscopicity is the most restrictive in its application. The wood capacity for water sorption from its surroundings leads to a series of interconnected technological problems, which are limiting. Problems related to increased wood moisture include dimensional swelling, variation of density, and increased susceptibility to biodegradation. All these issues may result in irreversible damage to wood structures.

These inconvenient characteristics are mainly due to the hydroxyl groups from the macromolecules in the wood cell wall. Such OH groups are highly prone to hydrogen bonds. Besides, numerous micro cavities in the cell walls serve as means for the movement of free water within the wood [1]. Linking of these reactive sites or blocking the cell wall micro cavities are good strategies to make wood less hygroscopic and improve its dimensional stability.

Therefore, several techniques used to modify the chemical structure of the wood rely on the substitution or elimination of reactive hydroxyl groups on the cell wall. These techniques can be of thermal nature, such as thermo rectification [2] or hydro thermal treatment [3], thermochemical, as the treatment with heated oil [4], as well as thermo mechanical modification with heat compression [5]. In addition, the technique of cold plasma deposition [6] and the preparation of wood/polymer composites by *in situ* polymerisation [7,8] are used mainly to increase hydrophobicity and dimensional stability in wood.

The fabrication of wood/polymer composites (WPC) by *in situ* polymerisation of unsaturated monomers within wood pores (vessels and capillaries) has gained considerable attention in recent decades. That is because not only does WPC have easy applicability in the industry, but also, the treatment does not degrade the structural components of the wood.

In order to develop this process, studies have been performed in several countries such as Canada [9,10], Poland [11], India [12], China [13], Malaysia [7], Sweden [14], Turkey [15], Brazil [16], and others. These studies used low quality wood from fast growing plantations such as pine, poplar, beech, and rubber. The prepared composites by *in situ* polymerisation of monomers (e.g. methyl methacrylate, glycidyl methacrylate, styrene, acrylonitrile, furfuryl alcohol, and others) were water repellent, as well as dimensionally stable.

The interest of the use of methyl methacrylate (MMA) in these composites centres on the characteristics of this monomer. MMA monomer is inexpensive and accessible, mainly due to the large

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production in the Asian industry (China, Singapore and South Korea), has easy synthesis, is stable, translucent, and can be catalysed by different methods. However, due to a lack of interaction between the poly(MMA) and wood [9,17], we tested the application of methacrylic acid (MAA) as a cross-linker and coupling agent in order to promote a cross-linked copolymer graphitised onto the wood cell wall. We also used glycidyl methacrylate (GMA) in order to compare the results, since wood/polymer composites prepared by *in situ* polymerisation using the GMA are found in the literature [13,18,19].

This work was encouraged because copolymers based on weak acids such as poly(MAA) are of great interest in various application fields [20–22] due to the ability of the system to change significantly upon variations according to applications and synthesis. The presence or absence of specific end-groups can also cause significant changes in the final material properties as well as in the polymer reactivity, mainly after subsequent copolymerisation reactions [23]. In this context, the application of poly(MMA-*co*-MAA) and poly(MMA-*co*-GMA) as reinforcement for low quality woods is interesting and viable.In light of these considerations, we aim to evaluate the hygroscopicity and thermochemical properties of pine wood/polymer composite prepared by *in situ* polymerisation of methyl methacrylate (MMA) using glycidyl methacrylate (GMA) and methacrylic acid (MAA) as cross-linkers.

2. Material and methods

2.1. Materials

Pinus taeda wood was provided by a local sawing company (Madarco, S.A.) from Pelotas, RS, Brazil. Pinewood samples were prepared from defect free wood, cut into blocks of 1.5 × 1.5 × 2.5 cm^3 (thickness, width and length, respectively) for dimensional stability, water uptake, and contact angle tests. 15 samples were used for the tests in each composite and control wood, totalling 90 samples.

All chemicals were purchased from Sigma–Aldrich and used as received. Benzoyl peroxide (BPO) obtained from Vetec Química Fina (Brazil) was used as the heat catalyst.

2.2. Preparation of wood/polymer composites

The samples were oven-dried at 90 ± 2 °C, until constant weight (∼2 days) and then cooled in a silica gel desiccator. The monomeric solutions were prepared according to Table 1 and 1.5 wt.% of benzoyl peroxide was added and homogenised in the solution by magnetic stirrer.

The samples were submitted to vacuum at 600 mmHg during 30 min using a stainless cylinder. After that, the solution was released into the cylinder followed by pressurization by compressed air at 6 atm for 1 h. After impregnation, the excess chemicals were wiped off from the surfaces. Then, the samples were wrapped in aluminium foils and underwent to polymerisation at 90 ± 2 °C for 10 h.

Table 1
Specification of the pine wood/polymer composites.

Code treatment	%			wt.%
	MMA	GMA	MAA	BPO
W (control)	–	–	–	–
W/M	100	–	–	1.5
W/M:G (2:1)	66.5	33.5	–	1.5
W/M:G (3:1)	75	25	–	1.5
W/M:A (2:1)	66.5	–	33.5	1.5
W/M:A (3:1)	75	–	25	1.5

MMA: methyl methacrylate; GMA: glicidil methacrylate; MAA: methacrylic acid; BPO: benzoyl peroxide (the letters of the code treatments corresponding to – W: wood; M: methyl methacrylate; G: glicidil methacrylate; A: methacrylic acid).

2.3. Weight percent gain (WPG)

Weight percent gain (WPG) after polymer loading was calculated according to Eq. (1), as previously mentioned in other studies [7,9,12,24].

$$\mathrm{WPG} = \frac{W_\mathrm{p} - W_0}{W_0} \times 100 \qquad (1)$$

where W_p = weight of sample after the treatment; W_0 = weight of sample before the treatment.

2.4. Infrared spectroscopy (ATR-IR)

The infrared spectra was qualitatively used for evaluating the chemical structure of untreated pine wood and the wood/polymer composite samples were measured by a Nicolet Nexus 570 equipment, with attenuated total reflectance device (ATR-IR), in direct transmittance at a resolution of 4 cm^{-1} for 32 scans in the range of 700 cm^{-1} to 4000 cm^{-1}. The alignment of the light equipment and the background spectra were ensured before all the tests.

2.5. Thermal analysis (TGA and DSC)

The thermogravimetric curve (TG) and the derivative (DTG) were obtained in a DTG-60 equipment from Shimadzu. For this, we used an inert atmosphere with nitrogen gas flow of 50 ml min^{-1}, temperature range between 25 and 600 °C, and heating rate of 10 °C min^{-1}. The weight of the samples ranged from 5–8 mg inside a platinum pan for allocating the samples in the device.

Shimadzu DSC-60 was the employed equipment. DSC thermograms were obtained from 3–4 mg of sample into an aluminium pan immersed in an inert nitrogen atmosphere (gas flow of 20 ml min^{-1}) at a heating rate of 10 °C min^{-1}. Samples were heated from room temperature to 100 °C and kept under isothermal conditions for 10 min, after which they were heated to 600 °C.

2.6. Dynamic wettability

The dynamic wettability was evaluated on 5 samples (stabilised at 20 °C temperature and 65% relative humidity), in the tangential and radial anatomical sections of each composite and control woods. Measurements of wettability were performed using a Dataphysics 0CA goniometer (sessile droplet method). The contact angle was determined by the placement of a deionized water droplet (5 μl) on three distinct points (randomly selected) of each sample (15 measurements per anatomical section) and in different times, namely after 5, 20, 35, 50, 65,80 and 95 s.

2.7. Water uptake tests

The hydrophobicity of the composites was evaluated by the percentage of weight of water absorbed (%WA) and water absorption rate (AR). The %WA and AR curves were established by measuring the weight of the samples after 2, 4, 8, 12, 24, 48, 72 and 96 h of immersion in fresh water, in order to prepare a absorption kinetics. The % WA and AR were calculated by the Eqs. (2) and (3), respectively.

$$\%\mathrm{WA} = \frac{W_\mathrm{f} - W_\mathrm{i}}{W_\mathrm{i}} \times 100 \qquad (2)$$