NOTE

Kunio Tsunoda

Preservative properties of vapor-boron-treated wood and wood-based composites

Received: January 26, 2000 / Accepted: March 22, 2000

Abstract The treatability of wood (sapwood of *Cryptomeria japonica* D. Don) and wood-based composites (particleboard, waferboard, medium-density fiberboard, plywood) with vapor-boron was good, and the treated materials proved to be resistant to decay fungi and subterranean termites in laboratory bioassays. No difference in effectiveness was noted between vapor-boron and liquid-boron treatment of wood. Toxic threshold values determined for solid wood were 0%–0.24%, 0.26%–0.51%, and 0.26%–0.51% BAE (boric acid equivalent), respectively, against the white-rot fungus *Trametes versicolor* (L.: Fr.) Pilat, the brown-rot fungus *Fomitopsis palustris* (Berk. et Curt.), and the subterranean termite *Coptotermes formosanus* Shiraki. A concentration of less than 1% BAE seemed sufficient to control biological attacks on composites, although the toxic limits could not be determined more accurately because of the tested range of boron retention. High boron retention was needed to meet the performance requirements for slow-burning materials when a fire-retardant agent was not incorporated into the glue line.

Key words Vapor-boron treatment · Trimethyl borate · Decay resistance · Termite resistance · Fire resistance

Introduction

Boron compounds have been used to treat green lumber by a rapid dip-diffusion process because of low treatment cost, high insecticidal and fungicidal effectiveness, unchanged color of the treated lumber, and relatively low toxicity.[1–7] As reviewed previously[8] boron and related compounds have proved effective in retarding fire in wood and wood-based composites owing to their coating effect, with a heat-molten membrane formed on the substrate surfaces during fire. A retention level of approximately 12% (w/w) boric acid gave a good fire-retardant quality to sliced veneers of *Chamaecyparis obtusa* Endl.[9]

Vapor-boron treatment has been investigated in New Zealand and the United Kingdom to improve treatment efficiency (shortened processing and storage time, reduced cost, and environmental soundness) and to understand the preservative and mechanical performance of treated materials.[10–19] All of these studies were concerned with the use of a borate ester, trimethyl borate, as a potential chemical agent for vapor-boron treatment of wood products. The chemical reaction of trimethyl borate with moisture within the wood or wood-based composites results in deposition of boric acid, forming methanol as a by-product. A possible reaction is:

$$B(OCH_3)_3 + 3H_2O \rightarrow H_3BO_3 + 3CH_3OH$$

Vinden et al. indicated that the reaction took place instantaneously when vaporized trimethyl borate came in contact with wood, and that the treatment temperature was not significant for retention so long as it was high enough to evaporate the chemical introduced into the treatment vessel. They also demonstrated that the moisture content of wood was critical for the retention obtained by such a hydrolytic reaction using 100 × 50 mm radiata pine sapwood.[10] Murphy and Turner, who investigated the effects of moisture content and treatment time on the treatability of wood-based composites, found that retention increased with the moisture content, and levels of penetration adversely decreased in oriented strand boards. Other board materials tended to show a similar tendency, whereas retention and penetration levels varied among the various board types when tested at moisture contents of 0%, 2%, and 4%. Treatment time proved to be significant, leading to higher retention in oriented strand boards at a moisture content of 2%.[11] Decay test results of the wood-based composites well supported the applicability of the vapor-boron treatment. At a retention of 0.7% BAE, decay was satisfactorily suppressed, as the percent mass loss was less than 2% in any of

K. Tsunoda (✉)
Wood Research Institute, Kyoto University, Uji, Kyoto 611-0011, Japan
Tel. +81-774-38-3661; Fax +81-774-38-3664
e-mail:tsunoda@termite.kuwri.kyoto-u.ac.jp

the wood-based composites when the mass loss of untreated controls exceeded 15%.[12]

A series of papers that addressed the mechanical properties (modulus of rupture, modulus of elasticity, impact strength, internal bond strength) and physical properties (swelling, mass increase after water soaking, dimensional stability, hysteresis over a range of 30%–90% moisture content) of wood-based composites concluded that vapor-boron treatment did not have any significant negative effect on most of the mechanical and physical properties, except for a slight reduction in the impact strength at the higher retention of boric acid.[15–17,19] Flame retardance seems obtainable with wood-based composites through vapor-boron treatment without any of the serious disadvantages of the current liquid-phase treatments.[16]

This paper describes the applicability of vapor-boron treatment to solid wood and wood-based composites in terms of decay and termite and fire resistance of the treated materials according to Japanese Industrial Standard (JIS) and Japan Wood Preserving Association (JWPA) standard methods.

Materials and methods

Test specimens

Sapwood specimens were prepared from *Cryptomeria japonica* D. Don in dimensions of 20mm (T) × 20mm (R) × 10mm (L). Five commercially available wood-based composites were tested as well: particleboard (PB-A) [resin PF; thickness 15.2mm; air-dried specific gravity (ADSG) 0.73]; particleboard (PB-B) (resin PMF; thickness 15.2mm; ADSG 0.79); aspen waferboard (WB) (resin PF; thickness 15.2mm; ADSG 0.63); medium-density fiberboard (MDF) (resin UMF; thickness 15.2mm; ADSG 0.64); and hardwood plywood (PW) (resin PF; thickness 15.5mm; ADSG 0.67). Specimens in dimensions of 22cm × 22cm × thickness were obtained from these wood-based composites.

Treatment and test specimen assignment

Solid wood specimens were dried to 10%–15% moisture content before placing them in a treatment chamber preheated to 60°–65°C. Trimethyl borate (TMB) (Aldrich, Milwaukee, WI, USA) was introduced into the chamber under vacuum to start the chemical reaction in the wood specimens; they were left there for 15min, and then pressure was slowly returned to the ambient condition. The amount of TMB was adjusted to obtain the desired retention of boric acid (target retentions were 1, 2, 3, 4, 5kg/m^3). Another set of specimens were impregnated with an aqueous solution of boric acid under vacuum to prepare matched retentions for comparison. A total of 23 replicates were prepared for each treatment (18 for the decay test and 5 for the termite test). Additional specimens were prepared to determine the retention of boric acid by a standard chemical analysis.

For the wood-based composites, the cutting edges of the test specimens were sealed with epoxy resin to prevent overloading the boric acid. Treatments were conducted at approximately 70°C under vacuum to produce three levels of retention, with five replicates for each treatment. A single board for each treatment was assigned for chemical analysis of boric acid. Specimens for decay and termite tests (2.5cm × 2.5cm × thickness) were obtained from a single board of each treatment group. Additional repeated treatments of the test wood-based composites were conducted to increase boron retention, and the treated materials were tested only for their fire resistance.

Decay test

The laboratory decay test was conducted according to JIS K 1571[20] using unweathered specimens of *C. japonica* sapwood and wood-based composites. Three specimens were exposed to a monoculture of the white-rot fungus *Trametes versicolor* (L.: Fr.) Pilat (FFPRI 1030) or the brown-rot fungus *Fomitopsis palustris* (Berk. et Curt.) (FFPRI 0507) in a glass jar at 26° ± 2°C for 12 weeks. Three decay jars were used to test nine replicates of each treatment against the two decay fungi. The percent mass loss was calculated from the difference in oven-dried weights of each specimen before and after the decay test.

Termite test

The termite test was conducted according to the JWPA Standard 11(1).[21] A test duration of 5 weeks was applied to the wood-based composite samples because of their large size (25mm × 25mm × thickness). Five replicates were tested. The percent mass loss of the specimens and the mortality of the termites were calculated after a termite bioassay.

Fire resistance test

The fire resistance test (surface test) was carried out with composite materials by a Japanese standardized test method (JIS A 1321).[22] The specimens (22cm × 22cm × thickness) were fitted into the heating furnace so the area of heated surface was limited to 18 × 18cm; they were then heated for 10min. A single board for each treatment level was used for the preliminary test, and two replicates were used for the later tests with higher boron-loading composites.

Results and discussion

Retention of boric acid in wood and composite materials

In general, the increase in weight due to the treatment is used to determine chemical retention in the treated substrate. However, some moisture is removed from the sub-

Table 1. Biological resistance of boron-treated sapwood of *Crypotomeria japonica*

Treatment	Retention		Mass loss by decay (%), mean ± SD		Mass loss by termites (%), mean ± SD	Termite mortality (%), mean
	kg/m^3	% BAE	*Trametes versicolor*	*Fomitopsis palustris*		
Vapor phase	0.9	0.24	0	6.5 ± 15.83	6.0 ± 1.55	96.8
	2.4	0.67	0	0	2.0 ± 0.42	100
	3.0	0.83	0	0	1.4 ± 1.24	100
	4.0	1.12	0	0.4 ± 0.67	2.7 ± 0.84	100
	5.3	1.46	0	0	1.5 ± 0.29	100
Liquid phase	0.9	0.26	0	14.9 ± 16.00	3.3 ± 0.45	100
	1.8	0.51	0	0	1.5 ± 0.95	100
	2.7	0.75	0	0	1.1 ± 0.62	100
	3.8	1.06	0	0	0.9 ± 0.38	100
	4.6	1.27	0	0	0.6 ± 0.43	100
Untreated controls			52.9 ± 7.72	59.7 ± 2.49	20.8 ± 2.03	7.2

BAE, boric acid equivalent

Table 2. Biological resistance of vapor-boron-treated composites

Composite	Retention (% BAE)	Mass loss by decay (%), mean ± SD		Mass loss by termites (%), mean ± SD	Termite mortality (%), mean
		Trametes versicolor	*Fomitopsis palustris*		
Particleboard (PB-A)	0	17.3 ± 0.79	2.0 ± 1.29	3.3 ± 0.75	50.7
	1.64	0	0	0	100
	4.20	0	0	0	100
Particleboard (PB-B)	0	18.7 ± 0.68	1.7 ± 0.33	2.8 ± 0.59	27.3
	0.85	0	0	0	100
	2.88	0	0	0	100
Waferboard (WB)	0	39.1 ± 3.69	60.3 ± 3.69	7.5 ± 0.52	33.6
	1.14	0	0	0	100
	3.19	0	0	0	100
Medium-density fiberboard (MDF)	0	7.7 ± 1.20	2.3 ± 0.32	2.2 ± 0.25	49.3
	2.29	0	0	0	100
	5.74	0	0	0	100
Hardwood plywood (PW)	0	15.5 ± 1.79	0.6 ± 0.1	2.3 ± 0.25	63.3
	0.64	0	0	0	100
	2.17	0	0	0	100

strate during the initial vacuum period, and the substrate absorbs both boric acid and methanol when vapor-boron treatment is applied. The boric acid retention, therefore, was chemically determined with sapwood of *C. japonica* and five wood-based composites according to the established titration technique in the present study. The analytical data are shown in Tables 1, 2, and 3.

Decay resistance

Review of early studies indicates that retention of 2.0 kg/m^3 or 0.5% (w/w) of boric acid is high enough to prevent decay in laboratory tests.[7,23–27] The results in Table 1 well support previous findings. Growth of *T. versicolor* was suppressed at the lowest test retention of 0.9 kg/m^3 (0.25% BAE), whereas *F. palustris* caused some decay of the treated wood specimens at the same retention with mean mass losses of 6.5% and 14.9% for vapor-boron- and liquid-boron-treated wood specimens, respectively. A retention level of approximately 2.0 kg/m^3 (0.55% BAE) appeared to be high enough to control the fungus regardless of the treatment method.

As the retention varied with wood-based composite types, it seemed impossible to determine threshold values of boric acid for decay and termite attacks on the tested materials. However, the lowest retention level (0.64% BAE for hardwood plywood) was effective in controlling both decay fungi and termites (Table 2). Retentions similar to those of solid wood were possibly required to protect wood-based composites from such biodegradation, as nondurable aspen waferboards were well protected from decay at 0.5% BAE when treated with disodium octaborate tetrahydrate.[28–30]

Termite resistance

There was no difference in termiticidal efficiency of boron for vapor and liquid treatments, as shown in Table 1. Boron-treated wood and wood-based composites were resistant to the subterranean termite *C. formosanus* at retentions of 0.5% BAE and higher in the current tests (Tables 1, 2). That figure was within the range of toxic

Table 3. Fire resistance of vapor-boron-treated composites

Composite	Retention (% BAE)	Performance					
		Deformation	Width of cracks on the unheated face	Afte flame (s)	Temperature-time area (°C·min)	Fuming coefficient (CA)	Mass loss after heating (g)
PB-A 1	8.6	None	None	29	205.0	85.7	57.1
PB-A 2	8.4	None	None	42	251.5	118.4	64.5
PB-B 1	5.0	None	None	58	238.1	169.9	69.0
PB-B 2	5.0	None	None	60<	238.1	187.4	69.7
WB 1	10.0	None	None	60<	238.3	74.4	56.6
WB 2	20.3	None	None	60<	231.1	74.8	51.9
MDF 1	10.4	None	None	60<	261.8	74.6	64.3
MDF 2	15.7	None	None	21	185.6	59.3	51.1
PW 1	5.8	None	None	45	215.0	65.1	47.3
PW 2	6.4	None	None	49	225.8	57.6	49.2
Required performance for slow burning materials		None	≤1/10 of thickness	≤30	≤350	≤120	

threshold values reported previously with the borates using the same subterranean termite species.[31–35]

Fire resistance

Preliminary tests with five wood-based composites showed that none of them met the performance requirements for slow-burning materials in the standard because of low boron retention, which ranged from 1.59% BAE for PW to 6.36% BAE for MDF. Therefore, detailed data for these tests are omitted here.

Results with repeatedly treated samples are shown in Table 3. Only 2 of the 10 tested wood-based composites (PB-A 1 and MDF 2) met the performance requirements. Based on the failure of the "after flame" requirement, careful attention should be paid to the selection of adhesives applied to the composites if fire resistance is required for the products. Although the amount of boron varied with composite type, and no previous study was concerned with the experimental results of the fire resistance of vapor-boron-treated wood-based composites, it seems that a minimum of 10% BAE is needed to meet the performance requirements for slow-burning materials.[9]

Conclusions

Vapor-boron-treated wood and wood-based composites proved to be as resistant as those treated with an aqueous solution of boric acid against decay fungi and subterranean termites in the laboratory. Further investigations should be undertaken to evaluate the efficacy of vapor-boron treatment under service conditions in the field. Much higher boron loading was needed to provide wood-based composites with fire resistance when compared with that required for biological resistance, although careful selection of the adhesive and addition of a fire-retardant agent to the glue line might reduce the boron loading to meet the performance requirements for fire-resistant composites.

References

1. Carr DR (1959) Boron as a wood preservative. Rec Ann Conv Br Wood Preserv Assoc 105–135
2. Cockcroft R, Levy JF (1973) Bibliography on the use of boron compounds in the preservation of wood. J Inst Wood Sci 6(3):28–37
3. Bunn R (1974) Boron compounds in timber preservation: an annotated bibliography. New Zealand Forest Service technical paper no. 60
4. Dickinson DJ, Murphy RJ (1989) Developments of boron-based wood preservatives. Rec Ann Conv Br Wood Preserv Assoc 35–42
5. Drysdale JA (1994) Boron treatments for the preservation of wood: a review of efficacy data for fungi and termites. The International Research Group on Wood Preservation document no. IRG/WP 94-30037
6. Grace JK (1997) Review of recent research on the use of borates for termite prevention. In: Proceedings of the 2nd international conference on wood protection with diffusible preservatives and pesticides. Forest Products Society Madison, WI, USA, pp 85–92
7. Tsunoda K (1999) Application of borates to wood preservation (in Japanese). Mokuzai Hozon (Wood Preservation) 25:48–58
8. Ishihara S (1989) Boron and its compounds as wood fire retardants (in Japanese). Mokuzai Hozon (Wood Preservation) 15:248–260
9. Ishihara S (1981) Synergistic effect of alkali metals on fire proofing properties of boric acid-containing melamine-formaldehyde condensates (in Japanese with English summary). Zairyo (J Soc Mater Sci Jpn) 30:725–730
10. Vinden P, Fenton T, Nasheri K (1985) Options for accelerated boron treatment: a practical review of alternatives. International Research Group on Wood Preservation document no. IRG/WP/3329
11. Murphy RJ, Turner P (1989) A vapour phase treatment of manufactured wood based board materials. Wood Sci Technol 23:273–279
12. Turner P, Murphy RJ, Dickinson DJ (1990) Treatment of wood based panel products with volatile borates. International Research Group on Wood Preservation document no. IRG/WP/3616
13. Burton R, Bergevoet T, Nasheri K, Vinden P, Page D (1990) Gaseous preservative treatment of wood. International Research Group on Wood Preservation document no. IRG/WP/3631

14. Bergevoet A, Burton R, Nasheri K, Page D, Vinden P (1992) Gaseous boron treatments of wood and wood products. International Research Group on Wood Preservation document no. IRG/WP/3691-92
15. Hashim R, Dickinson D, Murphy R, Dinwoodie J (1992) Effect of vapour boron treatment on mechanical properties of wood based board materials. International Research Group on Wood Preservation document no. IRG/WP/3727-92
16. Murphy RJ, Dickinson DJ, Turner P, Wickens PJ, Hashin R (1993) Vapor boron treatment of wood composites: production of wood-based composite products. In: Preston AF (ed) IUFRO symposium, Orlando, Florida. Forest Products Society, Madison, WI, USA, pp 49–56
17. Hashim R, Murphy RJ, Dickinson DJ, Dinwoodie JM (1994) The mechanical properties of boards treated with vapor boron. For Prod J 44(10):73–79
18. Turner P, Murphy RJ (1995) Treatment of timber products with gaseous borate esters. Part 1. Factors influencing the treatment process. Wood Sci Technol 29:385–395
19. Hashim R, Murphy RJ, Dickinson DJ, Dinwoodie JM (1997) The physical properties of boards treated with vapor boron. For Prod J 47(1):61–66
20. JIS K 1571 (1998) Qualitative standards and testing methods of wood preservatives
21. JWPA standard 11(1) (1992) Test method for evaluating effectiveness of termiticides for treatments by brushing, spraying and dipping
22. JIS A 1321 (1975) Testing method for incombustibility of internal finish material and procedure of buildings.
23. Harrow KM (1950) Toxicity of water-soluble woo-preservatives to wood-destroying fungi. NZ J Sci Technol B31(5):14–19
24. Baechler RH, Roth HG (1956) Laboratory leaching and decay tests on pine and oak blocks treated with several preservative salts. Proc Am Wood Preservers Assoc 52:24–34
25. Becker G (1959) Contribution to the knowledge of the efficacy of boron compounds against wood-destroying insects and fungi. Holz Roh Werkstoff 17:484–489
26. Findlay WPK (1960) Boron compounds for the preservation of timber against fungi and insects. Pest Technol March: 124–126
27. Yalinkilic MK, Yusuf A, Yoshimura T, Takahashi M, Tsunoda K (1996) Effect of vapor formalization of boric acid treated wood on boron leachability and biological resistance. In: Proceedings of the 3rd Pacific Rim bio-based composites symposium, December 1996, Kyoto, pp 544–551
28. Laks PE, Quan X, Palardy RD (1991) The effects of sodium octaborate tetrahydrate and zinc borate on the properties of isocyanate-bonded waferboard. In: Proceedings of the adhesives and bonded wood products symposium, Seattle, November 1991, pp 144–157
29. Laks PE, Manning MJ (1994) Inorganic borates as preservative systems for wood composites. In: Proceedings of the 2nd Pacific Rim bio-based composites symposium, Vancouver, Canada, November 1994, pp 236–244
30. Laks PE, Manning MJ (1995) Preservation of wood composites with zinc borate. International Research Group on Wood Preservation document no. IRG/WP 95-30074
31. Williams LH, Amburgey TL, Parresol BR (1991) Toxic thresholds of three borates and percent wood weight losses for two subterranean termite species when feeding on treated wood. In: Proceedings of the 1st international conference on wood protection with diffusible preservatives, November 11 Nashville, 1990. Forest Products Society proceedings no. 47355, 129–133
32. Su N-Y, Scheffrahn RH (1991) Laboratory evaluation of disodium octaborate tetrahydrate (TIM-BOR®) as a wood preservative or bait-toxicant against the Formosan and eastern subterranean termites (Isoptera: Rhinotermitidae). International Research Group on Wood Preservation document no. IRG/WP/1513
33. Grace JK, Yamamoto RT, Tamashiro MT (1992) Resistance of borate-treated Douglas-fir to the Formosan subterranean termite. For Prod J 42(2):61–65
34. Mauldin JK, Kard BM (1996) Disodium octaborate tetrahydrate treatments to slash pine for protection against Formosan subterranean termite and eastern subterranean termite (Isoptera: Rhinotermitidae). J. Econ Entomol 89(3):682–688
35. Tsunoda K (1999) Application of borates to wood preservation. 2. Field evaluation and applicability to the preservative treatment of composites (in Japanese). Mokuzai Hozon (Wood Preservation) 25:251–262