IMPROVEMENT OF THE DURABILITY OF HEAT-TREATED WOOD AGAINST TERMITES

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ABSTRACT

Thermal modification is an attractive alternative to improve the decay durability and dimensional stability of wood. However, thermally modified wood is generally not resistant to termite attacks, limiting the field of application of such materials. One way to overcome this drawback is to combine thermal modification treatment with an additional treatment. One such treatment is the impregnation of a boron derivative associated with appropriate vinylic monomers, which takes advantage of the thermal treatment to polymerise these monomers for boron fixation. Using this strategy, we recently showed that an impregnation of borax (2 or 4% boric acid equivalent) dissolved in a 10% aqueous solution of polyglycerolmethacrylate followed by thermal treatment under nitrogen at 220°C protects wood from both termite and decay degradations, even after leaching. Additionally, wood samples treated with a 10% polyglycerolmethacrylate aqueous solution and subjected to thermal treatment at 220°C presented improved resistance to termites while avoiding boron utilization. Based on these results, we investigate the effect of impregnation with two types of vinylic monomers, which are already used in the presence of boron, followed by thermal treatments at different temperatures. We evaluate termite and decay durability of wood to evaluate if thermal modification associated with light chemical modification could be a solution for utilization of thermally modified materials in termite-infested areas.

Keywords: Chemical modification, decay, durability, *Fagus sylvatica*, *Pinus sylvestris*, *Reticulitermes flavipes*, thermal treatment.

INTRODUCTION

Wood thermal modification has been the subject of increasing interest over the last decades and is currently considered one of the most promising non-biocide alternatives to improving the performance of low natural durability wood species (Militz 2002, Esteves and Pereira 2009, Gérardin 2016). However, even if wood decay resistance and dimensional stability are improved, termite resistance is not sufficient to permit its use in termite-infested areas (Mburu et al. 2007, Shi et al. 2007, Surini et al. 2012, Sivrikaya et al. 2015). On the contrary, thermally modified wood is generally more susceptible to termite attacks than untreated wood (Sivrikaya et al. 2015, Salman et al. 2016). Termite

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resistance improvements to thermally modified wood are crucial for future development of thermo-modified materials. In this context, it was recently demonstrated that thermo-modified wood samples previously impregnated with boron in the presence of water soluble vinylic monomers, which are used to limit boron depletion, induced full protection of samples from termite attack and decay (Salman et al. 2014, Salman et al. 2016). Surprisingly, it was also observed that control samples treated with polyglycerolmethacrylate only and cured at 220°C were resistant to termites, while thermally modified blocks without treatment were strongly degraded. Considering the increase in interest in developing non-biocide wood protection treatments, it is critical to test mild chemical modifications based on the impregnation of vinylic monomers, followed by a thermal treatment that can lead to higher biological resistance. Even though previously developed chemical treatments, such as acetylation, DMDHEU or furfurylation, have claimed to enhance wood protection against termites (Wang et al. 2002; Gascón-Garrido et al. 2013), the advantages of the present approach is to reduce the chemical usage that is necessary to achieve wood protection. The aim of this paper is to evaluate different treatments based on thermal modification (150, 180, 200 and 220°C) of samples impregnated with a 5 or 10% aqueous solutions of two vinylic monomers, polyglycerolmethacrylate (PGMA) and polyglycerol/maleic anhydride adduct (AM/PG); we assess the durability of treated wood against different brown and white rot fungi as well as termites.

EXPERIMENTAL

Materials

Wood blocks (15 mm by 5 mm in cross section, 30 mm along the grain) of Scots pine sapwood (*Pinus sylvestris L.*) and beech (*Fagus sylvatica*) were used in this study. One hundred sixty-eight replicates were used for each treatment solution. Forty-two samples were used for each treatment temperature (150, 180, 200 and 220°C), and half of these samples were subjected to leaching. All chemicals were purchased from Fluka Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France). Polyglycerol was furnished by Solvay as a mixture of compounds with an average molecular weight of 242 (n ~ 3).

Synthesis of additives

Maleic anhydride/polyglycerol adducts (MA/PG) and polyglycerol methacrylate (PGMA) were synthesized according to previously published procedures (Roussel *et al.* 2001, Soulounganga *et al.* 2003).

Block impregnation

Maleic anhydride/polyglycerol adducts and polyglycerolmethacrylate were dissolved with distilled water at 5 and 10% (m/m). Wood blocks were oven dried at 103°C and weighed (m_0). Wood samples were placed in a beaker inside a desiccator equipped with a two-way tape and subjected to vacuum at 5 mbar for 15 min. The treatment solution was then introduced into the beaker so that all blocks were completely covered by the solution. Blocks were kept immersed for 30 min at atmospheric pressure, removed from the impregnation solution, kept for 16 hours at ambient temperature, dried at 103°C for 48 hours and weighed (m_1). Weight percent gain (WPG) was calculated according to the following formula:

$$WPG\ (\%) = 100\ \text{Í}(m_1 - m_0)/m_0$$

where m_0 is the initial anhydrous mass, and m_1 is the anhydrous mass of treated wood samples.

Heat treatment

Thermal modification was performed under nitrogen using a Carlo Erba GC oven. Samples were placed in a 500-mL reactor for 20 hours at four different temperatures (150, 180, 200 and 220°C). The oven temperature was increased by 20°C min^{-1} from ambient to final temperature. Weight loss due to thermal degradation (WL$_{TT}$) was calculated according to the formula:

$$WL_{TT}(\%) = 100 \, Í \, (m_1 - m_2) \, / \, m_1$$

where m$_1$ is the initial sample anhydrous mass before heat treatment, and m$_2$ is the anhydrous mass of the same sample after heat treatment.

Leaching procedure

Leaching was performed according to a procedure adapted from the NF X 41-569 standard (2014). Samples (twenty-one replicates) were immersed in 240 mL of distilled water and subjected to six leaching periods of increasing duration under continuous shaking at 20°C. Water was replaced after each leaching period after 1 hour, 2 hours and 4 hours. Samples were then removed and air-dried for 16 hours. Additional leaching periods were conducted for 8 hours, 16 hours and 48 hours with water replacement between each. Blocks were finally dried at 103°C for 48 hours and weighed (m$_3$). Weight loss due to leaching was calculated as follows:

$$WL_L \, (\%) = 100 \, Í(m_2 - m_3)/m_2$$

where m$_2$ is the pre-leaching initial anhydrous mass of wood samples after thermal treatment , and m$_3$ is the anhydrous mass of the thermally modified wood samples after leaching.

Thermogravimetric analysis

Thermo gravimetric analysis (TGA) was performed on 10-mg samples under nitrogen using a Mettler Toledo TGA/DSC STARe system to investigate the thermal behaviour of impregnated wood and vinylic monomers. The analysis was run under nitrogen at a purge rate of 50 mL/min. Approximately 20 mg of sample was heated from 25 to 220°C at a rate of 10 °C/min.

Decay tests

Decay resistance was evaluated according to a procedure modified from EN 113 (1986) described by Bravery (1979). Pine samples were exposed to *Coniophora puteana* ((Schumacher ex Fries) Karsten, strain BAM Ebw. 15) and *Poria placenta* ((Fries) Cooke sensu J. Eriksson, strain FPRL 280), while beech wood samples were exposed to *Coriolus versicolor* ((Linneus) L. Quélet strain CTB 863 A) and *Coniophora puteana* (six replicates for each fungus). Sterile culture medium was prepared from malt (40 g) and agar (20 g) in distilled water (1 L) and placed in 9-cm diameter Petri dishes. After jellification of the medium, each Petri dish was inoculated with a small piece of mycelium of freshly grown pure culture and incubated for 2 weeks at 22°C and 70% relative humidity, providing full colonization of the surface by mycelium. All wood samples were autoclaved at 121°C for 20 min.; three specimens (two treated and one control) were placed in each Petri dish. Each experiment was conducted in tripli-

cate. Virulence controls were also performed on twelve specimens of untreated Scots pine and beech. Incubation was carried out for 16 weeks at 22°C under 70% RH in a climatic chamber. Once the fungal exposure was complete, mycelium was removed, and specimens were weighed in order to evaluate their moisture content at the end of the fungal exposure. The specimens were then dried at 103°C, and their final weight recorded. The moisture content at the end of the test (data not shown) and mass losses were determined. Mass loss (ML) was expressed as a percentage of initial oven-dry weight of the wood sample according to the formula:

$$ML\ (\%) = 100 \times (M_{0\ OR\ 2\ OR\ 3} - M_4)/M_{0\ OR\ 2\ OR\ 3}$$

where m4 is the wood sample's final anhydrous mass after fungal exposure, m0 is the initial dry mass of the control sample, m2 is the anhydrous mass of PGMA or MA/PG impregnated (or not) wood samples cured at different temperatures before leaching, and m3 is the anhydrous mass of PGMA or MA/PG impregnated (or not) wood samples cured at different temperatures after leaching.

Termite resistance tests

Termite resistance was evaluated using *Reticulitermes flavipes* (ex. *santonensis*) termites using a non-choice test based on the guidelines of the European standard EN 117 (2013). Prior to the test, each sample was dried at 103°C in order to obtain its anhydrous initial weight (m_0, or m_1 or m_2). For each set of treatments, three replicates were tested for their resistance to termites. Each sample was placed in a 9-cm diameter Petri dish containing 40 g of Fontainebleau sand (4 volume of sand / 1 volume of deionized water). The samples were placed on plastic mesh in order to avoid water saturation. A total of 50 termite workers, one nymph and one soldier were then introduced to the sand. Fifteen controls of pine sapwood or beech were tested in the same manner. The Petri dishes were placed in a dark climatic chamber at 27°C with relative humidity > 75%. After 4 weeks, the samples were removed and cleaned of sand, and the termite survival rate was calculated. The samples were dried at 103°C, and their weight loss was calculated as a % of initial weight.

RESULTS AND DISCUSSION

Tables 1 and 2 show weight percent gains obtained after impregnation with two vinylic monomers and *in situ* resin formation as well as the weight loss caused by thermal modification with or without subsequent leaching for pine and beech samples.

Table 1. Weight change and standard deviation of pine sapwood samples impregnated with different additive concentrations and subjected to heat treatment at different temperatures.

Additive	Concentration (%)	WPG (%)	Temperature (°C)	WL_{TT} (%)	WL_L (%)
PGMA	5	8,79±0,87	150	1,36±0,29	2,78±0,32
			180	3,54±0,65	2,07±0,32
			200	7,74±1,16	2,53±0,55
			220	13,95±2,07	2,85±1,85
PGMA	10	16,89±1,49	150	1,44±0,27	3,7±1,54
			180	4,01±0,81	2,53±0,65
			200	8,51±1,5	2,45±0,38
			220	14,02±2,44	3,57±0,32
AM/PG	5	7,63±0,83	150	1,33±0,23	2,49±0,32
			180	3,49±0,46	2,17±0,28
			200	6,92±0,96	3,25±1,13
			220	11,34±2,1	4,41±2,69
AM/PG	10	16,14±1,45	150	1,85±0,22	3,9±0,41
			180	4,67±0,52	2,04±0,47
			200	7,81±0,98	4,24±1,76
			220	13,25±2,05	5,01±2,84
–	–	–	150	0,46±0,21	2,06±0,65
			180	2,11±1,29	2,05±1,64
			200	5,55±1,28	1,33±0,32
			220	9,12±1,1	1,96±0,23

Table 2. Weight change and standard deviation of beech samples impregnated with different additive concentrations and subjected to heat treatment at different temperatures.

Additive	Concentration (%)	WPG (%)	Temperature (°C)	WL_{TT} (%)	WL_L (%)
PGMA	5	5,76±0,56	150	1,16±0,15	2,07±0,23
			180	2,7±0,51	1,35±0,19
			200	6,41±1,87	1,19±0,27
			220	15,31±2,31	0,9±0,42
PGMA	10	10,85±1,36	150	1,44±0,22	2,35±0,28
			180	3,8±0,63	1,61±0,25
			200	8,83±1,66	0,79±0,32
			220	14,81±2,87	0,87±0,4
AM/PG	5	5,35±0,74	150	1,58±0,22	2,33±0,47
			180	3,75±0,77	1,81±0,52
			200	6,16±1,49	2,20±0,63
			220	15,07±2,29	1,7±0,99
AM/PG	10	8,36±0,88	150	1,83±0,23	1,97±0,33
			180	4,43±0,95	1,33±0,39
			200	9,31±1,82	2,13±0,58
			220	13,21±2,25	1,82±0,52
–	–	–	150	0,43±0,22	1,34±0,23
			180	1,79±0,42	1,36±0,18
			200	6,92±2,34	1,28±0,4
			220	15,01±1,93	1,44±0,46

Weight percent gains depend directly on vinylic monomer concentration in the impregnation solution. Increasing the concentration from 5 to 10% increases the WPG obtained by a factor of two, with pine wood being more easily impregnated than beech wood.

Weight loss after curing increases with treatment temperature. Samples cured at low temperature present weak weight losses, while those treated at 220°C present weight losses up to 15% depending on the impregnation solution and wood species. Independent of treatment, beech samples present generally higher weight losses compared to pine samples impregnated and cured in the same conditions; these results corroborate previous results on the effect of wood species during thermal treatment (Chaouch *et al.* 2010, Chaouch *et al.* 2013). For a given curing temperature, weight losses of impregnated samples are always higher than those of non-impregnated samples, indicating a higher susceptibility of resin treated samples to heat compared to untreated samples. This behaviour may be due to either a lower resin thermal stability or an effect of impregnated vinylic monomers or polymers resulting from the latter on wood thermal stability Therefore, the thermal stability of different vinylic monomers alone or impregnated in pine samples has been investigated using thermo gravimetric analysis (Figure 1).
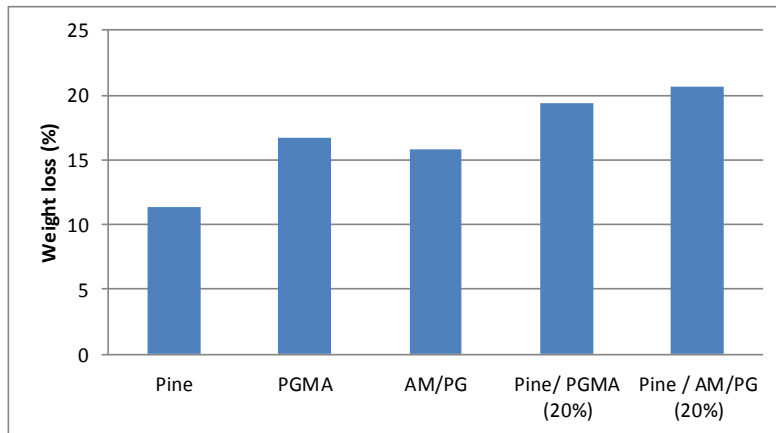
Figure 1. Weight losses recorded after 2 hours at 220°C by thermo gravimetric analysis.

According to results, resin is more sensitive to thermal degradation than pinewood as demonstrated by weight losses of 15,8 and 16,7% obtained for AM/PG and PGMA, respectively, compared to 11,3% for pine wood sawdust. The thermal behaviour of pine wood samples impregnated with a 20% aqueous solution of each vinylic monomer followed by polymerisation indicates a higher weight loss than with wood or resins alone. This behaviour shows the synergistic effect of wood and resins on the thermal stability of impregnated samples. Fixation of the two resins in wood was investigated after the leaching of the samples that were impregnated and cured at different temperatures (tables 1 and 2). Weight losses due to the leaching of extractives comprised between 1,33% and 2,06% for pine wood treated at different temperatures and between 1,28% and 1,44% for beech samples. At the same time, weight losses of pine samples treated with 5 or 10% of PGMA and cured at the different temperatures comprised between 2,07% and 3,47% indicating that a minimal amount of resin was leached from wood. No significant differences were observed between the different curing temperatures, indicating that polymerization of the vinylic monomers was effective from the lowest temperature of 150°C. Similar results were obtained for pine samples impregnated with AM/PG at different concentrations as well as for beech samples treated with the two vinylic monomers. According to these results, the polymerization and formation of resins occurred independently of curing temperature.

Decay resistances of treated and untreated pine wood and beech wood samples are presented in tables 3 and 4.

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Table 3. Weight losses and standard deviation of pine wood samples subjected to different brown rot fungi.

Treatment			Mass loss (%)			
Additive	Concentration (%)	Temperature (°C)	Unleached blocks		Leached blocks	
			Poria placenta	Coniophora puteana	Poria placenta	Coniophora puteana
PGMA	5	150	34,56 ± 3,81	38,09 ± 8,85	40,8 ±7,61	41,36 ± 11,43
		180	36,23 ± 8,10	21,63 ± 9,90	41,12 ± 9,54	36,41 ± 12,16
		200	24,57 ± 1,28	3,06 ± 2,57	27,64 ± 6,65	4,08 ± 1,36
		220	4,02 ± 2,37	0,64 ± 0,24	7,33 ± 2,32	0,51 ± 0,32
PGMA	10	150	40,07 ± 11,65	34,75 ± 4,78	37,3 ± 10,41	40,33 ±13,98
		180	34,42 ± 8,76	5,3 ± 1,79	36,85 ± 6,5	4,15 ± 1,44
		200	4,11 ± 2,03	1,3 ± 0,80	5,24 ± 2,19	2,26 ± 0,37
		220	1,18 ± 0,98	0,9 ± 0,39	0,92 ± 1,16	1,41 ± 0,81
AM/PG	5	150	41,79 ± 6,65	33,1 ± 4,98	41,95 ± 12,09	29,11 ± 10,11
		180	34,1 ± 8,40	11,75 ± 8,43	37,03 ± 11,03	22,75 ± 5,87
		200	22,96 ± 4,79	3,75 ± 2,96	25,57 ± 9,34	4,98 ± 3,65
		220	0,92 ± 1,20	0,69 ± 0,96	1,04 ± 0,70	0,37 ± 0,63
AM/PG	10	150	34,47 ± 10,54	13,17 ±2,68	31,67 ± 7,62	20,9 ± 6,74
		180	25,18 ± 9,96	4,61 ± 2,54	25,74 ± 6,89	6,2 ± 2,72
		200	5,48 ± 1,01	2,15 ± 0,97	11,25 ± 4,94	2,85 ± 1,54
		220	0,81 ± 0,09	0,48 ± 0,78	1,64 ± 0,06	0,93 ± 0,23
–	–	150	45,06 ±14,20	40,07 ± 10,43	49,73 ± 12,84	42,68 ± 11,92
		180	40,89 ± 9,16	40,92 ± 9,92	44,54 ± 11,43	41,61 ± 12,23
		200	23,98 ± 7,61	6,57 ± 2,39	30,6 ± 11,65	8,12 ± 3,27
		220	11,71 ± 3,31	3,97 ± 0,17	30,6 ± 11,65	5,02 ± 1,95
Control			50,41 ± 11,18	45,76 ± 7,22		

Table 4. Weight losses and standard deviation of beech wood samples subjected to different white rot and brown rot fungi.

Treatment			Mass loss (%)			
Additive	Concentration (%)	Temperature (°C)	Before leaching		After leaching	
			Trametes versicolor	Coniophora puteana	Trametes versicolor	Coniophora puteana
PGMA	5	150	41,68 ± 6,56	44,74 ± 2,47	45,01 ± 12,63	42,38 ± 3,40
		180	38,56 ± 3,37	40,89 ± 5,55	45,61 ± 8,23	42,71 ± 10,42
		200	27,2 ± 8,06	7,74 ± 3,45	26,28 ± 10,88	10,83 ± 4,86
		220	2,57 ± 1,95	0,19 ± 0,37	4,63 ± 0,82	0,85 ± 0,36
PGMA	10	150	44,03 ± 3,38	36,48 ± 3,65	42,46 ± 7,17	47,04 ± 6,94
		180	39,34 ± 3,38	28,54 ± 4,22	41,76 ± 4,11	30,12 ± 5,72
		200	20,18 ± 5,38	3,09 ± 1,05	21,84 ± 7,68	6,86 ± 2,57
		220	4,21 ± 2,73	0,7 ± 0,65	3,75 ± 3,51	0,28 ± 0,32
AM/PG	5	150	38,14 ± 3,53	35,18 ± 1,73	41,53 ± 5,42	32,75 ± 6,5
		180	33,56 ± 5,25	25,84 ± 4,86	36,02 ± 5,09	27,51 ± 7,98
		200	10,39 ± 5,28	5,04 ± 2,67	12,39 ± 3,07	3,53 ± 0,52
		220	1,59 ± 1,18	0,31 ± 0,2	2,87 ± 1,64	0,64 ± 0,28
AM/PG	10	150	36,65 ± 4,22	41,02 ± 11,95	40,91 ± 3,08	46,42 ± 7,84
		180	25,16 ± 6,45	14,79 ± 4,98	33,21 ± 6,17	20,31 ± 6,53
		200	12,01 ± 6,52	1,23 ± 0,65	12,26 ± 3,75	2,22 ± 0,22
		220	3,44 ± 1,98	0,24 ± 0,86	3,83 ± 2,7	0,92 ± 0,45
–	–	150	55,97 ± 11,37	55,97 ± 5,82	55,02 ± 8,69	48,79 ± 13,97
		180	50,98 ± 6,35	32,13 ± 8,63	55,61 ± 10,41	40,54 ± 12,36
		200	33,23 ± 8,31	21,18 ± 3,64	31,84 ± 7,41	27,25 ± 9,76
		220	4,46 ± 1,18	0,47 ± 0,75	3,89 ± 0,65	0,89 ± 0,82
Control			52,99 ± 8,84	49,54 ± 9,83	-	-

Independent of the nature and concentration of the vinylic monomers used, all blocks cured at 150 and 180°C present no improvement of durability compared to control samples. Curing at 220°C after vinylic monomer impregnation results in significant durability improvement; all samples were minimally attacked by the tested brown rot and white rot fungi. Treatments performed at 200°C generally did not improve decay durability, although some decay durability was observed in some cases depending on the vinylic monomer solution, fungal strain and wood species that were used. According to these results, it appears that thermal modification and treatment intensity, which are directly connected to final treatment temperature, are the primary considerations in the improvement of durability. The impregnation of low amounts of vinylic monomers in the wood have no effect on durability as demonstrated by mass losses recorded in samples cured at 150 and 180°C, similar to those observed for controls. At higher temperature (220°C), the improvement of durability is similar to that described in the literature during thermal modification (Hakkou *et al.* 2005, Welzbacher *et al.* 2007) indicating that a given level of thermodegradation of wood cell wall polymers should be reached to insure durability against fungi.

The effect of different treatments on termite resistance is described in tables 5 and 6.

Table 5. Weight losses and standard deviation of pine wood samples subjected to termite attack.

Treatment			Weight loss (%)		Survival rate (%)	
Additive	Concentration (%)	Temperature (°C)	Before leaching	After leaching	Before leaching	After leaching
PGMA	5	150	12,74 ± 1,2	15,68 ± 0,2	74	81
		180	13,58 ± 0,76	14,74 ± 1,25	64	77
		200	17,18 ± 3,01	20,79 ± 2,77	82	68
		220	4,17 ± 1,18	8,11 ± 1,5	23	35
PGMA	10	150	13,19 ± 1,44	13,45 ± 1,3	80	76
		180	14,09 ± 1,72	15,93 ± 0,68	73	84
		200	9,32 ± 2,55	13,66 ± 1,55	29	60
		220	3,95 ± 0,74	5,57 ± 2,31	8	24
AM/PG	5	150	9,07 ± 0,61	9,26 ± 0,57	57	53
		180	6,24 ± 1,52	9,55 ± 2,77	25	51
		200	9,11 ± 1,02	10,14 ± 2,57	45	45
		220	5,69 ± 0,51	6,74 ± 0,75	4	20
AM/PG	10	150	2,32 ± 0,58	3,57 ± 1,12	0	6
		180	2,68 ± 0,14	4,88 ± 1,69	0	15
		200	3,03 ± 0,96	4,59 ± 1,81	0	17
		220	1,66 ± 0,46	4,16 ± 0,22	3	5
–	–	150	10,26 ± 0,71	15,38 ± 2,43	66	79
		180	15,17 ± 1,04	17,82 ± 1,92	78	81
		200	16,64 ± 0,38	19,65 ± 3,36	78	79
		220	20,38 ± 4,87	21,75 ± 4,02	72	80
Control			10,64 ± 1,19		75	

Table 6. Weight losses and standard deviation of beech wood samples subjected to termite attack.

Treatment			Weight loss (%)		Survival rate (%)	
Additive	Concentration (%)	Temperature (°C)	Before leaching	After leaching	Before leaching	After leaching
PGMA	5	150	10,32 ±2,02	9,63 ±1,36	88	77
		180	9,26 ±0,97	11,41 ±1,01	76	73
		200	8,9 ±2,29	12,9 ±0,86	66	79
		220	5,41±0,03	8,91±2,05	27	45
PGMA	10	150	9,27 ±0,43	9,16 ±1,52	74	70
		180	8,38 ±1,61	9,21 ±0,43	64	72
		200	7,87 ±2,57	10,84 ±0,55	63	58
		220	3,38 ±2,35	6,45 ±2,98	17	40
AM/PG	5	150	6,08 ±1,26	6,3 ±1,66	53	44
		180	6,32 ±1,05	9,76 ±2,25	55	68
		200	5,75 ±2,16	8,29 ±0,43	47	61
		220	3,16 ±0,49	3,71 ±0,38	11	19
AM/PG	10	150	4,4 ±1,19	5,32 ±1,01	45	54
		180	3,51 ±0,11	5,9 ±0,44	32	45
		200	3,55 ±1,41	6,9 ±3,32	39	40
		220	2,39 ±0,24	3,4 ±0,49	0	17
–	–	150	7,96 ±2,15	9,32 ±1,05	73	73
		180	8,71 ±0,94	11,75 ±1,13	73	81
		200	10,26 ±2,11	14,74 ±1,75	85	84
		220	12,36 ±3,09	14,71 ±2,21	71	75
Control			13,82 ±2,14		82	

Without vinylic monomer impregnation, heat-treated as well as control wood samples were strongly degraded by termites. For both wood species, termite durability decreases with the intensity of thermal modification; samples cured at higher temperatures are generally more susceptible to termite attack than samples cured at lower temperatures. For pine wood, all heat-treated samples present a higher degree of attack than untreated samples, while for beech wood samples, controls were slightly more degraded than heat treated samples. In all cases, the rate of survival of termites at the end of the test is high, indicating that thermally modified samples were not toxic for termites. These results are in good agreement with the results reported by Sivrikaya *et al.* (2015): thermal modification did not improve durability of naturally non-durable species to termite attack. Similarly, Shi *et al.* (2007) reported that termite susceptibility of thermally modified aspen, jack pine, and yellow-poplar was comparable to that of untreated controls. At the same time, these authors reported that significantly higher termite attack occurred on thermally modified Scots pine wood compared to untreated wood.

The behaviour of resin-impregnated samples subjected to thermal modification is quite different. Indeed, contrary to non-impregnated samples, termite durability increases as the treatment temperature increases for both wood species. After thermal treatment at 220°C, resin impregnated samples present a significant durability improvement towards termite attack, with the mass losses being relatively low comparatively in all cases compared to those recorded for controls; the rate of termite survival is weak. The amounts of vinylic monomers in the impregnation solution positively influence the durability of wood; samples treated with a 10% vinylic monomer solution present the highest durability to termites. After leaching, the termite resistance decreases slightly for most of the treatments but remains better for impregnated heat-treated samples. These results corroborate our previous findings (Salman *et al.* 2016), suggesting a synergistic effect between chemical and thermal modifications for the improvement of termite durability. Considering the thermal stability of wood and different resins at 220°C reported in figure 1, it is assumed that different thermal degradations involving radical formation and possible recombination of these radicals may occur. These reactions may be the source of thermal degradation products presenting toxic properties for termites. Alternatively, the modification of wood cell wall polymers could render the modified wood substrate inadequate as a nutrition source for insects. The fact that durability is maintained after leaching suggests that the modification of the wood cell wall polymer is the primary reasons for the improvement of durability. This result suggests that the treatment may be considered as a non-biocide treatment. However, further experiments are necessary

to confirm these assumptions. From a more applied point of view, such treatments can be relatively easily applied at industrial scale, vacuum pressure impregnation and thermal modification technologies being already available. Even if the cost of vinylic monomers is difficult to estimate, it can be assumed that utilization of polyglycerol, considered as an industrial by-product, will not be limiting for the development of such treatments. Moreover, wood chemical modification with both polyglycerol derivatives may be considered as "non biocide" treatments as demonstrated by the important weight losses measured for samples cured at 150°C after exposure to termites or fungi. At higher temperature, chemical and thermal modifications appeared to act synergistically allowing achieving full protection of wood samples against termites and fungi without the any biocide utilization, which may be of valuable interest for the development of more environmentally wood preservation processes.

CONCLUSIONS

The results presented in this study confirm our previous findings that impregnation of aqueous solutions of vinylic monomers before thermal modification improves the termite durability of heat-treated wood. An impregnation of a 10% aqueous solution of maleic anhydride/polyglycerol adduct (MA/PG) or polyglycerolmethacrylate (PGMA) followed by thermal modification at 220°C improves the durability of the material towards termites, while control samples that were heat treated at 220°C were strongly attacked. At the same time, vinylic monomers impregnated in heat-treated samples impart high durability against decay due to the effect of thermal modification. In all cases, similar results were also obtained after leaching, indicating that such treatment would be appropriate for exterior applications. These combinations of chemical and thermal modifications therefore appear useful in termite-infested areas, providing additional application areas for heat-treated products. Termite durability improvements appear to be due to a synergistic effect between chemical and thermal treatments. Further investigations are necessary to study the exact reasons for this durability improvement and modification of wood cell wall polymers in the presence of vinylic monomers during thermal modification.

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