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State of progress of utilisation of supramolecular gels for formulations of water-soluble wood preservation salts

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ABSTRACT

This article is a compilation of the work done so far concerning the utilization of supramolecular hydrogels, built on low-molecular-weight amphiphilic molecules and containing boron salts conferring fungicidal properties. Mixing boron with thermoreversible hydrogels allows the formation of a supra molecular network incorporating boron and important amount of water upon gelification of the solution when the temperature decreases. Hydrogels obtained from several amphiphilic peptides, pseudo-peptides or various gelling molecules were impregnated in pine wood block using vacuum pressure treatment and subjected to leaching. Results indicated that incorporation of boron salts in the hydrogel network, allowed to protect effectively wood from degradation caused by the brown rot fungus *Poria placenta* even after leaching. It was assumed that these hydrogels are able to limit the leachability of boron salts.

Keywords: boron, decay, wood preservation, low-molecular-weight hydrogel, leachability, peptide gelator, glycerol derivative

1. INTRODUCTION

Supramolecular hydrogels have recently gathered increasing interest due to their wide range of applications in tissue engineering, sensing, drug delivery or water pollution control (Loos et al *2005*, Sagawa et al *2006*, Sangeetha and Maitra *2005*, Steed *2011*, Yanga and Zu *2007*). This type of gel is named "smart gel" because of their sensitivity to stimuli temperature, pH or agitation... They are obtained from low-molecular-weight amphiphilic molecules and they are made by the self-assembly of amphiphilic molecules through no covalent interactions including hydrogen bond, pi–pi stacking and Van der Waals forces. New Low Molecular Weight gelators based on amphiphilic dipeptides have been recently synthesized in our lab and their gelation behavior in water and different organic solvent was investigated (Gizzi et al *2009*, Pan and Dey *2011*, Pasc et al *2009*, Pasc et al *2010*, Patra et al *2010*). Indeed, despite the continuous interest in organogels and hydrogels of low-molecular-weight gelators, the molecular design and the corresponding gelation mechanism is still a challenge.

On another side, boron salts have been described as valuable alternatives for wood protection for non-ground contact applications. Disodium octaborate tetrahydrate (DOT), boric acid and borax are the most widely used boron-based wood preservatives. They possess many advantages such as being colourless, odourless, non corrosive, non flammable, inexpensive, having low vapour pressure and low toxicity for mammals and the environment, but suffer of an important

drawback due to their high susceptibility to leaching which limits their use in outdoor applications. Numerous studies have been described to reduce boron leachability involving mainly the use of organic chemicals to reduce boron solubility in water through formation of insoluble or hydrophobic complex (Baysal et al *2004*, Gezer et al *1999*, Kartal and Green *2003*, Kartal and Imamura *2004*, Kartal et al *2004* and *2009*, Mohareb et al *2002*, *2010*, *2011*, Mourant et al *2008*, Temiz at al *2008*, Thevenon et al *1997* and *1998*, Thevenon and Pizzi *2003*, Toussaint-Dauvergne *2000*). However, complexation reduced boron biodisponibility to fungi, limiting the application of such complex to develop antifungal treatment.

We present here results obtained from alternative formulation of boron salts in low-molecular-weight hydrogel built from different kind of gelators. The objective is to encapsulate mineral salt solubilized in water inside the hydrogel. Mixing boron with thermo-reversible hydrogels allows the formation of a supramolecular network incorporating boron and important amount of water upon gelification of the solution when the temperature decreases.

This article is a continuation of the previous paper related to synthesis of a pseudopeptidic hydrogelator and its utilization to improve boron retention in wood (Obounou-Akong et al *2012a, 2012b, 2013*). We make here a compilation of the different results obtained on the subject. Three gelators are concerned: an amphiphilic tripeptide (GlyGlyPheC10), a glycerol carbamate derivative (Glycerol-C14) and a catanionic system associating an amphiphilic dipeptide and lauric acid (AlaHisC8/C12).

Hydrogels obtained from these molecules and boron salt were impregnated in pine wood block using vacuum pressure treatment and subjected to leaching. Pine wood blocks have been exposed to fungi and termites.

2. MATERIAL AND METHODS

2.1 Synthesis of hydrogelators

All reactants were purchased from Acros Organics (Noisy le Grand, France) or Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France) or Alfa Aeasar (Johnson Matthey Company, Schiltigheim, France).

2.1.1 Di and tripeptide

General procedure for peptide coupling (between aminoacid or fatty amine):

In 40 mL of CH_3CN, were added 3.77 mmol of Boc-aminoacid, 1eq of BOP (1.67 g, 3.77 mmol), 2 eq of triethylamine (0.76 g, 7.54 mmol) and 1 equivalent of amino partner (3.77 mmol) (fatty amine or aminoacid). After adjusting the pH with Et_3N (7-8), the reaction mixture was maintained under stirring at room temperature for 15 hours. The precipitate was filtrated, washed successively with CH_3CN and diethyl-ether and dried. Recristallisation in CH_3CN gives in general a white solid. If no precipitate occurred, CH_3CN was evaporated under reduced pressure and the residue was introduced in ethyl acetate and the organic phases was washed successively with 20 mL of HCl 0.1 N, 20 mL of saturated $NaHCO_3$ and twice with 20 mL of saturated NaCl.

Then, the organic phase was dried on $MgSO_4$ and the solvent was removed under reduced pressure.

Boc deprotection :

Powder was dispersed in anhydrous diethyl-ether and then treated with anhydrous HCl gaz. The mixture was maintained under stirring at room temperature during 18 hours. After evaporation of the solvent, the product was a hygroscopic white powder.

2.1.2 Glycerol carbamate derivative

A mixture of glycerol carbonate (2g, 16.93 mmol), one equivalent of tetradecylamine (16.93 mmol), and 5 ml of methanol was heated under stirring at 65°C during 6 hours. Reaction was monitored by IR (ATR) to follow the deasappearence of C=O carbonate band (1790 cm^{-1}) and

appearance of C=O carbamate band (1700 cm^{-1}). After evaporation of solvent, the product was a white powder.

2.2 Blocks impregnation

Mini-blocks (15 by 5 mm in cross section by 50 mm along the grain) of Scots pine sapwood *(Pinus sylvestris* L.) were used. 16 replicates were used for each treatment. Samples were oven dried at 103 ºC for 48 hours and weighed to a precision of 0.001g (m_0). All treatments were performed using a single vacuum pressure impregnation. Two treatments were performed for hydrogelator agent involving impregnation of hydrogelator alone or with borax (5 %). Treatment solutions containing borax and hydrogelator were heated at 80°C before use to decrease their viscosity and impregnated immediately till hot. 5% borax solution was used as reference solution. Wood specimens were vacuum treated at 5 mbar for 30 min., impregnated with the treatment solutions and kept immersed for 2 hours at atmospheric pressure, and finally reweighed to determine solution uptake. Wood samples were kept for 16 hours at ambient laboratory temperature, dried at 103 ºC for 48 hours and weighed (m_1). Weight percent gain (WPG) was calculated as follows:

$WPG\ (\%) = 100 \times (m_1 - m_0)/m_0$

where m_0 is the initial dry mass of wood samples without treatment and m_1 is the dry mass of treated wood samples.

2.3 Boron leaching procedure

Leaching was performed according to a procedure adapted from the European standard ENV 1250-2 (European Committee for Standardization *1994*). Eight samples were immersed in 90 mL distilled water and subjected for six leaching periods of increasing duration under continuous shaking at 20°C. Water was replaced for each leaching period after 1 hour, 2 hours and 4 hours. Samples were then removed and kept air drying for 16 hours. Other leaching periods have been conducted for 8 hours, 16 hours and 48 hours with change of water between each. All leachates were collected and kept for boron analysis. After leaching procedure, blocks were dried at 103ºC for 48 hours and weighed (m_2). Mass Loss after leaching (ML) was calculated as follows:

$ML\ (\%) = 100 \times (m_2 - m_1)/m_1$

where m_1 is the dry mass of treated wood samples and m_2 is the dry mass of treated leached wood samples.

2.4 Boron analysis

Boron content was analyzed after mineralization of treated or untreated wood blocks subjected or not to leaching. For this purpose, blocks were ground to fine sawdust and dried at 103°C until constant mass. 1 g of sawdust was placed in a 100 mL Erlenmeyer flask and 15 mL of concentrated nitric acid added. The flask was heated at 80°C until reddish-brown fumes stop. Hydrogen peroxide (15 mL) was added drop-wise, and the flask heated at 80°C until total dissolution of organic material. After cooling, the solution is transferred in a 100 mL volumetric flask, rinsed with distilled water and completed to 100 mL. The boron contents was determined using a Varian SpectrAA 220 FS atomic absorption spectrometer with standard solutions comprising between 25 and 1,000 mg L^{-1}.

2.5 Decay test

Sterile culture medium (20 ml), prepared from malt (40 g) and agar (25 g) in distilled water (1 L), was placed in 9 cm Petri dishes, inoculated with a small piece of mycelium of a freshly grown culture of *Poria placenta* and incubated during 2 weeks at 22°C and 70% HR to allow full colonization of the medium by the mycelium. For each treatment, three blocks (two treated and one control) were placed in a Petri dish under sterile conditions and the experiment repeated four

times. Simultaneously with the test series, pine sapwood samples were exposed to *Poria placenta* as virulence controls. Incubation was carried out for 16 weeks at 22°C under controlled humidity conditions of 70% RH in a climatic chamber WTB BINDER TYP KBF 240. At the end of the test period (16 weeks), mycelia were removed and all specimens were oven dried to constant mass at 103°C and weighed. Weight loss (WL) was expressed as a percentage of the initial oven-dry weight of wood sample according to the formula:

$WL\ (\%) = 100 \times (m_{0 \text{ or } 1 \text{ or } 2} - m_3)/m_{0 \text{ or } 1 \text{ or } 2}$

where m_3 is the final dry mass of wood samples after the fungal exposure.

2.6. Termite resistance tests

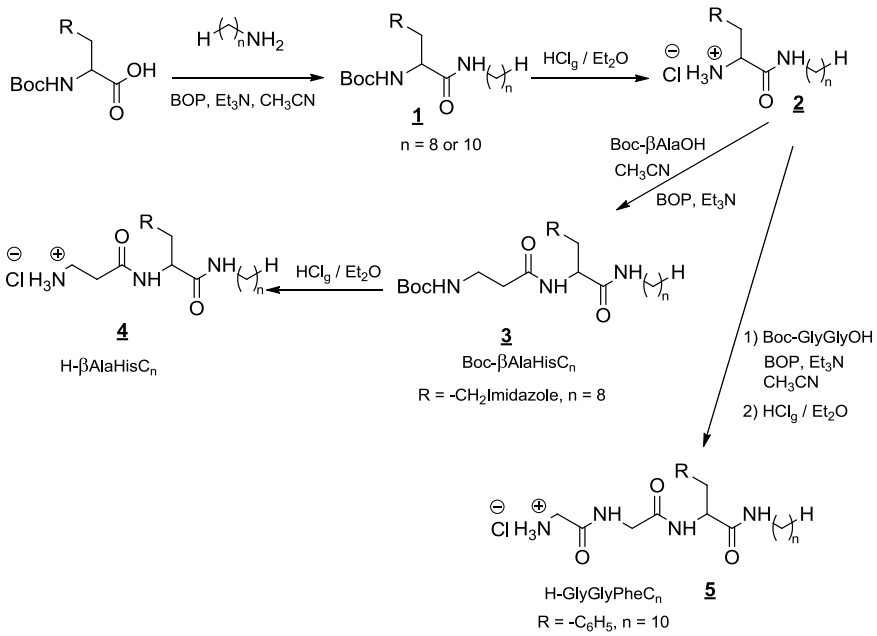
Pine (*Pinus sylvestris*) sapwood of dimensions (30x20x5mm^3, L,R,T) treated, un-leached and leached were used for non choice termite test. Prior to the termite test, each sample was dried at 103°C to get its anhydrous initial weight. For each set of treatment and controls, 3 replicates were tested for their resistance towards *Reticulitermes flavipes* (ex. *santonensis*) termites.

Each sample was introduced in a Petri dish (Ø 9 cm) containing 20g of Fontainebleau sand (sand 4 vol / deionized water 1 vol). The samples were placed on a plastic grid, in order to avoid waterlogging. Onto the sand, 100 termite workers, 5 nymphs and 5 soldiers were introduced. Pine sapwood controls (30x20x5mm^3) were tested in the same manner.

The test devices were placed in a dark climatic chamber at 27°C, RH > 75%. An observation was done twice a week and the sand was wetted when necessary. After 5 weeks, the samples were taken out from the test devices. Each sample was cleaned from the sand, visually rated according to the EN117 criteria (European Committee for Standardization *1990*), and the survival rate of the termites is calculated. Samples were dried at 103°C and weight losses calculated.

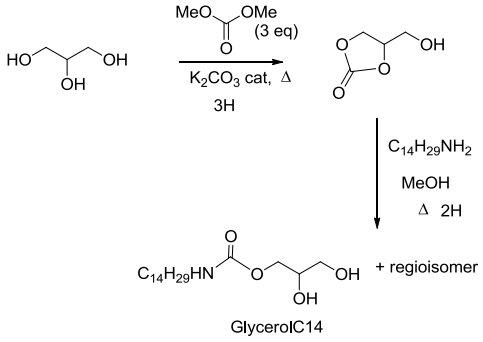
3. RESULTS AND DISCUSSION

The synthesis of the di or the tripeptide (beta-AlaHisC8 and GlyGlyPheC10) was performed in four steps using classical protection/deprotection and coupling peptide synthesis procedures. The first step involved the reaction of the fatty amine with the histidine (His) or the phenylalanine (Phe) moiety. The carboxylic acid was then activated with BOP, a classical activating agent in peptide synthesis, to lead rapidly and efficiently Boc-AA-NHC_nH_{2n+1} intermediate. Boc protecting group was removed quantitatively with gaseous hydrochloric acid dissolved in diethyl ether and the resulting amine coupled with Boc-Ala-OH or Boc-GlyGly-OH activated by BOP. Subsequent deprotection of the Boc protecting group with gaseous chlorhydric acid leads to the desired di or the tripeptide in its ammonium form (scheme 1).



Scheme 1: synthesis of the peptide-derived gelators

The synthesis of the carbamate derivative of glycerol corresponds to a very simple procedure. The first step is the synthesis of glycerol carbonate from dimethyl carbonate and glycerol under mild conditions. Dimethyl carbonate was used in a molar excess (3:1) to shift the reaction equilibrium towards the product, K_2CO_3 was added as catalyst and the reaction was carried out for 3H under reflux. Carbonate glycerol was obtained in a quantitative yield after distillation of methanol produced as by-product and un-reacted dimethyl carbonate under reduced pressure. In the second step, a simple mixture of fatty amine and glycerol carbonate in a little quantity of methanol leads to the carbamate in a mixture of region-isomers due to the different way of opening of the carbonate. (Scheme 2)



Scheme 2: synthesis of glycerol carbamate

Hydrogels were formed from tripeptide or from glycerol carbamate by introducing 5% of borax (50 g / L) and 2 % of GlyGlyPheC10 (20 g / L) or 3% of Glycerol C14 (30 g / L) in respectively 93 mL and 94 mL of water. The dispersion was first heated to 80°C until total solubilization of the reactants, slowly cooled to room temperature and allowed to stand until formation of the hydrogel. These conditions correspond to the best optimized conditions using the minimal gelator agent quantity leading to a gel-to-solution transition taking place between 60 to 70°C. In the case of the catanionic gelator (AlaHisC8/C12), the hydrogel was formed by mixing 100 mL of 5% borax solution (pH 10) with 180 mg (9 mM) of lauric acid and 120 mg (3 mM) of HCl.H-beta-Ala-His-NHC_8H_{17}. The dispersion was first heated to 80°C until total solubilization of the

reactants, slowly cooled to 4-5°C and allowed to stand until formation of the hydrogel. These conditions correspond to the best optimized conditions using the minimal gelator agent quantity (0.3% w/w) leading to a gel-to-solution transition taking place between 60 to 70°C. Lauric acid was chose for its ability to interact with amine moiety of beta-AlaHisC8 through acid-base interaction leading to self-assembly of solubilized molecules into hydrogels, similarly to results described by Suzuki (Suzuki et al, 2007).

To check the validity of the concept of hydrogels utilization to reduce boron leachability and develop new wood protection treatments, Scots pine sapwood blocks were impregnated with a 5% borax solution (w/w) in the presence or not of hydrogelator. Wood impregnation was performed using classical vacuum pressure. To allow impregnation of solutions containing hydrogelator, these latter were heated at 80°C and impregnated till hot. After impregnation, blocks were kept at room temperature, dried at 103°C and subjected to water leaching using several leaching periods of increasing duration under continuous shaking at 20°C. Weight percent gains and boron contents before and after leaching are reported in table 1.

Table 1. Weight percent gain and boron content before and after leaching

Treatment	WPG (%)	ML (%)	Boron content (mg / g dry wood)[a]	
			before leaching	after leaching
5% Borax	3.0 ± 0.3	-4.4 ± 0.8	8.3	0.73
2% Gel (GlyGlyPheC10)	0.7 ± 0.2	-2.2 ± 0.9	0.67	0.42
3% Gel (GlycerolC14)	1.3 ± 0.3	- 1.1 ± 0.2	0.76	0.25
0,3% Gel (AlaHisC8/C12)	0.4 ± 0.3	-5.4 ± 6.8	-	-
2% Gel (GlyGlyPheC10) / 5% Borax	5.4 ± 0.6	-2.7 ± 0.4	9.5	7
3% Gel (GlycerolC14) / 5% Borax	5.0 ± 0.6	-1.8 ± 1.3	7.5	6.8
0,3% Gel (AlaHisC8/C12) /Borax 5%	9.2 ± 3.0	-2.8 ± 2.7	-	-
Control	-	-2.6 ± 0.3	0.2	-

[a] precision ± 5%

Impregnation of 5% borax solution allows obtaining boron retention of 3.0% corresponding to a boron content of approximately 8.3mg of atomic boron per gram of dry wood based on the molecular weight of sodium tetraborate decahydrate (M = 381.37 g $mole^{-1}$). Considering a wood density of 500 kg per cubic meter, this value corresponds to approximately 24 kg of boric acid equivalent (BAE) per cubic meter, which is far above the toxic limit of 1 kg BAE/m^3 set for wood protection under outdoor conditions (Lloyd *1998*, Pezron et al *1988*). These value are similar to value reported in the literature (Lloyd et al., 1990; Mohareb et al., 2011) and above the toxic limit of 1 kg BAE/m3 set for wood protection under outdoor conditions (Drysdale, 1994; Schoeman and Lloyd, 1998).

Impregnation of gel alone has practically no effect on the weight percent gain due to small amounts of gelator agents used. Impregnation of gelator agents with borax lead to weight percent gain superior to borax alone. This may be due to the effect of temperature used to perform impregnations in the presence of gelator agents, while impregnation of borax alone was performed at room temperature. After leaching, all WPGs were inferior to zero indicating that most of the impregnated chemicals were leached out during leaching procedure.

Determination of Boron content showed very low values of boron in control and hydrogelator treated blocks. 5% borax treated wood in the presence or not of hydrogelator indicated boron content of approximately 8 to 9 mg of boron per gram of dry wood, which is far above the toxic limit of boron reported in the literature. After leaching, all boron is leached out from borax treated blocks, while quite all boron initially present in wood remains after leaching for blocks treated with borax and hydrogelators.

Treated and untreated, leached or unleached blocks were then exposed to *Poria placenta* during 16 weeks and mass losses due to fungal attack determinated (table 2).

Table 2. Weight losses of Scots pine sapwood blocks exposed to *Poria placenta*

Treatment	WL (%)	
	before leaching	after leaching
5% Borax	0.6 ± 0.2	71.5 ± 4.8
0,3% Gel (AlaHisC8/Lauric acid)	-	26.3 ± 8.6
0,3% Gel (AlaHisC8/C12)/Borax 5%	-	1.1 ± 0.9
2% Gel (GlyGlyPheC10)	67.2 ± 3	60.2 ± 3.3
3% GlycerolC14	49.4 ± 29.4	50.7 ± 24.8
2% Gel (GlyGlyPheC10) / 5% Borax	0.5 ± 0.3	0.6 ± 0.4
3% Gel (GlycerolC14)/ 5% Borax	0.5 ± 0.2	0.8 ± 0.4
Control	72.0 ± 1.8	-

Weight losses recorded after 16 weeks exposure to *Poria placenta* indicated a significant improvement of decay durability of blocks treated with borax in the presence of gelator agents comparatively to controls and blocks treated with borax alone. Indeed, mean weight losses of blocks treated with 5% borax in the presence of gel were inferior to 1 %, while weight losses of control and borax alone treated leached blocks were of 72 and 71.5% respectively. Impregnation of gel alone has no effect on wood durability confirming effect of gel on boron retention and consequently on decay durability. Contrary to results previously described in literature suggesting that complexation reduces biological activity of boron (Mohareb et al *2002*, Lloyd *1998*, Obanda et al *2008*) and similarly to our previous work using hydrogel (Obounou-Akon et al *2012*), utilization of these new hydrogels to reduce boron leachability have no effect on boron bio-disponibility and consequently on it fungicidal activity towards *Poria placenta*.

To assess termites' resistance and check the influence of hydrogels on boron retention, leached and unleached samples treated or not with Borax with or without hydrogels were subjected to termite attack using a laboratory test for five weeks. The results are reported in table 3.

For all the controls, the survival rate of the workers is above 50% and the attack is strong, thus is test is valid. The results for the borax treated samples were rather predictable. When un-leached, the amount of borax (5%) is far above the threshold for termites (Pezron *1988*). On the other hand, when leached, Borax on its own cannot remain in the wood and the attack is strong. Both gels (glycerol and GlyGlyPhe) have no effect on termite attack or survival. When Borax is added to glycerol gel, it is interesting to see that when un-leached, the results are comparable to those obtained with Borax alone, meaning that the gel has no impact on the active ingredient. After leaching, it appears clearly that some Borax is still available within the wood. Borax is not a repellent active ingredient, thus the termites have to ingest some wood before dying. Thus, despite no termite worker have survived, and that the weight loss of the wood is much lower than the one obtained for leached Borax alone or controls, the visual rating appears as average to strong.

Table 3. Survival rate, visual rating and weight losses of Scots pine sapwood blocks exposed to *Reticulitermes flavipes*

Treatement	Number of survival termites Workers (W)/Nymphs(N)/Soldiers(S)	Visual rating	Weight loss (%)
5% Borax before leaching	0W/0N/0S	0	2.66
	0W/0N/0S	0	3.16
	0W/0N/0S	0	3.33
5% Borax after leaching	37W/1N/1S	4	8.68
	29W/1N/1S	4	11.14
	18W/1N/1S	4	10.93
3% GlycerolC14 before leaching	63W/3N/1S	4	14.89
	60W/0N/1S	4	11.32
	58W/0N/1S	4	12.64
3% GlycerolC14 after leaching	54W/1N/1S	4	12.48
	45W/0N/2S	4	10.14
	61W/2N/1S	4	13.78
3% Gel (GlycerolC14)/ 5% Borax before leaching	0W/0N/0S	0	2.21
	0W/0N/0S	0	2.86
	0W/0N/0S	0	2.32
3% Gel (GlycerolC14)/ 5% Borax after leaching	0W/2N/0S	4	6.09
	0W/0N/0S	4	3.52
	0W/0N/0S	3	3.08
2% Gel (GlyGlyPheC10) before leaching	59W/2N/1S	4	16.77
	32W/0N/1S	4	9.68
	47W/0N/1S	4	9.10
2% Gel (GlyGlyPheC10) after leaching	64W/1N/1S	4	14.52
	68W/1N/2S	4	17.26
	47W/2N/0S	4	11.55
2% Gel (GlyGlyPheC10) / 5% Borax before leaching	0W/0N/0S	1	4.36
	0W/0N/0S	1	3.99
	0W/0N/0S	1	4.17
2% Gel (GlyGlyPheC10) / 5% Borax after leaching	34W/3N/1S	4	11.20
	12W/2N/1S	4	7.52
	34W/1N/1S	4	10.56

Similar trends are observed with GlyGlyPhe gel. For this combination, the visual rating and the weight loss of the samples suggest that (1) the active ingredient is may be less accessible and/or less active, (2) GlyGlyPhe gel retains less boric acid than for the glycerol gel.

4. CONCLUSIONS

The results presented in this study confirm the effectiveness of hydrogels to retain boron in wood allowing development of new strategies to reduce boron leachability from treated wood. Small

amounts of hydrogelators, comprised between 0.2 and 3 %, improve boron retention in wood allowing its protection against the brown rot fungus *Poria placenta* and termites (*Reticulitermes flavipes*) even after leaching, while blocks treated with the same concentration of Borax are strongly degraded after leaching. Nature of hydrogelator influences more or less the obtained results, the glycerol derivative (GlycerolC14) leading to better results than the amphiphilic tripeptide (GlyGlyPheC10). These two hydrogelators are not sensible to the pH contrary to the catanionic system. Determination of boron content by atomic absorption before and after leaching confirm the ability of hydrogels to retain Boron in treated wood, most of the boron impregnated in the wood remaining after leaching. According to these results, hydrogels appear as valuable additives to improve boron fixation in wood and develop friendly environmentally wood preservation formulations.

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