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Termite and fungal resistance of *in situ* polymerized tributyltin acrylate and acetylated Indonesian and USA wood

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Termite and fungal resistance of *in situ* polymerized tributyltin acrylate and acetylated Indonesian and USA solid wood

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ABSTRACT

Wood [Indonesian pine (IP), Indonesian Jabon (IJ) and USA southern yellow pine (USP)] was either *in situ* polymerized with tributyltin acrylate (TBTA) or acetylated and then exposed to termite and fungal degradation both in laboratory tests and field exposure. The TBTA woods had an average weight percent gain (WPG) of 11% for IP, 12% for IJ, and 10% for USP. The acetylated woods had a WPG of 15-27% for IP, 16% for IJ, and 12-21% for USP. All levels of TBTA and acetylation treatments were effective against the brown-rot fungus *Tyromyces palustris* and the white-rot fungus *Coriolus versicolor* in laboratory testing. Resistance to subterranean termites [*Coptotermes gestroi* (Wasmann)] and dry wood termites [*Cryptotermes cynocephalus* (Light)] was shown in laboratory tests with all treatments. After one year of field testing in Indonesia (AWPA Standard E7-93), TBTA treated specimens gave a grade number of 8 for all 3 woods compared to 0 for the untreated controls (based on a 10 - point scale.) The acetylated specimens gave a grade number of 4 for IP, 8 for IJ, and 6 for USP. Scanning electron microscopy (SEM) showed polymer located in the lumen of the earlywood and latewood of selected TBTA treated specimens, but at low overall polymer weight gain the lumens were not evenly filled. Termite field testing continues on all treated wood specimens.

Keywords: termite, fungus, acetylation, *in situ* polymerization, tributyltin acrylate, wood preservation, scanning electron microscopy

INTRODUCTION

Termite, as well as fungal degradation, causes extensive destruction in wood in Indonesia as well as many parts of the world. Existing wood treatments for protection against biodegradation are mainly based on toxicity, but there are other ways of protecting wood. Suttie reviews new strategies for wood protection, pointing out the main methods of preventing fungal attack on wood by: killing the fungus (toxicity); rendering the food source unusable (chemically modify); preventing the wood from becoming wet (chemically modify); or interfering with the chemicals that the wood-destroyers use to break the bonds (biochemical methods) (Suttie 1997). He discusses the biochemical methods, natural timber extractives, restricting water ingress, and chemical modification.

In Indonesia, chromated copper arsenate (CCA) had been the only preservative used to treat timber for use in cooling towers and the most common in treated wood for housing applications, but it was banned in 1994 (Permadi et al. 1998). New environmentally friendly technologies to protect wood and wood based products from biodegradation are needed. Products need to be not only environmentally friendly, but also non hazardous to human beings as well. One such technology involves *in situ* polymerization of bioactive polymers in the lumens of the wood. The mechanism of effectiveness may still be toxicity, but it is envisioned as a controlled release system, therefore holding the toxicant in place longer (Ibach 1996) (Ibach and Rowell 1995). Conventional wood treatments disperse the preservative in the wood without chemical anchoring, therefore having a greater leaching rate. With bioactive polymers the duration of protection and optimum release of toxicant can be controlled by the polymer matrix properties. Thus, the environmental hazard can be minimized.

Another technology involves chemically modifying wood by acetylating the hydroxyl groups to change the hydrophilic nature of the cell wall polymers of wood. The hydroxyl groups of the wood components are reacted with chemical reagents, resulting in stable, covalently bonded group attachment (Rowell et al. 1994). The modification should be more environmentally friendly. The mechanism of effectiveness is not based on toxicity, but perhaps substrate modification or moisture exclusion at the glycosidic hydrolysis site that is required by the degrading enzyme (Ibach and Rowell 1999).

Various bioactive compounds were evaluated for fungal resistance (Ibach 1996), but not termite resistance. The present paper takes one bioactive *in situ* polymerization treatment, tributyltin acrylate (TBTA), and acetylated wood and looks at not only fungal resistance, but also termite resistance. The ultimate goal is to treat woods to obtain a high resistance against all biodeterioration.

MATERIALS AND METHODS

The wood species used were Indonesian pine (IP), Indonesian Jabon (IJ), and USA southern yellow pine (USP). The catalyst for acrylic polymerization was 2,2′-Azobis-(2,4-dimethylvaleronitrile) from Polysciences, Inc., Warrington, PA.♣ The crosslinker was trimethylolpropane trimethacrylate (TMPTM) and the solvent was acetone. Both were from Aldrich Chemical Company, Milwaukee, WI. The acetic anhydride was from Pfizer, USA.

♣ The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Treatments:

Tributyltin acrylate:

Tri-n-butyltin acrylate (TBTA) was synthesized according to the literature (Ibach 1996) (Rowell 1983) (Mendoza 1977) (Montermosa et al. 1958) (Shostakovskii et al. 1961).

$$(C_4H_9)_3SnOSn(C_4H_9)_3 + 2(H_2C{=}\overset{\displaystyle H}{C}-\underset{\displaystyle OH}{C}{=}O) \rightarrow 2(CH_2{=}CH-C({=}O)-O-Sn(C_4H_9)_3) + H_2O$$

The ASTM D 1413 standard method for treating wood specimens was followed with a few modifications (ASTM 1976). Wood specimens (19 mm x 19 mm x 300 mm and 19 mm x 19 mm x 10 mm) were oven dried at 105 °C. They were then placed in a treating chamber and the system was evacuated for one hour with a water aspirator (30 mm Hg). Treating solutions were prepared just prior to treatment. A solution consisting of 5% TBTA, 0.4% catalyst, and 5% crosslinker in acetone was admitted into the treating chamber until the solution covered all the specimens, and then held for 5 minutes. Specimens were held in place with a glass weight to prevent floating. The vacuum was released and the chamber was brought to atmospheric pressure. The specimens were allowed to soak for 30 minutes in the solution, removed, wiped of excess solution, wrapped immediately in aluminum foil and then placed in a 52 °C oven, flushed with nitrogen and allowed to polymerize overnight. The foil was removed, specimens oven-dried and weight percent gain (WPG) calculated. After TBTA polymerization in IJ there was polymerized material on the surface of the 19 mm x 19 mm x 300 mm specimens that was brushed off before weighing.

Acetylation:

Oven dried wood specimens were immersed in acetic anhydride for two weeks, and then subsequently heated at 120 °C for 24 hours. The specimens were washed with water to remove excess anhydride and by-product acetic acid and they were dried again. The acetylation level was indicated by WPG, based on the original oven-dried weight of the wood specimens.

$$\text{Wood-OH} + CH_3\text{-}C(=O)\text{-}O\text{-}C(=O)\text{-}CH_3 \rightarrow \text{Wood-O-}C(=O)\text{-}CH_3 + CH_3\text{-}C(=O)\text{-}OH$$

Biological Testing:

Laboratory:

Fungal test:
The resistance to fungi was evaluated using a 12-week soil block test as per standard procedure (JWPA 1992). Decay resistance tests were carried out using *Tyromyces*

palustris a brown-rot fungus and separately with *Coriolus versicolor* a white-rot fungus with all three wood species.

Dry wood termite test:
TBTA treated, acetylated, and untreated control wood specimens (19 mm x 19 mm x 10 mm) were tested using the dry wood termite *Cryptotermes cynocephalus* (Light) (Hadi et al. 1995) (Hadi and Febrianto 1991). Fifty healthy and active nymphae of the dry wood termite were put into each box, and the boxes were put in a dark room at an average temperature of 20 to 32 °C and 81 to 89 percent relative humidity (RH) for 10 weeks. At the end of the test nymphae mortality and wood weight loss were determined.

Subterranean termite test:
TBTA treated, acetylated, and untreated control wood specimens (19 mm x 19 mm x 10 mm) were tested using the subterranean termite *Coptotermes gestroi* (Wasmann) in laboratory testing. Each wood specimen was put in an acrylic cylindrical tube (sized 60 mm height and 80 mm diameter), and to each tube was put 150 workers and 15 soldiers of nymphae. A wet tissue was placed in each tube to maintain humidity. The tubes were put in a dark room at an average temperature of 20 to 32 °C and 81 to 89 percent relative humidity (RH) for 5 weeks. At the end of the test the percentage weight loss of each specimen was determined as well as nymphae mortality.

Field test:

TBTA treated, acetylated, and untreated control wood specimens (19 mm x 19 mm x 300 mm) were exposed to in-ground field testing (AWPA 1993). Wood specimens were vertically buried in an arboretum, with 25 cm below ground. The test was carried out in Bogor, Indonesia, which has an average of 3552 mm/year rainfall, RH 80 % and 25 °C temperature. After 12 months specimens were inspected and percentage weight loss was determined. The protection level for each wood specimen was observed using the rating system shown in Table 1.

Table 1. – Rating system for field test termite resistance.

Protection Level	Condition of Wood Specimen
10	Sound. 1 to 2 small nibbles permitted
9	Slight evidence of feeding to 3% of cross section
8	Attack from 3 to 10% of cross section
7	Attack from 10 to 30% of cross section
6	Attack from 30 to 50% of cross section
4	Attack from 50 to 75% of cross section
0	Failure

Microscopic Analysis:

Scanning electron microscopy (SEM) was performed on selected specimens with a Joel 840 instrument. Longitudinal sections were gold coated, and the earlywood and latewood were observed at 150x and 250x magnifications, respectively. Representative pictures were taken of both earlywood and latewood.

RESULTS AND DISCUSSSION

Treatments:

Weight percent gains of TBTA and acetylated wood specimens are shown in Table 2. After treatment, the TBTA treated woods had an average WPG of 11% for IP, 12% for IJ, and 10% for USP. The acetylated woods had a WPG of 15-27% for IP, 16% for IJ, and 12-21% for USP. The WPG range for acetylated specimens is due to the different sample sizes. The smaller specimens for laboratory testing (19 mm x 19 mm x10 mm) had higher weight gains than the larger specimens for outdoor exposure (19 mm x 19 mm x 300 mm).

Table 2. Weight percent gain (WPG) of TBTA and acetylated wood specimens.

Wood species	Treatment	WPG
Indonesian Pine	TBTA	11
	Acetylation	15-27
Indonesian Jabon	TBTA	12
	Acetylation	16
U.S. Pine	TBTA	10
	Acetylation	12-21

Biological Testing:

Laboratory:

Both the TBTA treated and acetylated woods were resistant to attack by the brown-rot fungus, *T.palustris* (Table 3) and the white-rot fungus, *C.versicolor* (Table 4). At 5% TBTA and 5% crosslinker, these results are similar to the results using *Gloeophyllum trabeum* (Ibach 1996) (ASTM 1976). For acetylated wood, resistance to most decay fungi has been reported at WPGs of 15% - 20% (Rowell 1991) (Goldstein et al. 1961) (Tarkow et al. 1950).

The moisture content of the untreated specimens increased significantly after exposure to each fungus (Table 3 and Table 4). Overall, the specimens exposed to the white-rot fungus have higher moisture contents than the brown-rot specimens, yet all treatments have lower moisture contents than untreated controls for all three woods. Whether by mechanism of moisture exclusion or polymer bulking, the treated woods have lowered the moisture content and the result is no weight loss from degradation.

Weight losses of wood specimens and mortality of dry wood termites after 10 weeks are shown in Table 5. Both the TBTA treated and acetylated specimens showed resistance to dry wood termite attack in laboratory testing. Weight losses were significantly decreased for all treatments. The termite mortality increased for all treated specimens.

Weight losses of wood specimens and mortality of subterranean termites after 5 weeks are shown in Table 6. As with the dry wood termites, both the TBTA treated and acetylated specimens showed resistance to subterranean termite attack. Weight losses were significantly decreased. The acetylated IJ gave the highest weight loss of 3.5%. Termite mortality was 100% after 5 weeks for all treatments.

Field test:

The weight losses and protection level of TBTA treated, acetylated, and untreated controls after one-year of outdoor exposure are shown in Table 7. The TBTA specimens gave a protection level of 8 for all three wood species. This consists of attack from only 3 to 10% of the cross section compared to the control of 0, which is total failure. At the same time the weight losses were significantly decreased to 3.7% for IP, 6.3% for IJ, and 3.4% for USP. The acetylated IJ specimens gave an overall protection of 8 with 8.6% weight loss, while the USP gave protection level of 6 (attack from 30 to 50% of cross section) with 41% weight loss, and IP gave a protection level of 4 (attack from 50 to 75% of cross section) with 61% weight loss.

A comparison of U.S. southern pine wood and flakeboard untreated controls show essentially the same weight loss and termite survival in a 4-week subterranean termite test (Rowell et al. 1987). Even at the highest acetyl weight gain for both southern pine and aspen flakeboards, weight loss caused by termite attack was not completely stopped. Perhaps it was due to the severity of the test, but it is also known that the intestinal protozoa in termites decompose cellulose to acetic acid and that acetic acid accounts for 85% of all acids produced from cellulose fermentation in termites. Therefore, since termites can live on acetic acid, it is not surprising that acetylated wood is not completely resistant to termite attack.

In a worldwide, (four continent) in-ground stake test of acetylated composite boards, the most aggressive field exposure was in Bogor, Indonesia where all the controls failed in 3 months (Rowell et al. 1997). Yet, it was found in this study that acetylation of wood material imparts excellent protection against microbial decay and termite attack in most of the locations if a high degree of acetylation (about 20% acetyl content) is attained. With this in mind, looking at our field results, besides the aggressiveness of the Bogor field site, one explanation for the lower protection level and weight loss of the acetylated wood specimens may be explained by the weight gains of less than 20% with some of the specimens. Termite field testing continues on the treated wood specimens.

Microscopic Analysis:

Scanning Electron Microscopy (SEM) of IP, IJ, and USP TBTA treated woods shows polymer located in the lumen of both the earlywood and latewood. The latewood micrograms of untreated controls and TBTA treatment are presented in Figures 1-6. Compared to the untreated controls (Figures 1, 3, and 5), the 5%TBTA/5% crosslinker treated woods (Figures 2, 4, and 6) show polymer in the lumens, but not completely full. This is to be expected at such low overall weight gains of 10-12%. The USP TBTA treated wood is comparable to previous micrograms (Ibach 1996). Since earlywood SEM micrograms showed similar treatment, only latewood pictures are presented.

SUMMARY AND CONCLUSION

In situ polymerization of TBTA into Indonesian pine, Indonesian Jabon, and USA southern yellow pine at low polymer weight gain is possible as confirmed by SEM micrograms. TBTA and acetylation lower the percentage moisture content and are effective against both brown-rot (*T.palustris*) and white-rot (*C.versicolor*) fungal attack in laboratory tests. Both treatments impart resistance to subterranean termites [*Coptotermes gestroi* (Wasmann)] and dry wood termites [*Cryptotermes cynocephalus* (Light)] in laboratory testing. After one year of rigorous Indonesian outdoor exposure testing, TBTA and acetylation treatments give high protection, but not complete biological resistance. Higher WPG treatment levels of TBTA or acetylation may impart complete termite resistance. Collaborative research continues on biological resistance of chemically modified wood.

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Table 3. – Weight loss percentage and moisture content of three woods after exposure to *Tyromyces palustris*, a brown-rot fungus, for 12 weeks in laboratory testing.

Wood species	Treatment	Weight loss %	M.C.*%
Indonesian Pine	TBTA	0	37.0
	Acetylation	0	32.6
	Control	33.0	79.6
Indonesian Jabon	TBTA	0	80.0
	Acetylation	0	85.7
	Control	45.7	192.7
US Pine	TBTA	0.3	40.7
	Acetylation	0	38.3
	Control	29.6	70.9

*M.C. = Moisture content of wood after 12 week exposure.

Table 4. – Weight loss percentage and moisture content of three woods after exposure to *Coriolus versicolor*, a white-rot fungus, for 12 weeks in laboratory testing.

Wood species.	Treatment	Weight loss %	M.C.%
Indonesian Pine	TBTA	0	58.1
	Acetylation	0	63.7
	Control	19.6	179.7
Indonesian Jabon	TBTA	0	102.2
	Acetylation	0	95.2
	Control	39.7	227.4
US Pine	TBTA	0	54.4
	Acetylation	0	68.0
	Control	18.4	165.2

Table 5. – Weight loss percentage of wood specimens and nymphae mortality of dry wood termite, *Cryptotermes cynocephalus* (Light), after 10 weeks in laboratory testing.

Wood species	Treatment	Weight loss %	Mortality %
Indonesian Pine	TBTA	1.5	100
	Acetylation	1.9	99
	Control	9.3	42
Indonesian Jabon	TBTA	1.4	100
	Acetylation	1.9	95
	Control	16.5	31
US Pine	TBTA	1.9	100
	Acetylation	1.6	98
	Control	8.4	49

Note: starvation mortality 99% and with tissue 58%

Table 6. – Weight loss percentage of wood specimens and nymphae mortality of subterranean termite, *Coptotermes gestroi* (Wasmann), after 5 weeks exposure.

Wood species	Treatment	Weight loss %	Mortality %
Indonesian Pine	TBTA	1.4	100
	Acetylation	1.7	100
	Control	9.9	70
Indonesian Jabon	TBTA	1.5	100
	Acetylation	3.5	100
	Control	12.5	83
US Pine	TBTA	1.7	100
	Acetylation	1.6	100
	Control	10.0	78

Note: starvation mortality 100% and with tissue 92%

Table 7. – Weight loss percentage and protection level of acetylated, TBTA treated and untreated control wood specimens after one-year of outdoor exposure.

Wood species	Treatment	Weight loss %	Protection Level
Indonesian Pine	TBTA	3.7	8
	Acetylation	61.2	4
	Control	95.5	0
Indonesian Jabon	TBTA	6.3	8
	Acetylation	8.6	8
	Control	98.9	0
US Pine	TBTA	3.4	8
	Acetylation	41.0	6
	Control	92.2	0

Figure 1. SEM of Indonesian Pine latewood control (250x).

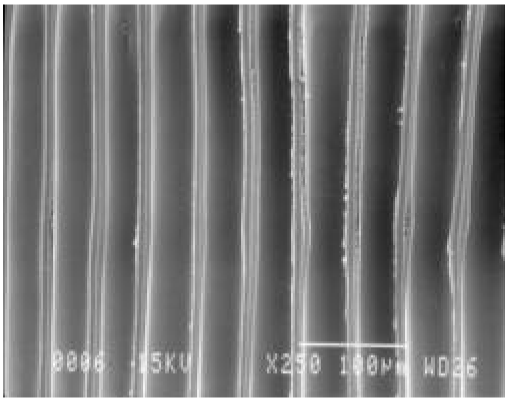


Figure 2. SEM of TBTA treated Indonesian Pine latewood (250x).

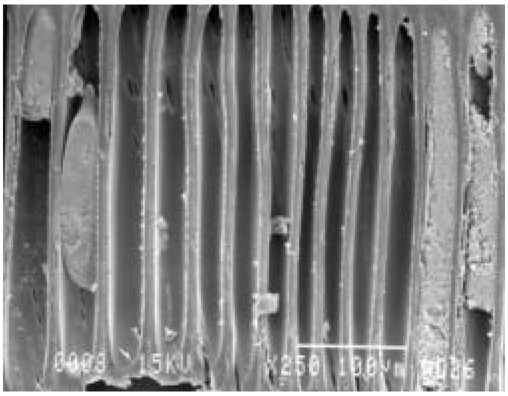


Figure 3. SEM of Indonesian Jabon latewood control (250x).

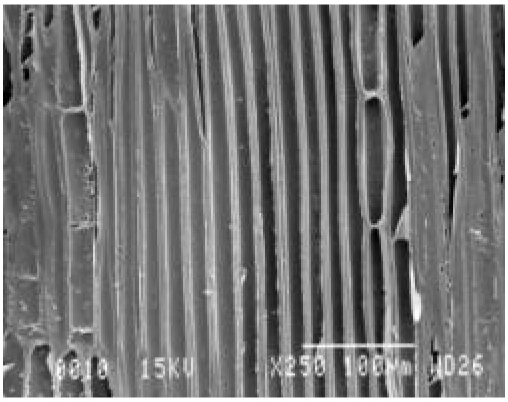


Figure 4. SEM of TBTA treated Indonesian Jabon latewood (250x).

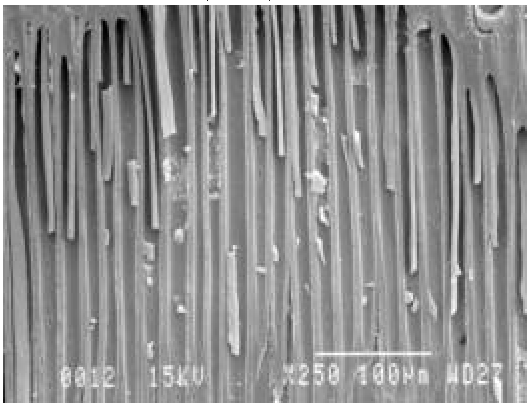


Figure 5. SEM of United States Pine latewood control (250x).

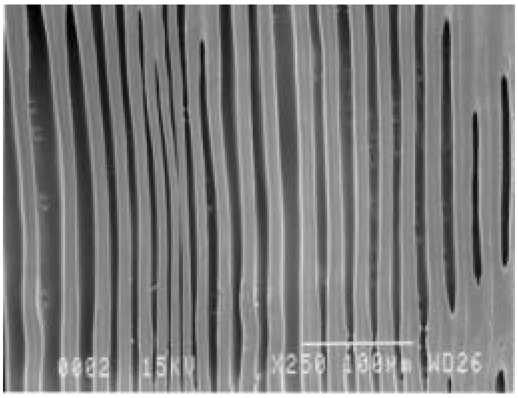
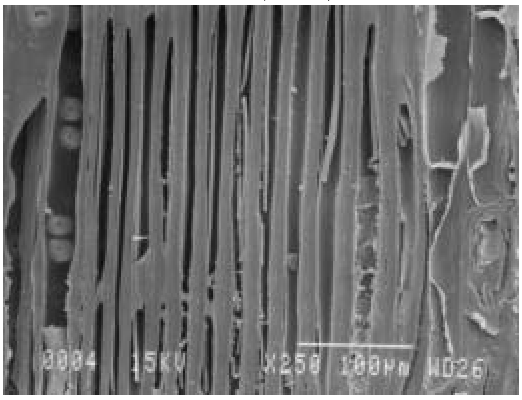


Figure 6. SEM of TBTA treated United States Pine latewood (250x).



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