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NOTE

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Enhancement of the biological resistance of wood by phenylboronic acid treatment*

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Abstract Phenylboronic acid (PBA) was tested in terms of boron leachability from treated wood. In addition, the fungal and termiticidal efficacy of PBA-impregnated sugi (*Cryptomeria japonica* D. Don) wood was tested against the decay fungi *Coriolus versicolor* (L. ex Fr.) Quel. and *Tyromyces palustris* (Berk. et Curt) Murr., representing white-rot and brown-rot fungi, respectively, and the Formosan subterranean termite *Coptotermes formosanus* Shiraki. Ion chromatography analysis of hot water extracts of treated wood before and after leaching indicated that PBA is considerably resistant to water leaching, and saturation of the treatment solution increased the fixation ratio of boron in wood, whereas boric acid could not remain in wood impregnated even with the saturated solution. Decay test results revealed the excellent bioactive performance of PBA. Wood treated with 0.34% PBA solution was found resistant to both decay fungi, even after running-water leaching for 10 days and treatment with 1.00% PBA completely inactivated the Formosan subterranean termite for the leached specimens. Weight gain levels were 0.18% w/w ($0.46 kg/m^3$) and 0.99% w/w ($2.49 kg/m^3$) for these concentration levels, respectively, after being leached by running water. Contrary to the general belief that boron is a slow-acting toxicant against termites and unable to prevent mass loss of treated wood, PBA acted rapidly, and the mass loss caused by termites was low.

Key words Phenylboronic acid · Boron leachability · Decay resistance · Termite resistance · Wood preservation

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Introduction

Boronic acids belong to a family of organic boron derivatives expressed by the formula $RB(OH)_2$. These compounds have been reported to have biological activities such as sterilizing effects on flies.[1] Some members of the closely related group of borinic acids (general formula R_2BOH) have been reported to have antifungal effects.[2] Boronic acids are expected to have the ability to inhibit certain enzymes of decay fungi by interacting with the active sites.[3] In final reports on this matter, phenylboronic acid [$C_6H_5B(OH)_2$] (PBA) (Fig. 1), which is the simplest arylboronic acid commercially available, was found to have fungicidal activity against basidiomycete decay fungi.[4–6] The toxic oral LD_{50} dose of PBA for the rat is 740 mg/kg, whereas a 2660 mg/kg dose of boric acid (BA) is required for the same level of efficacy.[7] No environmental toxicity was reported for PBA, similar to other environmentally safe boron compounds.[7]

Studies on the use of PBA as a wood preservative are few and relatively recent.[4–7] It has been suggested in those studies that other properties of PBA, such as its leachability from treated wood, antiinsect properties, and effect on wood strength, must be determined before the potential of PBA as a wood preservative can be fully known. The present study therefore deals with the leachability of boron and the biological resistance of wood treated with PBA.

Experimental

Chemicals and treating conditions

Sapwood blocks of sugi (*Cryptomeria japonica* D. Don) were prepared in dimensions of 20 mm (T) × 20 mm (R) × 10 mm (L) for impregnation treatment (T = tangentially; R = radially; L = longitudinally). Air dried specimens were used. PBA was applied at concentrations of 0.34%, 0.50%, 1.00%, and 2.00% (w/w) in aqueous solution. Leachability

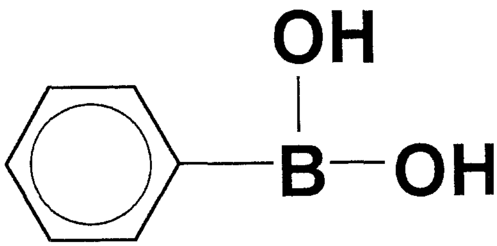


Fig. 1. Chemical structure of phenylboronic acid

and biological test results of conventional BA treatment (in aqueous solutions of 0.25%, 1.00%, and 4.70%) (saturated solution at 20°C) were also included in the study to compare the relative efficiencies of the two chemicals.[8] Specimens were subjected to 30 min of vacuum at 760 $mmHg^{-1}$ followed by 30 min of diffusion in the treatment solutions. All the treatments were duplicated under the same conditions. Weight gains of the chemicals were calculated from the initial and final oven dry weights.

Leachability

Leachability tests were conducted according to Japanese Industrial Standard (JIS) A 9201–1991. Water leaching and evaporation were conducted for 10 cycles. Leaching was performed in deionized water stirred by a magnetic stirrer (400–450 rpm/min) for 8 h at 25°C and specimens were dried for 16 h at 60°C consecutively for each cycle. After each leaching period the leachate was sampled for analysis by ion chromatography (IC) using the Yokogawa-Hokushin Electric IC 500P 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. A refractive index detector (ERC-7511; Erma Tokyo, Japan) was used. To determine the fixed amount of boron in wood, specimens at each retention level before and after leaching and ground to fine powder were subjected to hot water extraction (HWE) for 3 h; the filtered HWE extracts were then analyzed with IC. The IC analyses were conducted according to the literature.[9]

Biological tests

Prior to the biological tests, wood specimens were subjected to running-water leaching for 10 days at ambient temperature, with a 4-h vacuum application per day. The vacuum was intended to increase the severity of leaching by introducing water into the wood blocks. Preliminary laboratory trials on the severity of cyclic and running-water leaching of PBA-treated wood with the applied vacuum condition resulted in less weight gain of wood. Thus running-water leaching with occasional vacuum application was preferred in this study to create more severe leaching before the biological tests.

Decay resistance test

A monoculture decay test was conducted according to JIS A-9201-1991, using the brown-rot fungus *Tyromyces palustris* (Berk. et Curt) Murr. FFPRI 0507 and the white-rot fungus *Coriolus versicolor* (L. ex Fr.) Quel. FFPRI 1030. The test blocks were sterilized in gaseous ethylene oxide after measuring their original dry weight. The blocks in the glass jars in which the fungal mycelia grew were kept at 26°C for 12 weeks. Nine replicates were made for each treatment. The extent of the attacks was determined based on the percent mass loss.

Termite resistance test

Four untreated and treated test blocks were exposed to subterranean termites (*Coptotermes formosanus* Shiraki) in accordance with Japan Wood Preserving Association (JWPA) standard 11 (1)-1992. Each wood block was placed at the bottom of a cylindrical test container with a plaster bottom (80 mm in diameter). A total of 150 termite workers were introduced into each test container with 15 soldiers. The assembled containers were set on damped cotton pads to supply water to the blocks and kept at 28°C and >80% RH in the dark.

Termite mortality was determined after 3 days and at the end of each of the following 3 weeks from the beginning date of the test. The mass loss of the test blocks caused by termite attacks was determined after 3 weeks of exposure.

Results and discussion

Weight gain, leachability, and possible fixation mechanism of boron

The weight gains of specimens treated with PBA and BA before cyclic leaching are shown in Fig. 2. The same concentration resulted in the same weight gain of wood after both PBA and BA treatments (at 1.00% concentration the weight gain was 3.54% w/w for both chemicals). This result reflects the absorption similarity of the woods under the same impregnation conditions.

The boron concentration in the leachates was found to be low by IC. Therefore the IC results from the HWEs were used as a base for the leachability assessment. PBA and BA apparently differed in their leachability pattern of boron (Figs. 3, 4). Boron detected in the HWEs of PBA-treated wood before and after leaching revealed that much of the boron was fixed in the wood and could be only partly solubilized by hot water extraction. In addition, saturation of the treatment solution resulted in more fixation of boron in the wood after PBA treatment (Fig. 3).

Boron in the HWEs of BA-treated wood became undetectable by IC after leaching. In other words, all detectable boron was removed from wood by water, regardless of the retention level of BA (Fig. 4). These results are in good agreement with data from Peylo and Willeitner.[10]

Evidently, increasing the solution strength can provide better fixation of boron with PBA impregnation, whereas BA is definitely leached out regardless to the loading amount in wood.

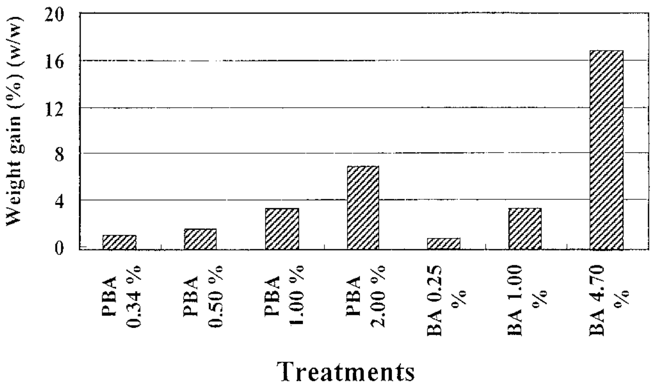


Fig. 2. Weight gain of sugi wood treated with phenylboronic acid (*PBA*) and boric acid (*BA*) with the concentrations of the aqueous solutions

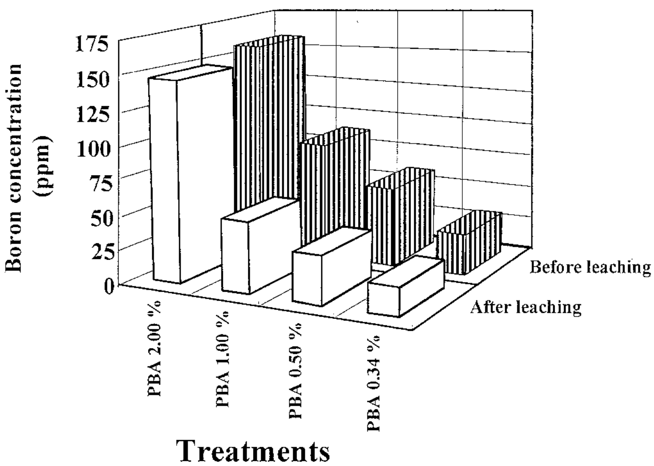


Fig. 3. Boron concentration in hot water extracts (HWEs) of PBA-treated wood

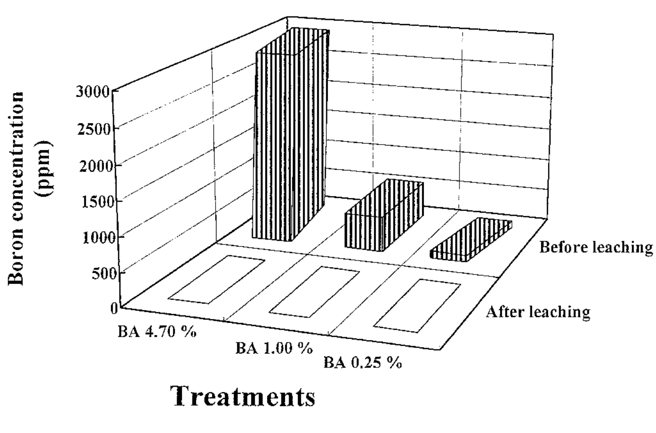


Fig. 4. Boron concentration of HWEs obtained from BA-treated wood

The apparent difference of boron stability after PBA and BA treatment is likely due to their chemical interactions with wood. BA readily forms complexes with 1-methoxy-2-hydroxy benzene and 1,2-dimethoxy benzene groups in lignin.[11,12] PBA has two reactive OH^- groups linked to the boron molecule (Fig. 1), so PBA is likely to be connected to wood by bonds similar to those of BA. As suggested by Lloyd[3] for PBA–polyol complexation, a hypothetical structure of the wood–PBA interaction is proposed in Fig. 5. Such a connection probably makes boron more stable to water leaching than the borates because water access to wood seems limited by the possible occupation of reactive sites of PBA (OH^- groups) by wood or other PBA molecules. An increasing tendency of boron fixation by saturation of PBA solution (Figs. 2, 3) supports this assessment.

On the other hand, the stability of boron depends on the strength of the boron–oxygen bond (B-O).[13] Boron became almost completely undetectable in the HWEs of BA-treated wood after being leached out by running water (Fig. 4), so it can be speculated that the strength of B-O bonding during the BA–wood interaction is less than that of water molecule–wood bonding through OH^- groups. In contrast, the PBA–wood connection seems much stronger to the extent of fixation capacity than that of BA, according to the leachability results.

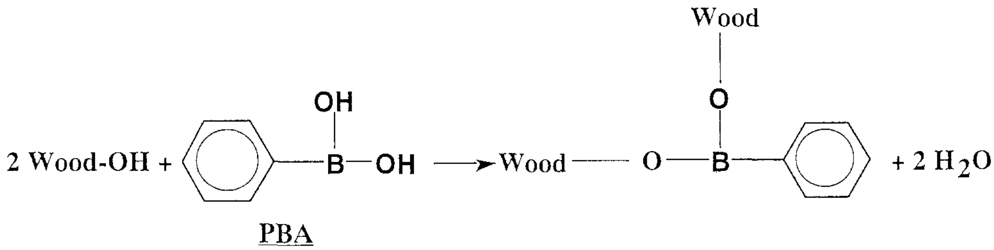
The permanence of PBA in wood after severe leaching is believed to lead to the development of new, alternative treatments of outdoor timber for long-term protection instead with those of the unstable boric compounds known to be easily leachable and hygroscopic.[6,8,14–16]

Decay resistance

Results of decay tests of sugi specimens untreated and treated with PBA and BA are shown in Figs. 6 and 7, respectively. The PBA-treated specimens were resistant to both of the decay fungi before and after leaching. Although the leaching process slightly increased the fungal attack for low weight gain with PBA, the mass loss remained at a reasonable level: 3.74% and 2.22% for *T. palustris* and 2.63% and 2.51% for *C. versicolor* at 0.34% and 0.50% treatment concentrations of PBA, respectively (Fig. 6). Wood treated with the 0.34% PBA solution was found resistant to both decay fungi, even after running-water leaching for 10 days. Therefore the threshold level of PBA against the two types of decay fungi appeared to be around 0.20% weight gain w/w ($0.46 kg/m^3$) for the leached specimens.

In contrast, the BA-treated wood, even at high loading levels with the saturated solution (17.0% w/w, or $42.08 kg/m^3$, before leaching) was strongly destroyed by fungal attack after leaching (Fig. 7). The determined threshold levels of PBA after leaching are within the required level limits of BA in nonleaching conditions.[17,18] Taking into account all other threshold levels recorded for boron compounds, which were summarized by Drysdale,[19] PBA appeared superior by maintaining its bioactivity even after severe leaching conditions.

Fig. 5. Possible structure of wood–PBA interaction



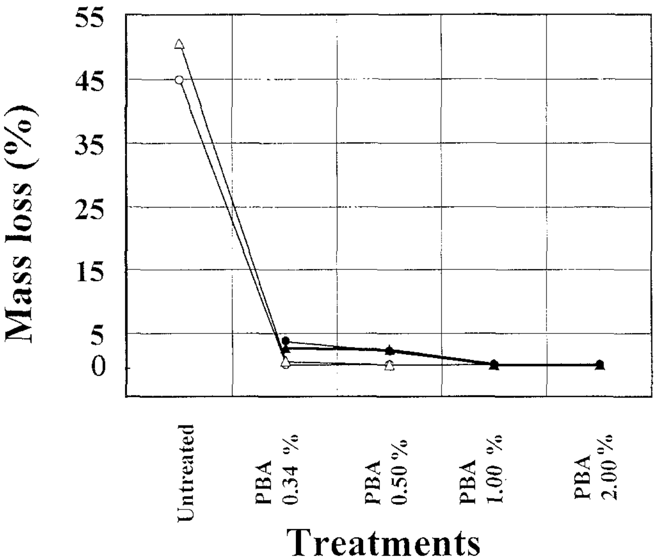


Fig. 6. Mass loss of PBA-treated sugi wood subjected to decay test. *Open circles*, before leaching – *Tyromyces palustris*; *filled circles*, after leaching – *T. palustris*; *open triangles*, before leaching – *Coriolus versicolor*; *filled triangles* after leaching – *C. versicolor*

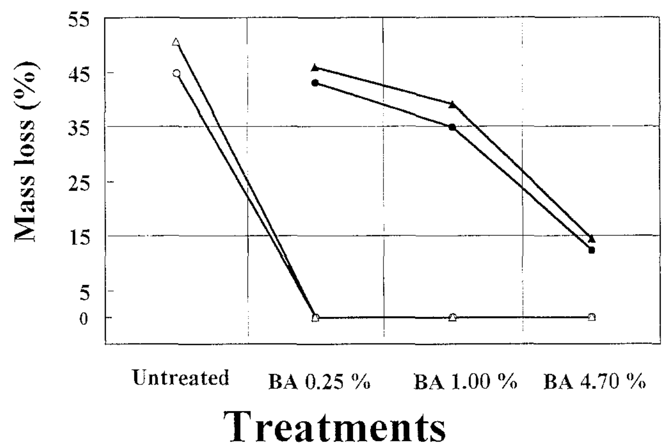


Fig. 7. Mass loss of BA-treated sugi wood subjected to decay test. See Fig. 6 for explanation of symbols

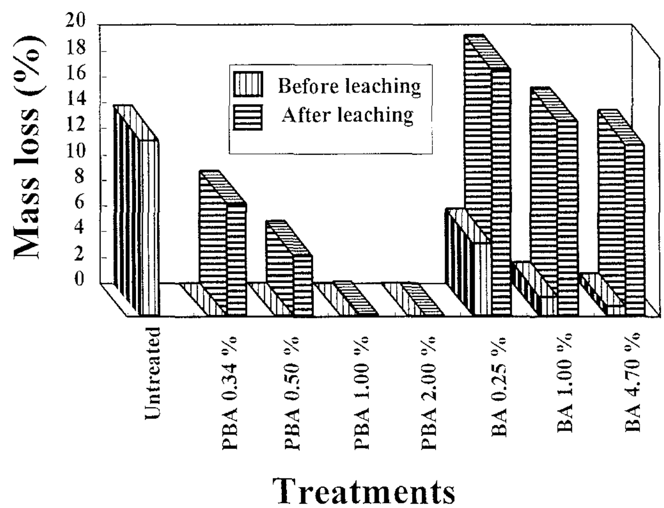


Fig. 8. Mass loss of sugi wood after exposure to termites for 3 weeks. The percentages represent the concentration in aqueous solutions

Termite resistance

The PBA-treated wood specimens were subjected to a forced feeding test of the Formosan subterranean termite *C. formosanus*. Mass loss and termite mortality of test specimens after exposure to termite attack for 3 weeks are shown in Figs. 8–10 for both PBA- and BA-treated wood.

No mass loss was recorded for PBA-treated wood before leaching, whereas there was considerable loss for the BA-treated wood even after treatment with the saturated solution (Fig. 8). Moreover, BA lost much of its protection against termites after leaching regardless of the weight gain, and the mass loss caused by termites reached levels similar to that of the control; for wood with lower retention the loss was considerably more than that of the control.

In contrast to BA, PBA showed excellent termiticidal performance before and after leaching. Complete elimination of termite attack was accomplished by PBA treatment with 1.00% concentrated solution in leached specimens. The weight gain of wood at this concentration was 0.99% w/w (2.49 kg/m^3) after leaching. A much lower concentration of PBA achieved total termite inactivation before leaching. With 100% mortality of termites there was no mass loss during the second week of exposure after treatment with 0.34% PBA (Fig. 8).

On the other hand, PBA differed from conventional boron treatment in regard to acting against termites, according to the mass loss and mortality levels after leaching (Fig. 8–10). Boron is a known slow-acting toxicant that kills termites when they ingest treated wood rather than by

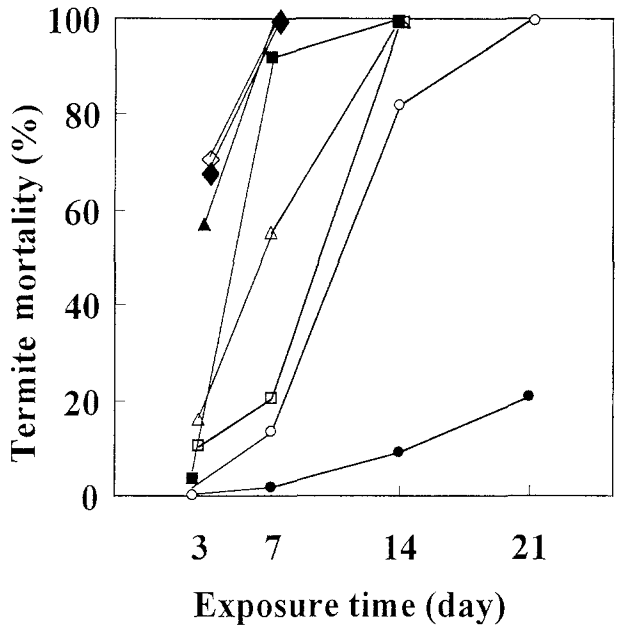


Fig. 9. Mortality levels of *Coptotermes formosanus* during exposure of unleached PBA- and BA-treated sugi wood. *Filled circles*, untreated; *filled squares, triangles, diamonds*, 0.34%, 0.50%, 1.00% PBA, respectively; *open diamonds*, 2.00% PBA; *open circles*, 0.25%, *squares, triangles*, 1.00%, 4.70% BA, respectively

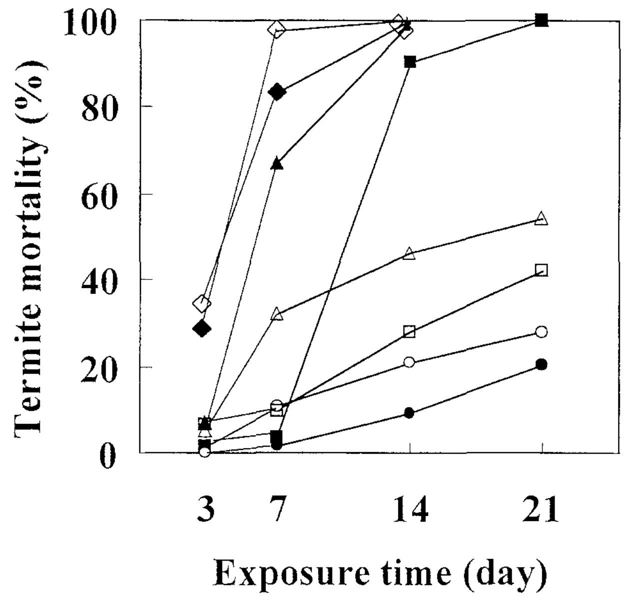


Fig. 10. Mortality levels of *C. formosanus* during exposure of leached PBA- and BA-treated sugi wood. See Fig. 9 for explanation of symbols

contact.[20] As a consequence, a considerable amount of wood mass is lost almost unavoidably even at high concentrations of boric acid and borax, and the protective ability of boron sharply decreases when treated wood is water-leached, which gradually attracts termite attacks during the wet season.[6,8,20] In contrast, PBA was able to avoid mass loss of wood under termite attack and maintained its protective effect after leaching.

Total inactivation of termites could be accomplished within 3 days with PBA treatment at a concentration of 0.50% and higher before leaching. PBA 0.34% attained this level of mortality after 1 week of exposure (Fig. 9), whereas BA achieved total inactivation only after 2 weeks' exposure of specimens treated with a saturated solution (Fig. 10).

The high efficacy of PBA against termites was exhibited by the markedly lower weight gain by the PBA-treated wood. Moreover, there was minor loss of mass and high termite mortality in the leached specimens.

Conclusions

Phenylboronic acid was tested in terms of boron leachability and biological resistance. Results indicated that PBA is markedly resistant to water leaching, whereas BA was readily leached from treated wood. The boron leaching rate was reduced by increased retention of PBA in wood, independent of the weight gain after BA treatment.

Wood treated with 0.34% PBA solution was found resistant to *T. palustris* and *C. versicolor*, even after running-water leaching for 10 days. The corresponding weight gain was 0.2% w/w (0.46 kg/m^3) for the threshold level of PBA, whereas BA-treated wood, even at a high loading level with the saturated solution, was badly damaged by fungal attack after leaching. Weight gain was 17.0% w/w (42.08 kg/m^3) for this concentration of BA before leaching.

The PBA showed excellent termiticidal performance before and after leaching. Treatment with 1.00% PBA totally inactivated the Formosan termite *C. formosanus* after leaching. The corresponding weight gain was 0.99% w/w (2.49 kg/m^3) after leaching. Contrary to the general belief that boron compounds are slow-acting toxicants against termites, resulting in an unavoidable mass loss in wood treated with borates, PBA acted rapidly, and the mass loss caused by termite attack was low for PBA-treated wood.

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