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Boron addition to non- or low-formaldehyde cross-linking reagents to enhance biological resistance and dimensional stability of wood

M. K. Yalinkilic, E. D. Gezer, M. Takahashi, Z. Demirci, R. Ilhan, Y. Imamura

Boric acid (BA) and phenylboronic acid (PBA) were added into aqueous solutions of non- or low-formaldehyde reagents; dimethylol dihidroxy ethyleneurea (DMDHEU), glutaraldehyde (GA) and glyoxal (GX), in order benefit from their potential synergistic effects in wood. Boron addition to GA improved the anti-swelling efficiency (ASE) of wood while other combinations resulted in some decreases. Ion chromatography analysis of boron leaching supported the presumption on boron-GX complexion referred to ASE changes in the presence of boron. Although such complexations seemed to reduce boron leaching, boron appeared to decrease cross-linking efficacy of GX and to a lesser degree of DMDHEU to the wood cell wall which was understood from declining ASE of wood after boron addition. Boron addition to these reagents considerably improved the decay resistance against *Tyromyces palustris* and *Coriolus versicolor*, which are the representative test fungi of brown- and white-rot in Japanese Industrial Standard (JIS) A-9201-1991, respectively. PBA had somewhat less contribution to decay resistance of GX most possibly due to chemical complexation. GA proved superior in decay resistance to the other two reagents. Mass loss due to the Formosan termite *Coptotermes formosanus* attack could be reduced to a minimum with total inactivation of termites by PBA addition. BA retention did not suffice to impart complete termite resistance after ten cycles of severe weathering of the specimens. Thus, BA was found appropriate to be added to the used cross-linking agents in such service conditions where decay risk is high while PBA combinations should be preferred if termite damage prevailes.

Borsäurezusatz zu vernetzenden Reagenzien ohne und mit geringem Formaldehydgehalt zur Verbesserung der biologischen Widerstandsfähigkeit und der Dimensionsstabilität

Borsäure (BA) und Phenylborsäure (PBA) wurden zu folgenden Reagenzien ohne oder mit geringem Formaldehydgehalt in wäßriger Lösung zugesetzt: Dimethylol-dihydroxyethylen-Harnstoff (DMDHEU), Glutaraldehyd (GA) und Glyoxal (GX), um mögliche synergistische Effekte im Holz zu nutzen. Borsäurezusatz zu GA verbesserte die ASE-Eigenschaften von Holz, während andere Kombinationen zu einem geringfügigen Abfall führten. Ionenchromatographie der Borauswaschung stützten die Vermutung, daß die Änderung des ASE in Gegenwart von Borsäure auf Borsäure-GX-Komplexe zurückzuführen ist. Diese Komplexe verringern zwar die Borauswaschung, verringern aber auch die Vernetzungsfähigkeit des GX mit der Zellwand und in geringerem Maße auch des DMDHEU. Das wurde aus dem abnehmenden ASE nach Borzugabe gefolgert. Die Borzugabe zu den genannten Reagentien erhöht beträchtlich die biologische Resistenz gegen *Tyromycetes palustris* und *Coriolus versicolor*, die im japanischen Standardtest als als Vertreter für Braun- bzw-Weißfäulepilze verwendet werden. PBA liefert einen geringeren Beitrag zur Resistenzerhöhung durch GX, wahrscheinlich aufgrund der Bildung von Komplexen. GA erwies sich den anderen Reagenzien als überlegen. Massenverluste durch Angriff von Termiten (*Coptotermes formosanus*) konnten minimiert werden durch Zusatz einer PBA-Lösung. Das Rückhaltevermögen von BA war nicht ausreichend um nach 10-maliger Bewitterung die Termiten zu inaktivieren. Daher ist BA eher geignet als Zusatz zu Vernetzungsreagenzien, wenn Pilzbefall abzuwehren ist, während PBA-Kombinationen bei Gefahr von Termitenbefall vorzuziehen sind.

1 Introduction

Boron wood preservatives have several great advantages for application as wood preservatives including a broad spectrum of activity against insects and fungi, low mammalian toxicity, low volatility, and they are colorless and odorless (Murphy 1990). However, they are generally leachable from treated wood in ground contact. In addition, because of their hygroscopic characters, they are likely to increase water sorption of wood after high boron loading that may effect dimensional stability (Yalinkilic et al. 1995a, b). Water repellent polymers or hydrophobic reagents and phenolic resins have been tried to reduce

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boron leachability and increase dimensional stability as well as providing high biological and fire resistance (Ryu et al. 1992; Peylo and Willeitner 1995; Su et al. 1997; Murphy et al. 1995; Yalinkilic et al. 1996; Yalinkilic et al. 1997a). Compatibility of boron with the accompanying chemical appeared to have a profound effect on the treated wood properties (Lloyd 1993; Yalinkilic et al. 1997a). Dual treatments with boron- incorporated systems are also a matter of cost and time. Therefore, boron addition to treatment solutions of compatible chemicals in a single impregnation process appears to be more practical.

Among the combination treatments, boron-formaldehyde incorporations had some remarkable improvements on decay and termite resistances (Yalinkilic 1996; Yalinkilic et al. 1997b). In addition, wood became more stable owing to the treatment with formaldehyde (Yusuf 1996). However, special care should be paid to this process due to the formaldehyde toxicity to the human body (Yusuf et al. 1995). Formaldehyde in the form of gas or aerosol – the effect of both is comparable – is very irritating to the mucous membrane. The pungent smell is noticeable even at concentration below 1 ppm. Therefore formaldehyde is a dangerous material to work with and has received the same rating as phenol (Knop and Scheib 1979). It has been reported that wood can be alternatively treated with non- or low-formaldehyde agents which have a similar cross-linking ability with the OH-groups of the cell wall (Frick et al. 1960, 1982; Hurwitz and Conlon 1958; Mehta and Mehta 1960; Mehta and Mody 1960). Yusuf et al. (1995) proved the dimensionally stabilizing effects of the ethylene urea type reagent dimethylene dihidroxy ethylene urea (DMDHEU), glutaraldehyde (GA) ($OHCCH_2CH_2$-CH_2CHO), and glyoxal (GX) (OHCCHO) on wood. Since these are applied as aqueous solutions, boron addition to the treatment solution in a single treatment system ought to be possible. Therefore, the present study dealt with such single treatment systems in which boron is expected to increase biological resistance while cross-linking agents would provide dimensional stability in addition to potential boron fixation through reducing water access to wood or possible chemical complexation with boron through oxygen bonds.

2 Materials and methods

2.1 Chemicals and treatment conditions

Boric acid (BA) and phenylboronic acid (PBA) were used as boron compounds. They were separately added to chosen non- or low-formaldehyde reagents to obtain 1% final boron concentration in the 5% DMDHEU and GA aqueous solutions and 20% GX solution. Pad-dry-cure treatment with non- or-low-formaldehyde reagents were performed according to Yusuf (1996). A 30 min pre-vacuum was applied to the specimens, which were prepared from sugi (*Cryptomeria japonica* D. Don) sapwood with the size of 20 (T) × 20 (R) × 10 (L) mm, before introducing the treatment solutions into an evacuated chamber. Specimens were left there for a one week diffusion until they sank to the bottom, and then were air-dried for 1 week. Then 10 pieces of the test blocks were preheated in a 3.5 l glass vessel for 20 min at 120 °C, and dried under vacuum. From a commercial bomb, four hundred ml of gaseous SO_2 were added to the glass vessel by a syringe. The glass vessel was maintained at the same temperature for 12 h. Impregnations and the following curing process were duplicated under the same conditions for each series of the treatment. Subsequently, boron-free specimens were rinsed thoroughly in running water for several days eliminating the unreacted reagent from the wood while boron-added ones were subjected to a cyclic leaching process.

The weight gains in percentage were determined from the oven-dried weights before treatment and after leaching of the treated specimens.

2.2 Dimensional stability

Test blocks were soaked in water and evacuated until they submerged to the bottom. They were then oven – dried at 60 °C for three days. Swelling values both in water-swollen and oven-dry state were determined using a digital micrometer (0.01 mm unit) to calculate the volumetric swelling. From the difference of the swellings for test and control specimens the anti-swelling efficiency (ASE) was calculated (Norimoto and Grill 1993):

$$\mathrm{ASE}(\%) = \frac{Su - S}{Su} \times 100 \ ,$$

where Su is of untreated wood volumetric swelling and S is of treated ones.

Bulking efficiency (BE) of the treatments was determined on the oven-dry basis measured prior to treatment and after leaching:

$$\mathrm{BE}(\%) = \frac{Vof - Voi}{Voi} \times 100 \ ,$$

where Vof is the final oven-dry volume after leaching of treated specimens and Voi is the same for untreated wood.

2.3 Leachability test

The leachability test was conducted according to the Japanese Industrial Standard (JIS A 9201-1991) under ion chromatography principles (Small 1989). Wood specimens were exposed to leaching cycles in deionized water stirred by a magnetic stirrer (400–500 rpm) at 25 °C for 8 h and to evaporation cycles in an oven at 60 °C for 16 h. After each leaching period, leachate was sampled to analyze boron with ion chromatography (IC) using IC 500P of Yokogawa-Hokushin Electric, equipped with an ion exclusion column. Analytical conditions were as follows: sample injection: 100 μl; column: SCS5-052 + SCS5-252; temperature: 40 °C; effluent: 1 mM H_2SO_4; flow rate: 1 ml/min; detector: refractive index detector (Erma, Inc., ERC-7511). Hot water extracts (HWE) of leached and unleached specimens of PBA-added combination treatments were prepared for ion chromatographic analysis, because the boron concentration was very low even in the concentrated leachates of PBA combinations. In addition, HWE of leached specimens of BA-added combinations were also subjected to ion chromatography in order to reveal remained boron in wood after a severe weathering process. Details of the preparation method of HWE with the boiling test were described earlier (Yalinkilic et al. 1997b, c).

2.4
Biological assay
Decay and termite tests were conducted to highlight the performance of retained boron in wood after ten severe leaching cycles. Leached specimens of combination treatments were used for biological tests.

2.4.1
Decay test
A mono culture decay test was conducted according to JIS A-9201-1991 using a brown-rot fungus, *Tyromyces palustris* (Berk. et Curt) Murr. [Fungal accession number of Forestry and Forest Products Research Institute, Tsukuba, Japan (FFPRI) 0507] and a white-rot fungus, *Coriolus versicolor* (L. ex Fr.) Quél. [FFPRI 1030]. Test blocks were sterilized with gaseous ethylene oxide after measuring their oven-dried weights. Three wood samples of the same treatment were kept in glass jars containing a medium of 250 g quartz sand + 80 ml nutrient solution with a fully grown fungal mycelia on it and then incubated at 26 °C for 12 weeks. Three replicates were arranged for each decay fungus. The extent of the fungal attack was determined based on the percentage of mass loss.

2.4.2
Termite test
Leached specimens were exposed to subterranean termites in accordance with the Japanese Wood Preservation Association (JWPA) Standard No. 11-1 (1992). A test wood block was placed at the center of the plastered bottom of a cylindrical test container (80 mm in diameter). One hundred and fifty *Coptotermes formosanus* Shiraki "workers" and 15 "soldiers" were introduced into each test container. The assembled containers were set on dampened cotton pads to supply water to the blocks and kept at 28 °C and >88% RH in the dark for three weeks. Termite mortality was determined regularly, and mass loss of a test wood due to termite attack was determined based on the differences in the initial and final weights of the block. Four replications were made for each treatment.

3
Results and discussion

3.1
Weight gain and dimensional stability
Weight gain, ASE, and BE levels of treated wood are given in Table 1. BA and PBA addition to GA increased the ASE levels of wood. Both boron compounds, however, caused some decrease in the ASE of wood when they were added to DMDHEU and more distinguishably when added to GX. BA addition to GX resulted in an ASE four times lower than that of solely GX treated wood. On the other hand, BE of used aldehydes in wood generally decreased after boron addition in comparison with their sole treatments. Since the chemical bonding desired between the cross-linking reagents and the wood cell wall is of major consideration (Rowell 1984), the reduction in ASE with boron-GX and -DMDHEU treatments account for the probable decrease of the cross-linking efficacy of these aldehydes in wood after boron addition. This may either be due to chemical complexation between the reactive sites of these chemicals instead of cross-links with wood, or due to the probable instability of established bonds regarding leaching stresses, as well as the possible occupation of reactive groups of the aldehydes and wood by boron-oxygen bonds (Yalinkilic et al. 1996). Acidity levels of fresh treatment solutions before and after boron addition also suggest some chemical interaction among boron and GX and to some lesser extent DMDHEU (Table 1). DMDHEU might have undergone a "gelation" reaction with boron depending upon the functionality levels of OH-groups (Knop and

Table 1. Weight gain, ASE and BE levels of wood treated with boron-non or low-formaldehyde combination systems

Tabelle 1. Gewichtszuwachs, ASE und Dimensionsstabilität (BE) von Holz nach Behandlung mit Kombinationen von Borsäre und vernetzenden Reagenzien ohne und mit geringem Formaldehygehalt

Chemical[b]	Concentration (%)	pH of fresh solution	Weight gain (% w/w)[a] Before leaching	After leaching	ASE (%)	BE (%)
Non-or-low formaldehyde reagents						
DMDHEU	5	4.45	17.6 (1.0)	16.9 (1.9)	64.7 (7.1)	4.7 (0.1)
GA	5	3.46	16.3 (0.6)	15.1 (0.5)	38.8 (2.0)	5.9 (0.4)
GX	20	3.00	88.8 (4.6)	50.2 (2.4)	82.2 (6.0)	5.7 (0.3)
Boric acid (BA)-non or -low-formaldehyde reagents' combinations						
BA	1	5.27	3.5 (0.3)	0.2 (0.3)	–	–
DMDHEU+BA	5	3.09	15.6 (3.4)	13.6 (3.9)	60.3 (4.4)	3.8 (0.2)
GA+BA	5	3.58	15.5 (0.6)	13.1 (0.6)	51.5 (2.4)	4.0 (0.1)
GX+BA	20	1.47	74.5 (6.6)	57.1 (5.8)	23.4 (8.7)	2.5 (0.1)
Phenylboronic acid (PBA)-non or -low-formaldehyde reagents' combinations						
PBA	1	6.00	3.5 (0.2)	1.0 (0.1)	–	–
DMDHEU+PBA	5	3.76	19.5 (2.4)	19.5 (1.9)	45.5 (3.3)	3.6 (0.1)
GA+PBA	5	3.46	18.1 (3.3)	17.7 (2.5)	66.4 (8.4)	5.7 (8.4)
GX+PBA	20	2.27	75.8 (11.6)	71.3 (6.4)	65.9 (1.8)	4.1 (0.6)

[a] Standard deviations were included in the paranthesis
[b] DMDHEU: dimethylol dihydroxy ethylene urea, GA: glutaraldehyde, GX: glyoxal, ASE: anti-swelling efficiency, BE: bulking efficiency

Scheib 1979), which evidently resulted in an ASE decrease (Table 1). On the contrary, the increase of ASE caused by boron addition to GA may reflect the catalizing effect of boron on establishing strong bonds between GA and the wood cell wall (primarily with its phenolic components), similar to the phenol and formaldehyde reaction accelerated by the strong ortho-directing effect of boric acid (Knop and Scheib 1979). The directing effect of metal ions is explained by formation of chelates as transient compounds. Boron can also form chelate complexes with certain organic compounds in aqueous solutions (Lloyd 1993), BA was likely to establish such complexes with aldehydes, although this is yet to be established through the present findings.

PBA itself was found to be more stable in wood than BA (Yalinkilic et al. 1997b, c). As a consequence, the PBA-GA combination produced a higher ASE than BA addition that supports the assumed boron catalyzing effects of the reactions between phenolic cell wall components and used aldehydes. However, addition of DMDHEU and GX also resulted in some ASE decrease most likely similar to the adverse effect of boron on cross-linking efficacy. Leachability results may help to understand the potential complexation of used aldehydes and boron.

3.2 Boron leachability

Ion chromatography results from boron leaching showed that the ionic boron which appeared on chromatograms decreased in amount when boron was added to GA and DMDHEU (Table 2). However, much remarkable change occurred in the case of boron addition to GX, because ionic boron was extremely low in the leachates of wood treated with BA-added GX and it was no longer detectable in the leachates and HWE of wood treated with PBA-added GX (Fig. 1). Ionic boron was very low in the leachates of cyclic leaching in general, therefore, boron concentration in HWE was based on the boron leachability assessment of PBA involved treatments. Disappearance of the boron peak which usually appears at around 8.5 min detection time of chromatograms suggested that boron was no longer in its ionic free form in cases of PBA- or BA-addition into GX and to a lesser extent in the case of PBA-addition to DMDHEU. Boron is known to establish oxygen bonds with OH-groups of cell walls (Kubel and Pizzi 1982). Although no evidence was reported of such a linkage between BA and GX after cured in wood, boron was supposed to interact with reactive sites of GX, referring to the leachability and ASE results (Tables 1 and 2). Boron-oxygen bonds (with hydroxyl groups of lignin guaiacyl units, and in similar manner with the wood carbohydrates) are easily soluble, and hence easily leachable during wetting of the treated wood (Kubel and Pizzi 1982; Yalinkilic et al. 1996). However, boron released into the leaching water was at very low levels from wood treated with BA-added GX. In addition, no ionic boron was detected from HWE of PBA-GX combination (Table 2). This indicates that complexation of boron with GX may be strong enough to affect cross-linking efficiency of GX to wood resulting in low ASE of wood (Table 1). Accordingly, it can be speculated that boron stability is likely be possible by chemical complexation with a compatible cross-linking chemical in wood. However, some adverse effect of boron on the cross-linking efficacy of aldehydes should also be taken into account due to potential chemical complexations. Unlikely, GA, and to some lesser extent, DMDHEU did not cause considerable changes in ionic form of boron as observed from the chromatograms. As a result, they appeared more appropriate for boron combination systems in terms of dimensional stability of wood while GX increased the boron stability in wood.

3.3 Decay resistance

Mass losses of wood after exposure to *Tyromyces palustris* and *Coriolus versicolor* are given in Table 3. Among the used cross-linking agents, GA produced complete resistance of wood against the two test fungi. GX, and to some lesser extent, DMDHEU required supplemental treatment to be sufficiently resistant. These results are consistent

Table 2. Boron acid concentration in the leachates and hot water extracts (HWE) of treated wood
Tabelle 2. Borsäurekonzentration im Waschwasser und Heißwasserextrakt von behandeltem Holz

Leach cycle	BA	DMDHEU + BA	GA + BA	GX + BA
Boron concentration in cyclic leachates (ppm)				
1	460.0	187.6	257.6	51.6
2	14.7	103.7	40.3	14.4
3	1.7	42.8	18.0	8.2
4	Undetectable	5.9	5.1	7.6
5	-do-	3.1	2.7	6.0
6	-do-	Undetectable	Undetectable	4.5
7	-do-	-do-	-do-	3.7
8	-do-	-do-	-do-	Undetectable
9–10	-do-	-do-	-do-	-do-
Total	476.4	341.1	323.7	100.6
	PBA	DMDHEU + PBA	GA + PBA	GX + PBA
Boron concentration in HWE of PBA involved treatments				
Before leaching	67.7	58.5	50.9	Boron peak disappeared
After leaching	49.0	53.1	34.4	Boron peak disappeared

[a] DMDHEU: dimethylol dihydroxy ethylene urea, GA: glutaraldehyde, GX: glyoxal, BA: boric acid, PBA: phenyl boronic acid

with the previous studies with the same chemicals, reported by Yusuf et al. (1995), and Yusuf (1996). BA and PBA addition expectedly imparted total resistance to both agents and mass losses recorded at reasonable levels less than 3% (Table 3) which is designated in the related standards for complete resistance. This indicates that remaining boron even after severe leaching of specimens had still been sufficient to inhibit fungal activity in wood. However, the PBA-GX combination resulted in somewhat higher mass losses 3%, around than 4.4 and 4.9% caused by *Tyromyces palustris* and *Coriolus versicolor* degradation, respectively. Since boron was claimed to be much more effective against fungi in its free ionic form rather than in chemical complexes (Lloyd 1993; Lloyd et al. 1990), higher mass losses in the decay test can also be an indicator of potential chemical complexations between PBA and GX. Unlikely, the boron-GA combination was quite resistant against both types of decay fungi indicating that boron is still keeping its biological activity despite mixing with GA.

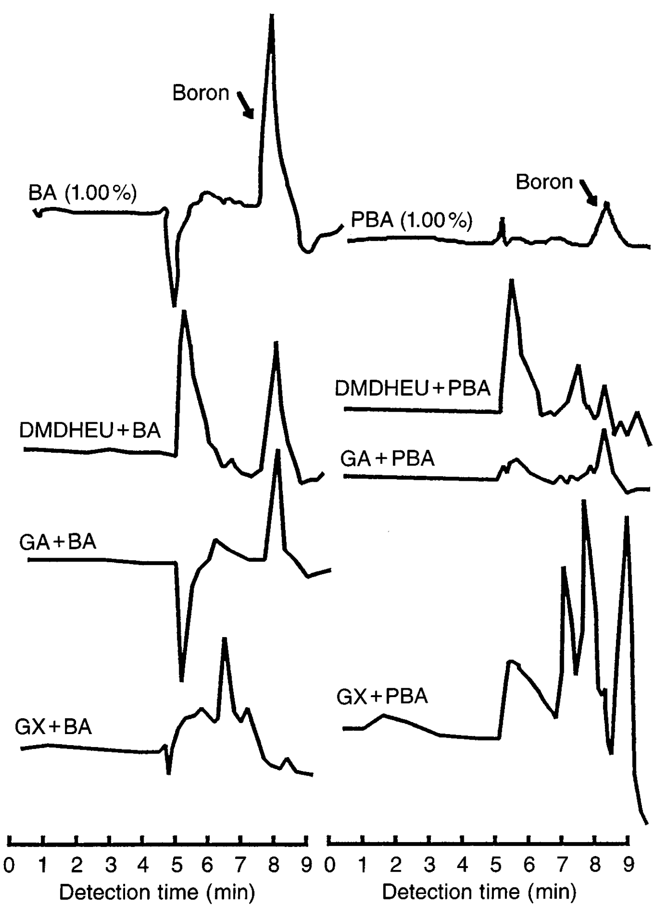

Fig. 1. Chromatograms of hot water extracts obtained from powder after treatment and curing with boron-non or low-formaldehyde agents before leaching BA: Boric acid, PBA: Phenylboronic acid, DMDHEU: Dimethylol dihidroxy ethylene urea, GA: Glutaraldehyde, GX: Glyoxal
Bild 1. Chromatogramme der Heißwasserextrakte von Holzmehl nach Behandlung und Vernetzen mit Borpräparaten ohne oder mit geringem Formaldehydgehalt vor dem Auswaschen: BA Borsäure; PBA Phenylborsäure; DMDHEU Dimethylol-dihydroxyethylen-Harnstoff; GX Glyoxal

3.4 Termite resistance

Mass losses of wood after exposure to termite attack and mortality percentages of *Coptotermes formosanus* over a three weeks incubation period are given in Tables 4 and 5.

Table 3. Mass loss of wood after exposure to the decay fungi *Tyromyces palustris* and *Coriolus versicolor* for 12 weeks
Tabelle 3. Gewichtsverlust von Holz nach 12-wöchigem Abbautest mit *T. palustris* und *C. versicolor*

Treatment[b]	Leaching	*Tyromyces palustris*	*Coriolus versicolor*
Mass loss (%)[a]			
Untreated	Unleached	44.6 (8.4)	50.5 (5.5)
DMDHEU	Leached	6.6 (1.7)	3.1 (0.6)
GA	Leached	0.6 (0.2)	0.7 (0.4)
GX	Leached	19.9 (1.0)	24.6 (2.4)
BA-non or -low-formaldehyde reagents' combinations			
BA	Unleached	0.0	0.0
BA	Leached	21.7 (4.8)	26.0 (4.9)
DMDHEU + BA	Leached	0.3 (0.05)	2.5 (0.2)
GA + BA	Leached	0.0	0.0
GX + BA	Leached	2.4 (0.9)	0.7 (0.08)
PBA-non or -low-formaldehyde reagents' combinations			
PBA	Unleached	0.0	0.0
PBA	Leached	0.0	0.09 (0.3)
DMDHEU + PBA	Leached	2.5 (0.3)	1.1 (0.5)
GA + PBA	Leached	0.9 (0.1)	1.3 (0.4)
GX + PBA	Leached	4.4 (0.2)	4.9 (0.5)

[a] Standard deviations were included in the paranthesis
[b] DMDHEU: dimethylol dihydroxy ethylene urea, GA: glutaraldehyde, GX: glyoxal, BA: boric acid, PBA: phenyl boronic acid

Table 4. Mass loss of wood after exposure to Formosan subterranean termite *Coptotermes formosanus* for 3 weeks
Tabelle 4. Gewichtsverlust nach 3-wöchigem Abbau durch Termiten (*Coptotermes formusanus*)

Treatment[b]	Leaching	Mean loss (g)	Percent loss
Mass loss (%)[a]			
Untreated	Unleached	0.131 (0.02)	13.7 (2.0)
DMDHEU	Leached	0.188 (0.02)	19.1 (2.8)
GA	Leached	0.065 (0.014)	6.4 (1.4)
GX	Leached	0.183 (0.04)	12.8 (2.1)
BA-non or -low-formaldehyde reagents' combinations			
BA	Unleached	0.014 (0.001)	1.5 (0.1)
BA	Leached	0.484 (0.44)	15.1 (0.4)
DMDHEU + BA	Leached	0.146 (0.02)	13.1 (2.3)
GA + BA	Leached	0.152 (0.02)	10.2 (1.6)
GX + BA	Leached	0.152 (0.02)	10.2 (1.6)
PBA-non or -low-formaldehyde reagents' combinations			
PBA	Unleached	0.0	0.0
PBA	Leached	0.001 (0.0)	0.1 (0.001)
DMDHEU + PBA	Leached	0.006 (0.001)	0.6 (0.1)
GA + PBA	Leached	0.005 (0.001)	0.5 (0.01)
GX + PBA	Leached	0.0	0.0

[a] Standard deviations were included in the paranthesis
[b] DMDHEU: dimethylol dihydroxy ethylene urea, GA: glutaraldehyde, GX: glyoxal, BA: boric acid, PBA: phenyl boronic acid

Table 5. Mortality rates of termite (*Coptotermes formosanus*) workers subjected to force-feeding test along with 3 weeks test duration (Mortality in brackets)
Tabelle 5. Letalität von Termiten-Arbeitern (*Coptotermes formosanus*) nach 3-wöchigem Freßtest (Sterberok in Klammern)

Treatment[b]	Leaching	3rd day	1st week	2nd week	3rd week
Mortality (%)[a]					
Untreated	Unleached	0.0	1.7 (2.9)	9.2 (2.1)	20.5 (8.3)
DMDHEU	Leached	0.3 (0.2)	8.0 (0.6)	18.3 (2.3)	33.0 (8.0)
GA	Leached	4.7 (1.3)	6.0 (2.7)	16.3 (3.0)	24.0 (6.7)
GX	Leached	5.1 (2.7)	10.6 (4.2)	23.2 (2.0)	39.0 (5.0)
BA-non or -low-formaldehyde reagents' combinations					
BA	Unleached	10.5 (3.5)	20.3 (5.0)	99.0 (1.0)	100.0 (0.0)
BA	Leached	5.0 (1.0)	9.6 (3.6)	28.0 (7.0)	42.0 (7.3)
DMDHEU+BA	Leached	2.0 (0.6)	4.6 (0.6)	16.0 (1.3)	26.7 (5.0)
GA+BA	Leached	0.4 (0.6)	1.5 (0.8)	13.8 (1.9)	28.5 (3.0)
GX+BA	Leached	3.6 (0.8)	10.0 (2.0)	23.5 (1.3)	35.1 (1.1)
PBA-non or -low-formaldehyde reagents' combinations					
PBA	Unleached	69.0 (12.8)	100.0 (0.0)	–	–
PBA	Leached	34.0 (7.0)	83.3 (10.4)	100.0 (0.0)	–
DMDHEU+PBA	Leached	7.3 (3.3)	16.7 (2.7)	95.7 (3.0)	100.0 (0.0)
GA+PBA	Leached	4.7 (1.3)	14.0 (2.5)	53.4 (3.5)	100.0 (0.0)
GX+PBA	Leached	6.7 (1.9)	7.3 (1.8)	50.7 (4.4)	100.0 (0.0)

[a] Standard deviations were included in the paranthesis
[b] DMDHEU: dimethylol dihydroxy ethylene urea, GA: glutaraldehyde, GX: glyoxal, BA: boric acid, PBA: phenyl boronic acid

Results indicated that used aldehydes did not impart any termite resistance to wood; (Table 5) therefore, the wood specimens need supplemental treatment, although GA could avoid excess mass loss after termite attack to half the extent of untreated wood. BA, surprisingly, had almost no termiticidal activity when added to the used cross-linking agents referring to resulting mass loss and mortality levels after boron addition (Tables 4 and 5). This might be mainly due to: (a) retained boron after severe leaching might not suffice to impart the required toxic effect to inactivate termite attack, because an almost four times higher amount of boron is necessary for termiticidal effectiveness of boron than that for the fungicidal threshold level (Drysdale 1994), (b) boron is a slow acting stomach poison and large amounts of mass losses are almost unavoidable at lower retention rates (Williams et al. 1990); (c) wood becomes more susceptible to termite attack when exposed to a temperature of over 100 °C for a long period of time (Doi et al. 1995 and 1996), or boron toxicity might change after being added to those agents, etc.

Contrary to BA, PBA could completely inactivate termite attack after the test period. The PBA-GX combination was the most effective treatment system regarding mass loss results while the PBA-DMDHEU combination yielded the highest termite mortality and killed almost all termites within two weeks (Tables 4 and 5). As a consequence, boron complexations appeared to have a reducing effect on PBA's decay resistance but not on its termiticidal activity and BA appeared appropriate to be added to DMDHEU, GA and GX where the decay risk is high, while PBA seemed preferable in cases where termite damage is dominant.

4 Conclusions

Boron was added to DMDHEU, GA and GX with the aim of reducing boron leachability while improving biological resistance and dimensional stability of wood in a single treatment process. Boron addition to GX and DMDHEU caused some decrease in ASE of treated wood, but interestingly improved the dimensional stability when added to GA. Leachability results suggested that some chemical interactions can be expected between boron and GX, since ionic boron was no longer detectable by ion chromatography when PBA, and to a lesser extent, BA were added into GX and then cured. DMDHEU and GA also showed some reducing effect on boron leachability.

BA and PBA addition to the used cross-linking agents considerably improved the decay resistance against *Tyromyces palustris* and *Coriolus versicolor*. Somewhat higher mass losses were recorded for PBA-GX combination treatments possibly due to chemical complexation referring to the related chromatograms. This finding was supportive to earlier conclusions on "high fungicidal activity of free ionic boron". After severe leaching of wood treated with BA-cross-linking reagent combinations, the retained boron was found not to show enough adequate termiticidal activity. However, PBA-addition to the used reagents attained complete resistance against termites. Thus, different boric compounds can show different physical, chemical and biological performances under certain conditions with the accompanying chemical combinations, and separate evaluations of boric compounds seemed necessary instead of generalization.

In conclusion, BA appeared to be appropriate to add the used cross-linking agents where decay hazard is high while PBA can be preferably added when termite attack is prevalent.

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