



Comparison of different treatments based on glycerol or polyglycerol additives to improve properties of thermally modified wood

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Abstract

Impregnation of European beech (*Fagus sylvatica*) with 10% w/w aqueous solution of different additives made from the reaction of glycerol or polyglycerol with glycidyl methacrylate or maleic anhydride followed by thermal modification at 150, 200 or 220 °C under inert conditions was investigated to evaluate potential synergies between chemical and thermal treatments. Treated and untreated wood were analysed to evaluate mass changes and bulking values after treatments, resistance of treatment to leaching, wettability, anti-swelling efficiency, modulus of elasticity (MOE), modulus of rupture (MOR), decay resistance against *Coriolus versicolor* and termite resistance against *Reticulitermes flavipes*. Results revealed that synergic effects between a combination of light chemical modification and thermal treatments can be observed at higher temperature treatments (200 and 220 °C), improving wood dimensional stability (approximately 80%), decay, and termite resistance properties. However, MOE and MOR values decreased by approximately 30% and 60%, respectively. Treated samples resulting from the combination of chemical and thermal treatment performed at 220 °C present improved durability against the termites *R. flavipes*.

1 Introduction

Non-biocidal wood preservation systems have been in demand since several decades. In general, these systems can be derived in the following two ways: thermal treatment and chemical modification (Gérardin 2016). Thermal treatment of wood is one of the alternative processes that have been widely studied and even applied in industrial scale to overcome the problem of wood dimensional stability (Militz 2002; Weiland and Guyonnet 2003; Esteves and Pereira 2009; Dubey et al. 2012) and decay durability (Kamdem et al. 2002; Hakkou et al. 2006). However, thermally modified woods present poor resistance to termites (Surini et al.

2012; Sivrikaya et al. 2015) limiting their utilization. On the other hand, chemical modifications involving impregnation of active chemicals into the wood is the other alternative to overcome the utilization of biocidal substances (Rowell et al. 2009; Esteves et al. 2011; Militz et al. 2011). Chemically modified woods, like furfurylated or acetylated wood, present better characteristics similar to those of most durable tropical wood species. Moreover, treatments can be applied to a lower temperature process minimizing degradation of wood compared to thermal treatment. The main drawback of these methods is their significant costs due to the large amount of chemicals required to achieve chemical modification.

In an attempt to find cost-effective wood modification systems, the use of a combination of wood thermal modifications in the presence of low concentrations of different derivatives of polyglycerol (polyglycerol-maleic anhydride and polyglycerol methacrylate) has been reported (Roussel et al. 2001; Soulounganga et al. 2004; Salman et al. 2014, 2016). These modifications allowed not only to improve wood properties similarly to what was generally observed in thermal modifications, but also to improve wood termite resistance in contrast to treatments performed only by heat. The use of polyglycerol in the additive formulation was

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based on the fact that the reticulated structure of this bio-sourced polyol obtained from glycerol permits the formation of different derivatives able to be fixed in the wood structure, consequently allowing stabilization of the wood cell wall polymers as a result of interactions of impregnated polymers with wood hydroxyl groups (Roussel et al. 2001; Soulounganga et al. 2004). However, polyglycerols [such as PG3 used in previous studies (Roussel et al. 2001; Soulounganga et al. 2004; Salman et al. 2014, 2016, 2017)], which are available from industry, present generally a low degree of polymerization, making them not so different from glycerol itself used as starting material. Consequently, the utilization of more easily available glycerol could be of interest to substitute PG3 avoiding previous dehydration of glycerol into polyglycerol. In order to evaluate the behaviour of the new glycerol-based additives (glycerol-maleic anhydride and glycerol methacrylate), this comparative study was carried out using either glycerol or polyglycerol-based additives to develop wood treatments based on a combination of light chemical modification and thermal treatments carried out at different temperatures (150, 200, 220 °C) under inert condition. As a substrate, European beech (*Fagus sylvatica* L.), known for its poor natural durability and low dimensional stability properties, was used in this study. Ultimately, the general goal of this study also was to develop a non-biocidal wood preservation system.

2 Materials and methods

2.1 Sample preparation

European beech wood samples with moisture content of approximately 10%, free from knots and defects were used in this experiment. Prior to the experiment, the wood samples were air-conditioned under ambient conditions [20 °C/60% of relative humidity (RH)].

All chemicals were purchased from Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France) as reagent grade. Polyglycerol was purchased from Novance (Compiègne, France) as a mixture of compounds with an average molecular weight (Mw) of 242 g mol⁻¹ (degree of polymerization ~ 3), with 99% in purity.

Four kinds of treatment solutions were investigated: polyglycerol/maleic anhydride adduct (PG-MA), glycerol/maleic anhydride adduct (Gly-MA), polyglycerol/glycidyl methacrylate (PG-GM), and glycerol-glycidyl methacrylate (Gly-GM). Four curing temperatures (103, 150, 200 and 220 °C) were tested during this study. For each additive solution, 96 samples measuring 30 × 15 × 5 mm³ and 40 samples measuring 190 × 20 × 5 mm³ (L, R, T) were used for the four curing temperatures. Samples were also treated at the four curing temperatures without any chemical treatment.

2.2 Additive formulation

PG-MA was made according to Roussel et al. (2001). 1 mol of polyglycerol (PG3, Mw = 242 g mol⁻¹) was reacted with 2 mol of maleic anhydride (MAH, Mw = 98.06 g mol⁻¹) in a beaker glass equipped with magnetic stirrer and glass watch, and heated at 80 °C for 3 h. The reaction was then stopped after disappearance of ATR-FTIR absorption of carbonyl group (C=O, stretch) of anhydride maleic reagent at about 1780 and 1853 cm⁻¹ and complete appearance of a characteristic ester band (C=O, stretch) of PG-MA at about 1715 cm⁻¹. The product was directly used without further purification and dissolved into distilled water so that the final concentration of the impregnation solution (additive solution) was 10% w/w. Gly-MA was prepared using the same procedure as for PG-MA.

PG-GM was made according to Soulounganga et al. (2004). 1 mol of polyglycerol (PG3, Mw = 242 g mol⁻¹) was reacted with 0.02 mol of 4-(dimethylamino)pyridine (4-DMAP, Mw = 122.17 g mol⁻¹) as a catalyst and 2 mol of glycidyl methacrylate (GM, Mw = 142.15 g mol⁻¹) in a beaker glass equipped with magnetic stirrer and glass watch, and heated at 70 °C for 15 min. The reaction was then stopped after complete appearance of a characteristic ester band (C=O, stretch) of PG-GM by means of ATR-FTIR at about 1716 cm⁻¹, and diminution of hydroxyl group (-OH, stretch) of polyglycerol at 3331 cm⁻¹ and epoxy group (stretch) of glycidyl methacrylate at 906 cm⁻¹. The product was directly used without further purification and dissolved in distilled water, so that the final concentration of the impregnation solution was 10% w/w. Just before the impregnation process, about 2% w/w of methylethylketonperoxide was added and mixed. Gly-GM was prepared using the same procedure as for PG-GM.

2.3 Wood modification

All oven-dried (103 °C until mass stabilization) beech samples were weighed (m_0) and their volumes were recorded (V_0), then exposed to vacuum conditions (8–10 kPa for 10 min) in an autoclave followed by the impregnation process in 10% w/w aqueous additive solution for 1 h under vacuum (5–10 kPa). Afterward, the pressure was brought to 100 kPa (ambient pressure), then the wood samples were exposed to a pressure of 1200 kPa for 1 h. Finally, the pressure was turned down to ambient condition. All samples were then air-conditioned for 24 h, dried at 103 °C, weighed until constant mass (m_1) and their volumes were re-recorded (V_1). Samples were then divided into four groups; one group that was only dried at 103 °C was kept, and the remaining three groups

were cured at 150, 200 or 220 °C for 20 h under nitrogen. All modified woods were then re-weighed (m_2) and their volumes were re-recorded (V_2). Non-impregnated beech woods were also prepared at each curing temperature as wood controls.

2.4 Leaching test

Leaching tests were conducted according to a procedure adapted from NF X 41-568 (2014). Six samples [$30 \times 15 \times 5 \text{ mm}^3$, (L, R, T)] from each treatment (additive-treated wood and wood control from different curing temperatures) were submerged in 72 ml of distilled water and subjected to six leaching periods (1, 2, 4, 8, 16, 48 h) under continuous shaking ($175 \text{ linear shakes min}^{-1}$) at 20 °C. Between the periods of 4 and 8 h, samples were removed and kept without water for 16 h. After leaching periods were completed, samples were dried at 103 °C for 48 h and re-weighed (m_3).

From the wood modification and the leaching test, mass changes were calculated using the following equation (Eq. 1):

$$\Delta m (\%) = 100 \times (m_1 \text{ or } m_2 \text{ or } m_3 - m_0) / m_0 \quad (1)$$

where Δm is the mass change of additive-treated wood or wood control at different curing temperatures before or after leaching process, m_0 is the initial mass of wood at 103 °C before treatment, m_1 is the mass of additive-treated wood at 103 °C, m_2 is the mass of additive-treated wood or wood control at higher temperature (150, 200 or 220 °C), and m_3 is the mass at 103 °C of additive-treated wood or wood control at different curing temperatures after leaching process.

Bulking values during wood modification were calculated from the following equation (Eq. 2):

$$\Delta V (\%) = 100 \times (V_1 \text{ or } V_2 - V_0) / V_0 \quad (2)$$

where ΔV is the percentage of bulking value of additive-treated wood or wood control at different curing temperatures during modification, V_0 is the dry volume of wood before treatment (initial volume), V_1 is the dry volume of additive-treated wood at 103 °C, V_2 is the dry volume of additive-treated wood and wood control at 150, 200 or 220 °C.

Weight loss due to leaching was calculated from the following equation (Eq. 3):

$$WL_L (\%) = 100 \times (m_1 \text{ or } m_2 - m_3) / m_1 \text{ or } m_2 \quad (3)$$

where WL_L is the percentage of weight loss value of additive-treated wood or wood control at different curing temperatures due to leaching, m_3 is the dry mass (at 103 °C) of additive-treated wood or wood control at different curing temperatures after leaching.

2.5 Wettability

Wettability was measured by the water drop test adapted from the method by Engonga et al. (1999). The contact angle of a water droplet on the wood surface was measured by means of Drop Shape Analysis system DSA10 MK2 instrument from Krüss. Contact angles of three samples [$30 \times 15 \times 5 \text{ mm}^3$, (L, R, T)] of additive-treated wood and wood control at different curing temperatures were measured precisely. For each measurement, the contact angle was recorded automatically every 22 s until 114 s.

2.6 Anti-swelling efficiency (ASE)

The method used in this study refers to Pfriem et al. (2012). Wood samples [$30 \times 15 \times 5 \text{ mm}^3$, (L, R, T)] from different curing temperatures were dried at 103 °C and their volumes were recorded (V_d). Samples were directly immersed in distilled water and placed under vacuum condition (10 kPa) for 30 min. Pressure was then returned to atmospheric pressure, and the samples were immersed in water for 24 h. Three cycles of drying-soaking system were conducted so that data of dried volume (V_d) and wet volume (V_w) in every cycle were collected. Swelling (S) and anti-swelling efficiency (ASE) values were calculated from the following equations (Eqs. 4 and 5), respectively.

$$S (\%) = (V_w - V_d) / V_d \quad (4)$$

where S is the percentage of swelling of the wood sample, V_d is the dry volume (at 103 °C) of the wood sample, V_w is the wet volume of the wood sample.

$$ASE (\%) = 100 \times (S_0 - S_1) / S_0 \quad (5)$$

where ASE is the percentage of anti-swelling efficiency of additive-treated wood or wood control from different curing temperatures, S_0 is the swelling of untreated wood, S_1 is the swelling of additive-treated wood or wood control from different curing temperatures.

2.7 Modulus of elasticity (MOE) and modulus of rupture (MOR)

These three point bending measurements were conducted according to EN 310 (1993). Samples of each additive-treated wood and wood control [$190 \times 20 \times 5 \text{ mm}^3$, (L, R, T)] were conditioned in a climatic chamber with the following conditions, at 22 ± 2 °C and relative humidity of $65 \pm 5\%$ RH, until constant mass. Dimensions of all samples were re-measured (l, b, t). The increment in load and displacement values of each sample was measured by means of INSTRON 4467 universal testing machine. MOE/MOR values were then calculated as follows (Eqs. 6 and 7):

$$MOE (\text{N/mm}^2) = [l^3 (F_2 - F_1)] / [4bt^3 (a_2 - a_1)] \quad (6)$$

where l is the distance between the centers of support in millimeters, b is the width of the sample in millimeters, t is the thickness of the sample in millimeters, $F_2 - F_1$ is the increase in load in newton on the cross section of the load-deformation curve, F_1 should be approximately 10% and F_2 approximately 40% of the breaking load, $a_2 - a_1$ is the increase in deflection at mid-length of the test sample (corresponding to $F_2 - F_1$).

$$\text{MOR (N/mm}^2\text{)} = (3 F_{\text{max}} l) / (2 bt^2) \quad (7)$$

where F_{max} is the breaking load in newton.

2.8 Decay resistance

Decay tests were performed according to the procedure described by Bravery (1978). Sterile culture medium prepared from malt (40 g) and agar (25 g) (purchased from Sigma-Aldrich) in distilled water (1 l), was placed in culture 9 cm Petri dishes, inoculated with a small piece of mycelium of a freshly grown pure culture of *Coriolus versicolor* Quélet (CV) [Linnaeus, CTB 863 A] and incubated for 2 weeks at 22 ± 2 °C and $70 \pm 5\%$ RH to allow full colonization of the medium by the mycelium.

Wood samples [$30 \times 15 \times 5$ mm³, (L, R, T)] were sterilized in an autoclave at 121 °C for 20 min. In each petri dish, three specimens (two treated and one untreated wood) were inserted. Each experiment was repeated three times. Virulence controls were also performed on nine specimens of beech wood. Incubation was carried out for 16 weeks in a climatic chamber (at 22 ± 2 °C and $70 \pm 5\%$ RH). Once the fungal exposure was completed, samples were cleaned carefully from the fungus. All samples were then oven dried at 103 °C for 48 h and weighed (m_4). Mass loss after decay test was calculated as follows (Eq. 8):

$$\text{ML (\%)} = 100 \times (m_0 \text{ or } m_1 \text{ or } m_2 \text{ or } m_3 - m_4) / m_0 \text{ or } m_1 \text{ or } m_2 \text{ or } m_3 \quad (8)$$

where ML is the mass loss of additive-treated wood or wood control from different curing temperatures before or after leaching due to decay, m_4 is the mass (at 103 °C) of wood sample after decay test.

2.9 Termite resistance

Durability against termite was examined by using the non-choice screening test based on EN 117 (2013) against *Reticulitermes flavipes* (ex. *santonensis*). All tests were performed on additive-treated wood and wood control from different curing temperatures, previously subjected to leaching, as well as untreated wood as virulence. Three replicates from each treatment were tested. Each sample

was put in 9 cm diameter Petri dish containing 40 g Fontainebleau sand (4 volume of sand/1 volume of deionized water). Plastic mesh was used as a support for sample to avoid water saturation. In total, 50 termite workers, one nymph, and one soldier were introduced in each Petri dish. The Petri dishes were placed in a dark climatic chamber at 27 ± 1 °C with a relative humidity of 75%. After 4 weeks, the samples were removed and cleaned off the sand, and the number of termites still alive (n) were counted to determine their survival rate (Eq. 9). The samples were dried at 103 °C, weighed, and mass losses due to termite attacks were calculated (Eq. 10).

$$\text{Survival rate (\%)} = 100 \times n / 50 \quad (9)$$

where n is the number of the remaining live termite workers after the test, while 50 is the number of the termite workers added for the test.

$$\text{ML}_t (\%) = 100 \times (m_3 - m_5) / m_3 \quad (10)$$

where ML_t is the mass loss due to the termite attack of additive-treated wood or wood control treated at different temperatures after leaching, m_3 and m_5 are respectively the dried mass (at 103 °C) of additive-treated wood and wood control treated at different temperatures before and after termite attack.

2.10 Thermogravimetric analysis (TGA)

This analysis was performed to investigate the thermal stability of additive, additive-treated wood, and untreated wood by means of TGA/DSC1-TMA/SDTA 84Xe instrument from Mettler Toledo equipped with STARE v.11 fr System program. Twenty milligram (± 1.00 mg) of pure polyglycerol, glycerol, all types of dried pure additives and dried fine powder samples of additive-treated and untreated wood at 103 °C curing condition were placed on alumina crucibles (their exact mass was weighed automatically by the instrument). Afterward, their thermal stabilities (based on the mass loss) at any level of temperature set were measured by the instrument.

Temperature (T), time (t), and gas flow rate (v) conditions were set as follows:

1. T = 25–103 °C, t = 8 min, air condition (v = 5 ml/min);
2. T = constant at 103 °C, t = 15 min, air condition;
3. T = 103–220 °C, t = 10 min, N₂ condition (v = 10 ml/min);
4. T = constant at 220 °C, t = 120 min, N₂ condition (v = 10 ml/min);
5. T = 220–300 °C, t = 8 min, N₂ condition (v = 10 ml/min);
6. T = constant at 300 °C, t = 60 min, N₂ condition (v = 10 ml/min);
7. T = 300–25 °C, t = 25 min, N₂ condition (v = 10 ml/min).

Mass loss data of the sample in every set of temperatures were recorded automatically. By knowing the mass loss data of each component in treated wood, a mass loss estimation of additive-treated wood could be calculated and a mass loss difference between actual and estimation could be projected as an interaction/behavior of the additive to the wood. Mass loss estimation and its difference with mass loss actual were calculated as follows:

$$\text{Mass loss TGA estimation} = [\text{Additive}] \times \text{MLA} + (1 - [\text{Additive}]) \times \text{MLB} \quad (11)$$

$$\text{Mass loss difference} = \text{Mass loss TGA actual} - \text{Mass loss TGA estimation} \quad (12)$$

where [Additive] is the percentage of additive in treated wood at 103 °C curing condition, MLA is the mass loss of pure additive, MLB is the mass loss of untreated beech wood (without additive).

2.11 Statistical analysis

Statistical analysis was performed by means of Minitab 16 software using one-way ANOVA with Tukey multiple comparison method ($\alpha=0.05$) for identifying differences

in response individually, and two-way ANOVA analysis of variance with $\alpha=0.05$ for identifying differences among the additives and differences among the curing temperatures.

3 Results and discussion

Data concerning mass changes during the different treatment steps and effect of chemical modifications on leaching and bulking properties of additive-treated wood and wood control from different curing temperatures are reported in Table 1.

Replacement of polyglycerol by glycerol in each additive formulation did not affect Δm values after impregnation of 10% w/w aqueous solution of the additives and drying at 103 °C. Due to thermally induced degradation, curing at higher temperatures caused in all cases a decrease in Δm values for both additive-treated wood and wood control, corroborating previous results using PG-MA and PG-GM at different concentrations and curing temperatures (Salman et al. 2014, 2017). Among the different treatments, treatments involving utilization of glycerol instead of polyglycerol presented the highest mass changes with negative values for higher curing temperatures indicating a stronger effect of thermal degradations due to temperature compared to the

Table 1 Mass changes before and after leaching, bulking values, and mass loss due to leaching of additive-treated wood and wood control at different curing temperatures

Temperature (°C)	Additive	Δm (%)		WL_L^b (%)	ΔV^c (%)
		Before leaching ^a	After leaching ^a		
103	PG-MA	10.0 ± 0.6 (ab)	2.0 ± 0.4 (c)	7.3 ± 0.9 (ab)	9.9 ± 1.7 (ab)
	Gly-MA	9.7 ± 0.5 (ab)	2.2 ± 0.4 (bc)	6.8 ± 0.5 (bcd)	11.5 ± 1.8 (ab)
	PG-GM	10.7 ± 0.7 (a)	1.6 ± 0.4 (c)	8.2 ± 0.9 (a)	10.4 ± 1.4 (ab)
	Gly-GM	7.6 ± 0.6 (cd)	0.6 ± 0.5 (cd)	6.4 ± 0.9 (bcd)	4.7 ± 2.3 (def)
	None	0 (h)	-1.4 ± 0.3 (ef)	1.4 ± 0.3 (hi)	0 (gh)
150	PG-MA	8.3 ± 1.2 (bcd)	5.6 ± 1.0 (a)	2.5 ± 0.6 (ghi)	8.9 ± 1.5 (abc)
	Gly-MA	8.9 ± 0.6 (abc)	4.6 ± 0.4 (a)	4.0 ± 0.4 (ef)	11.0 ± 1.3 (a)
	PG-GM	10.2 ± 1.1 (ab)	3.9 ± 0.7 (a)	5.8 ± 0.6 (cd)	11.5 ± 1.4 (a)
	Gly-GM	6.9 ± 0.6 (de)	1.4 ± 0.5 (c)	5.2 ± 0.4 (de)	5.4 ± 2.3 (de)
	None	-0.1 ± 0.2 (h)	-1.8 ± 0.2 (ef)	1.7 ± 0.3 (hi)	0.5 ± 0.2 (gh)
200	PG-MA	3.2 ± 1.5 (fg)	0.9 ± 1.5 (cd)	2.3 ± 0.9 (ghi)	7.4 ± 0.6 (bcd)
	Gly-MA	1.9 ± 1.2 (g)	-0.8 ± 1.9 (de)	2.6 ± 1.2 (fgh)	6.3 ± 0.7 (cd)
	PG-GM	5.0 ± 0.4 (ef)	2.3 ± 0.4 (cd)	2.6 ± 0.6 (ghi)	8.9 ± 0.5 (abc)
	Gly-GM	-1.4 ± 0.9 (hi)	-2.9 ± 0.6 (fg)	1.5 ± 0.4 (hi)	2.1 ± 0.7 (fg)
	None	-2.5 ± 0.4 (ij)	-4.2 ± 0.3 (gh)	1.7 ± 0.1 (hi)	-1.7 ± 0.7 (h)
220	PG-MA	-3.1 ± 1.2 (ij)	-5.3 ± 1.2 (h)	2.4 ± 0.6 (ghi)	2.9 ± 1.0 (efg)
	Gly-MA	-5.6 ± 1.2 (kl)	-8.9 ± 1.1 (i)	3.6 ± 0.4 (fg)	2.8 ± 1.7 (efg)
	PG-GM	-4.0 ± 1.0 (jk)	-5.9 ± 0.7 (h)	1.9 ± 1.0 (hi)	2.9 ± 2.6 (efg)
	Gly-GM	-7.2 ± 1.5 (l)	-8.6 ± 1.3 (i)	1.5 ± 0.7 (hi)	-2.6 ± 0.8 (h)
	None	-10.5 ± 1.1 (m)	-11.6 ± 1.0 (j)	1.2 ± 0.3 (i)	-6.4 ± 0.7 (i)

Value was the average of ^a6 replicates; ^b6 replicates; ^c5 replicates

Values followed by the same letter in parentheses do not differ significantly ($\alpha=0.05$) based on one-way ANOVA test using Tukey multiple comparison

increased mass due to additive impregnation. This result might be greatly influenced by the lower molecular mass of glycerol compared to polyglycerol. The result corroborates another similar study using glycerol in wood thermal modification indicating that glycerol could accelerate degradation during thermal treatments (Yan and Morrell 2014; Liu et al. 2018). At the same temperature, this effect was more pronounced in Gly-GM treatment compared to Gly-MA. Unlike the high polarity of carboxylic group of Gly-MA adducts, the lower polarity of methacrylic group of glycidyl methacrylate reduced the penetration of the additive into wood cell wall. The lowest bulking value (ΔV) of Gly-GM wood samples confirms the lower affinity of this additive to penetrate into the wood cell wall. In case of wood modified by maleic anhydride-based additives, the use of glycerol instead of polyglycerol was obviously not different for their Δm values particularly at 103 °C and 150 °C curing conditions. At 200 °C and 220 °C curing conditions, the difference became more apparent, where Gly-MA-treated wood showed higher mass loss, which was confirmed by the present TGA results.

Data concerning a thermal stability of all additive-treated woods and their pure additives are presented in Table 2.

Based on TGA data, all additive-treated woods present higher mass loss actual than untreated wood in the same analytical condition. The highest mass loss values observed was for Gly-MA-treated wood, followed by PG-MA, Gly-GM, and the last was PG-GM. These results confirm the Δm data that mass change values of wood treated with maleic anhydride-based additives gave higher mass loss than wood treated with glycidyl methacrylate-based additives. According to the mass losses obtained and estimation of TGA data, the higher mass loss difference of Gly-MA and PG-MA-treated wood compared to Gly-GM and PG-GM-treated

wood indicated that acidity associated with maleic anhydride-based additives could accelerate wood degradation. A more acidic property of maleic-anhydride based additives presumably was the cause of these phenomena. Similar results were also reported in a related research by Bodiriau et al. (2008) indicating that maleic anhydride-treated wood has lower thermal stability.

Based on the leaching data, samples treated with PG-MA present slightly higher resistance to leaching (lower WL_L values) than samples treated with Gly-MA at higher curing temperatures. However, leaching is important, particularly for samples dried at 103 °C, and decreased progressively as the curing temperature increased indicating that higher temperatures improved fixation of the product. These results might be due to the possibility of polyglycerol to lead to more reticulated structures, particularly at higher curing temperatures (150, 200, 220 °C). In contrast, PG-GM-treated wood shows slightly higher WL_L values than Gly-GM-treated wood at all curing temperatures. The less reactive methacrylic group in PG-GM or Gly-GM was a possible reason for their difficulties to reticulate within the wood, especially at lower curing temperatures (103 and 150 °C). On the other hand, mass losses (Δm) of wood control treated at 200 or 220 °C are more important than mass losses of additive-treated wood at the same temperature indicating that some impregnated additives still remain in wood after curing at high temperature. Considering the quantity of additives impregnated in wood, the observed mass losses indicate that some partial degradations of additives occurred during treatment. Nevertheless, the lower differences between mass changes (Δm) before and after leaching caused by heat-induced wood degradation at these higher

Table 2 Mass loss of pure additives, additive-treated and untreated wood based on TGA actual measurement and estimation

No.	Samples	Mass loss TGA (%)								
		Actual			Estimation			Differences		
		103–220 °C	220 °C	Total	103–220 °C	220 °C	Total	103–220 °C	220 °C	Total
		(8 min)	(2 h)	103–220 °C	(8 min)	(2 h)	103–220 °C	(8 min)	(2 h)	103–220 °C
1	PG-MA pure	4.91	7.29	12.2	–	–	–	–	–	–
2	Beech-PG-MA	3.88	10.92	14.8	1.41	9.92	11.33	2.47	1	3.47
3	Gly-MA pure	6.49	14.47	20.96	–	–	–	–	–	–
4	Beech-Gly-MA	4.74	13.13	17.87	1.6	10.64	12.24	3.14	2.49	5.63
5	PG-GM pure	1.22	7.91	9.13	–	–	–	–	–	–
6	Beech-PG-GM	2.37	9.42	11.79	1.06	9.96	11.02	1.31	-0.54	0.77
7	Gly-GM pure	3.47	19.9	23.37	–	–	–	–	–	–
8	Beech-Gly-GM	4.23	10.54	14.77	1.24	10.99	12.23	2.99	-0.45	2.54
9	Beech wood	1.04	10.2	11.24	–	–	–	–	–	–
10	PG pure	0.66	7.91	8.57	–	–	–	–	–	–
11	Gly pure	56.9	94.19	100	–	–	–	–	–	–

thermal conditions emerged obviously indicating a better additive fixation to the wood.

All additives induced an important bulking of wood cell wall with ΔV values between 4.7 and 11.5% proportional to Δm values. This bulking effect was still obvious after treatments at 150 °C, however, due to thermally induced degradation, it started to decrease for treatments performed at higher temperatures. Samples treated with Gly-GM at 220 °C presented high shrinkage similarly to heat-treated samples, while a low bulking effect was still visible for the three other treatments.

Data concerning dimensional stability and mechanical properties of additive-treated wood and wood control at different curing temperatures are presented in Table 3.

ASE values (at the cycle III) increased with the increase in curing temperature. Additive-impregnated wood showed higher ASE values than wood control at the same temperature indicating that dimensional stability of wood increased by incorporating chemical and thermal modification treatments. Among the additives, PG-MA and Gly-MA treatments gave higher ASE values than other treatments at all curing temperatures. Similar ASE values were also reported by Epmeier et al. (2004), using impregnation with 15–20% aqueous solution of Gly-MA made from 1/3 molar ratio of glycerol/maleic acid. Other related researches that also used maleic anhydride system for wood modification gave ASE

values superior to 40% (Iwamoto and Itoh 2005; Liu et al. 2012; Essoua et al. 2015). Glycerol-based additives gave slightly better results than polyglycerol-based additives independent of the curing temperature. This may be due to a better penetration of glycerol-based additives into the wood cell wall leading to a better dimensional stability. Yan and Morrell (2014) also reported similar results indicating that thermal treatment of glycerol-impregnated wood gave higher ASE due to the residual glycerol in the wood cell wall and/or in the lumen. In general, the increase in dimensional stability of additive-treated wood combined with heat treatment might be due to possible chemical modifications through formation of new chemical bonds between additives and wood or polymerization of additive into the wood structure, thermal modification reducing wood hydrophilicity and shrinkage through reticulation reaction.

MOE and MOR values of the additive-treated wood were always lower than those of untreated samples cured at the same temperature. Indeed, for the same treatment temperature, impregnation of wood samples with different additives resulted in a slight decrease in MOE and MOR independent of the nature of the additive indicating that interaction of impregnated additives within cell wall polymers induced wood strength loss. The reduction in these mechanical properties was probably influenced by the acidic property of the additive solution at the origin of wood polysaccharides

Table 3 Dimensional stability and mechanical properties of additive-treated wood and wood control at different curing temperatures

Temperature (°C)	Additive	ASE ^a (%)	MOE ^b (N/mm ²)	MOR ^b (N/mm ²)
103	PG-MA	46.1 ± 2.0 (ef)	9479 ± 1088 (c)	96 ± 18 (bcde)
	Gly-MA	46.5 ± 4.9 (e)	9205 ± 876 (c)	89 ± 11 (cde)
	PG-GM	32.1 ± 2.2 (gh)	9837 ± 1009 (c)	119 ± 15 (ab)
	Gly-GM	32.4 ± 1.7 (gh)	9827 ± 1174 (c)	112 ± 14 (abc)
	None	13.1 ± 3.8 (i)	12459 ± 1389 (ab)	132 ± 17 (a)
150	PG-MA	48.1 ± 4.6 (e)	10723 ± 748 (bc)	88 ± 11 (cdef)
	Gly-MA	55.0 ± 4.5 (de)	10392 ± 946 (c)	85 ± 14 (def)
	PG-GM	34.3 ± 7.6 (fg)	10480 ± 915 (c)	116 ± 18 (def)
	Gly-GM	23.6 ± 7.8 (ghi)	10395 ± 816 (c)	112 ± 15 (abc)
	None	21.6 ± 6.3 (hi)	12801 ± 1243 (ab)	134 ± 17 (a)
200	PG-MA	61.7 ± 3.2 (cd)	10328 ± 960 (c)	75 ± 9 (efg)
	Gly-MA	69.0 ± 4.6 (abc)	9283 ± 1381 (c)	63 ± 12 (fgh)
	PG-GM	51.6 ± 7.1 (de)	9904 ± 827 (c)	84 ± 15 (def)
	Gly-GM	54.3 ± 2.2 (de)	10584 ± 1253 (bc)	86 ± 16 (def)
	None	49.4 ± 2.5 (e)	12933 ± 2046 (ab)	102 ± 19 (bcd)
220	PG-MA	74.7 ± 4.4 (ab)	9254 ± 1048 (c)	53 ± 12 (gh)
	Gly-MA	78.2 ± 1.9 (a)	9318 ± 1523 (c)	54 ± 27 (gh)
	PG-GM	73.0 ± 4.2 (abc)	8902 ± 959 (c)	51 ± 7 (gh)
	Gly-GM	75.6 ± 6.7 (ab)	8888 ± 969 (c)	48 ± 11 (h)
	None	63.5 ± 2.3 (bcd)	10490 ± 1880 (c)	58 ± 11 (gh)

Value was the average of ^a4 replicates at 3rd cycle of ASE; and ^b10 replicates

Values followed by the same letter in parentheses do not differ significantly ($\alpha=0.05$) based on one-way ANOVA test using Tukey multiple comparison

degradation. According to Yan et al. (2011), the reduction in mechanical properties for glycerol-treated wood above 120 °C was assumed to be due to the degradation of hemicellulose and/or lignin network. A significant difference for the reduction in MOE for additive-treated wood in comparison with wood control is also presented according to one-way ANOVA test using Tukey multiple comparison at $\alpha=0.05$. MOR was in all cases more affected by the different treatments (chemical, thermal or thermochemical) than MOE. The effects of curing temperature behave differently according to MOE or MOR (Kuboijima et al. 2000; Boonstra et al. 2007; Yildiz and Gümüşkaya 2007). The MOE of heat-treated wood first increased with increase in the temperature, then decreased in a second time for higher temperatures, whereas the MOR will decrease continuously as temperature increases. This condition happened at 150 °C curing condition, where MOE of the differently treated samples increased comparatively to samples treated at 103 °C, while at higher temperatures (200 and 220 °C) it decreased gradually. On the other hand, MOR values decreased gradually with the increase in curing temperature. No significant differences were observed for MOR and MOE values when replacing polyglycerol by glycerol (based on Tukey comparison method).

Figure 1 reports the evolution of water contact angles with time on the surface of wood samples subjected to the different treatments.

Water contact angle measurement is a possible technique to study the modification performance (Moghaddam 2015).

Based on Fig. 1, wettability of the additive-treated wood and wood control decreased (contact angle increased) with the increase in curing temperature confirming some previous research that the surface of heat-treated wood behaved more hydrophobic (Pétrissans et al. 2003; Hakkou et al. 2005). At 103 and 150 °C, maleic anhydride-based additive treated wood, PG-MA and Gly-MA had more hydrophobic properties than glycidyl methacrylate-based additive treated wood. This may be due to a lower penetration of Gly-GM and PG-GM in the wood cell wall due to the lower polarity of these additives compared to Gly-MA and PG-MA resulting in the presence of hydrophilic polyol moiety on the wood surface. Nevertheless, both maleic anhydride- and glycidyl methacrylate-based systems have more or less similar wettability properties independent of the nature of the polyol used. In other words, the most important parameter influencing wettability was the curing temperature.

Results of decay and termite resistance analysis are presented in Table 4.

According to the results (Table 4), durability of additive-treated wood and wood control against *C. versicolor* (CV) was improved with the increase in curing temperature. Even though the resistance of beech against CV increased as the curing temperature increased, confirming literature data (Hakkou et al. 2006), a combination of thermal and chemical treatment improved efficiently its resistance capability. This is particularly obvious for treatments performed at 200 °C, where a combination of both treatments allowed good protection of un-leached treated samples, while heat-treated

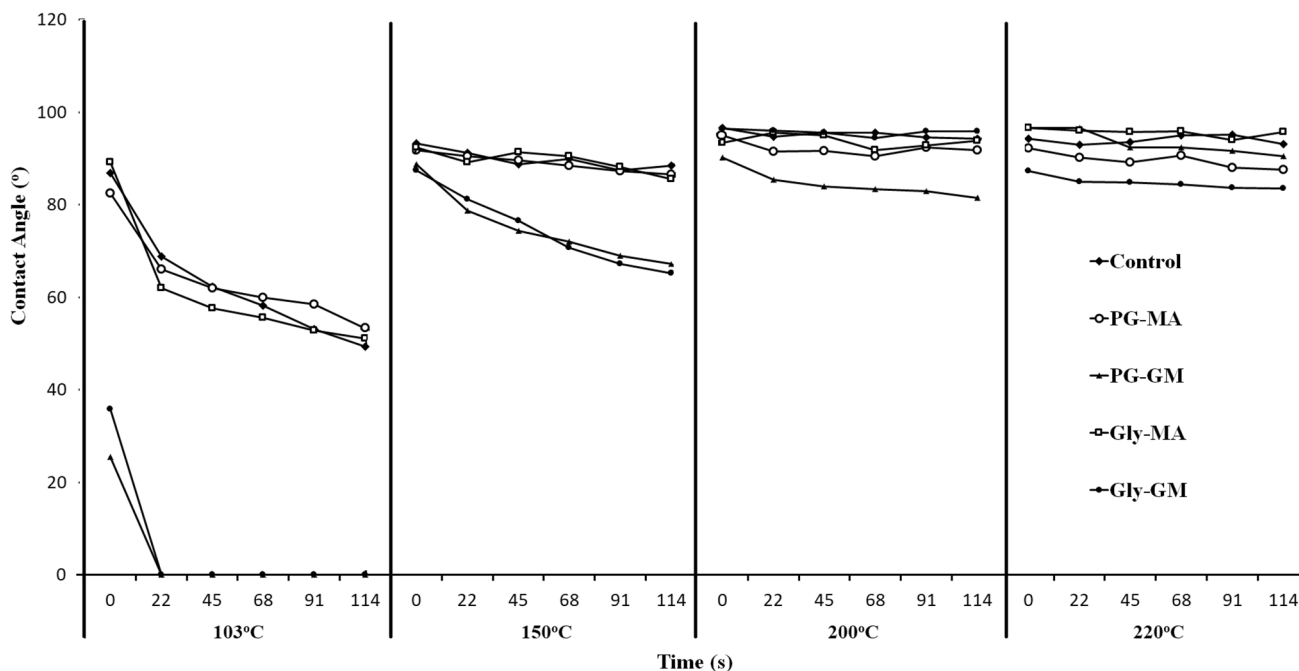


Fig. 1 Evolution of water contact angle on wood samples treated with the different additives and cured at different temperatures

samples without additive impregnation at the same temperature presented important mass losses under the experimental condition (according to Tukey comparison method). Additive impregnation permitted to envisage reduction in the severity of heat treatment conditions (temperature and duration) to achieve full protection of wood. After leaching, PG-MA and Gly-MA samples heat-treated at 200 °C were still resistant to CV degradation, while PG-GM and Gly-GM presented higher mass losses resulting probably from the leaching of the impregnated chemicals. In all cases, no significant difference was observed after the replacement of polyglycerol by glycerol. Impregnation of maleic anhydride-based additives followed by heat treatment at 200 °C highlighted a synergic effect between chemical and thermal treatments leading to a better decay resistance of wood samples compared to those treated at lower curing temperatures. These results are consistent with previous results (Salman et al. 2017). At 220 °C, all treatments permitted improvement of durability of beech samples against CV resulting from the cumulative effect of thermal and chemical modifications. Even if the temperature at 220 °C is believed to be responsible for durability improvement (Lekounougou et al. 2009; Gérardin 2016), further experiments will be necessary

in this case to evaluate more precisely synergistic effects between both treatments.

Termite resistance analysis was examined by non-choice screening tests using *R. flavipes* (Table 4). All additive-treated wood after leaching presented lower mass loss values against the termite than non-impregnated wood cured at the same temperature. In this latter case, increase in curing temperature has less effect on the improvement of the durability. Almost all additive-impregnated wood presented lower mass losses than un-impregnated samples even after leaching indicating a potentially beneficial effect of chemical treatment in this system. Further, at higher curing temperature, even though additive-treated samples were slightly attacked by the termites, the survival rates of the termites remained high indicating that the treatment can be considered as non-biocidal treatment. Reduction in degradation increased with the increase in curing temperature. Reduction in ML_t ranged between 4 to 65% depending on the additive used compared to the virulence sample. At 220 °C, PG-MA and Gly-MA-treated woods gave quite similar results indicating that there is no significant difference between glycerol and polyglycerol, while PG-GM-treated wood presented slightly better results than Gly-GM-treated wood. PG-MA

Table 4 Decay and termite durability improvement of wood blocks subjected to different treatments

T (°C)	Additive	Decay resistance		Termite resistance	
		ML (%) before leaching ^a	ML (%) after leaching ^b	ML_t (%) after leaching ^c	Survival rate ^c (%)
103	PG-MA	7.6 ± 1.1 (cd)	24.1 ± 5.2 (def)	3.9 ± 0.6 (ab)	3 ± 3 (cd)
	Gly-MA	7.85 ± 0.6 (cd)	29.3 ± 6.0 (cde)	3.7 ± 0.8 (ab)	0 ± 0 (d)
	PG-GM	7.8 ± 1.3 (cd)	45.3 ± 5.5 (a)	6.7 ± 3.5 (ab)	61 ± 15 (ab)
	Gly-GM	6.8 ± 0.6 (de)	45.0 ± 9.7 (a)	7.0 ± 1.5 (ab)	67 ± 10 (ab)
	None	24.2 ± 1.7 (a)	42.4 ± 6.3 (abc)	7.9 ± 3.8 (ab)	65 ± 5 (ab)
150	PG-MA	5.3 ± 3.1 (defg)	32.7 ± 3.2 (bcd)	5.4 ± 1.0 (ab)	51 ± 15 (ab)
	Gly-MA	3.5 ± 0.4 (efgh)	21.4 ± 1.9 (ef)	4.5 ± 0.7 (ab)	34 ± 3 (bcd)
	PG-GM	11.3 ± 5.8 (bc)	36.2 ± 2.4 (abc)	3.2 ± 1.1 (b)	29 ± 22 (bcd)
	Gly-GM	5.9 ± 1.0 (def)	30.9 ± 2.3 (cde)	6.9 ± 0.9 (ab)	77 ± 15 (a)
	None	21.2 ± 0.9 (a)	41.8 ± 7.4 (ab)	5.1 ± 1.2 (ab)	57 ± 6 (ab)
200	PG-MA	0.9 ± 0.5 (h)	3.1 ± 3.0 (g)	7.7 ± 1.2 (ab)	64 ± 12 (ab)
	Gly-MA	0.3 ± 0.3 (h)	0.7 ± 0.8 (g)	4.0 ± 1.5 (ab)	46 ± 7 (ab)
	PG-GM	3.6 ± 2.1 (efgh)	15.1 ± 2.3 (f)	4.8 ± 1.4 (ab)	47 ± 2 (ab)
	Gly-GM	2.7 ± 2.3 (fgh)	13.7 ± 7.4 (f)	5.8 ± 1.2 (ab)	63 ± 5 (ab)
	None	14.0 ± 2.1 (b)	21.3 ± 2.6 (ef)	9.7 ± 0.9 (a)	74 ± 2 (a)
220	PG-MA	0.0 ± 0.2 (h)	-0.4 ± 0.2 (g)	3.8 ± 0.7 (ab)	40 ± 7 (abc)
	Gly-MA	-0.3 ± 0.2 (h)	-0.2 ± 0.2 (g)	2.8 ± 1.8 (b)	41 ± 20 (abc)
	PG-GM	0.2 ± 0.3 (h)	3.3 ± 1.0 (g)	5.1 ± 5.3 (ab)	29 ± 30 (bcd)
	Gly-GM	0.2 ± 0.2 (h)	0.6 ± 1.0 (g)	5.8 ± 1.5 (ab)	62 ± 12 (ab)
	None	1.7 ± 1.2 (gh)	1.6 ± 0.9 (g)	8.6 ± 2.2 (ab)	55 ± 13 (ab)
Virulence		29.7 ± 1.3	51.2 ± 3.5	8.0 ± 1.0	81 ± 9

Value was the average of ^a6 replicates with five weeks incubation period; ^b5 replicates with twelve weeks incubation period; and ^c3 replicates. Values followed by the same letter in parentheses do not differ significantly ($\alpha=0.05$) based on one-way ANOVA test using Tukey multiple comparison.

Table 5 Differences among the additives and the curing temperatures according to the results of different parameter analysis using two-way ANOVA analysis of variance with confidence level 95%

Differences	Δm	ΔV^b		WL_L^a	ASE ^c	MOE ^d	MOR ^d	Decay resistance		Termite resistance	
		Before leaching ^a	After leaching ^a					ML before leaching ^a	ML after leaching ^b	MLt after leaching ^e	Survival rate ^e
Value	F(157.8) > P(0)	F(197.23) > P(0)	F(83.51) > P(0)	F(22.6) > P(0)	F(38.22) > P(0)	F(31.72) > P(0)	F(24.67) > P(0)	F(64.06) > P(0)	F(23.41) > P(0)	F(6.26) > P(0)	F(9.47) > P(0)
Additive											
PGMA	ab	b	a	b	a	b	c	bc	b	ab	b
GlyMA	b	ab	b	ab	a	b	c	c	b	ab	b
PGGM	a	a	a	a	b	b	b	b	a	ab	b
GlyGM	c	c	c	ab	b	b	b	bc	a	ab	a
None	d	d	d	c	c	a	a	a	a	a	a
Differences	Δm	ΔV^b		WL_L^a	ASE ^c	MOE ^d	MOR ^d	Decay resistance		Termite resistance	
Value	F(64.1.97) > P(0)	F(150.23) > P(0)	F(457.53) > P(0)					F(65.1) > P(0)	F(164.03) > P(0)	F(16.19) > P(0)	F(123.45) > P(0)
T Curing (°C)											
103	a	a	b	a	c	b	a	a	a	a	b
150	b	a	a	b	c	a	a	a	a	a	ab
200	c	b	c	c	b	ab	b	b	b	a	a
220	d	c	d	c	a	c	c	c	c	c	ab

Number of samples during analysis was ^a24; ^b20; ^c16; ^d40; ^e12; letter(s) in grouping are arranged from the highest (a) to the lowest range of the result values based on two-way ANOVA analysis; the same letter in one parameter analysis column means do not differ significantly ($\alpha=0.05$) based on confidence interval of two-way ANOVA analysis

and Gly-MA-impregnated samples cured at 103 °C presented the lowest mass loss compared to other treatments. Acidity of these additives could also be the possible reason of these better performances. At higher curing conditions, esterification reactions took place favoring fixation of these additives into the wood limiting acidity, which resulted in a decrease in termite durability.

According to analysis of variance using two-way ANOVA with 95% confidence level (Table 5), almost all additives treated wood presented significant differences compared to wood treated without additive. Among all the additives, wood treated with maleic anhydride-based additives (PG-MA and Gly-MA) showed higher differences in ASE, MOR, and ML due to decay test after leaching analysis in comparison with wood treated with glycidyl methacrylate-based additive and wood control. Effect of treatment temperature alone also influenced properties of the modified woods, however, treatments at low temperatures (103 and 150 °C) gave quite similar results for most of the examined properties (bulking, ASE, MOR, and ML due to decay before and after leaching analysis). Treatments at 200 and 220 °C gave on the other hand significant differences indicating that chemical modification with low concentration additives combined with thermal modification acted synergistically under these thermal conditions.

4 Conclusion

The results revealed that replacement of polyglycerol by glycerol did not induce an important change in the reactivity of additives prepared from maleic anhydride or glycidyl methacrylate. Depending on the investigated properties, utilisation of glycerol or polyglycerol may offer some slight advantages. In most cases, treatments involving glycerol (Gly-MA and Gly-GM) led to slightly better dimensional stability than treatments with polyglycerol (PG-MA and PG-GM), while more or less similar behaviours were observed for resistance to leaching, wettability, mechanical properties and biological durability tests at higher curing temperatures. Among all additives tested, maleic anhydride-based additives (Gly-MA and PG-MA) showed better performance compared to additives prepared from glycidyl methacrylate. Although in all cases the mechanical properties of the additive-treated woods were slightly lower than those of the wood control, a combination of chemical and thermal treatments permitted improvement of durability to *C. versicolor* and *R. flavipes* due to synergistic effect between the two kinds of treatment. These effects are particularly obvious at 200 °C for decay durability and 220 °C for termite durability tests, in particular for wood treated with maleic anhydride-based additives. However, further experiments will be necessary to investigate in more detail

these synergistic effects and their effect on wood durability. Glycerol could be used as a substitute agent for polyglycerol particularly in maleic anhydride-based additive. Ultimately, these results confirmed that a combination of chemical treatment with low additive concentration and thermal treatment could be an alternative as a non-biocidal wood preservation treatment.

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